

### 30. MINERALOGY AND GEOCHEMISTRY OF UPPER CRETACEOUS AND CENOZOIC SEDIMENTS FROM NORTH BISCAY BAY AND ROCKALL PLATEAU (EASTERN NORTH ATLANTIC), DSDP LEG 48

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#### ABSTRACT

One hundred and thirty samples of various Cretaceous to Pleistocene sediments from DSDP Sites 399 and 400 (north Biscay Bay) and 403 to 406 (south Rockall Plateau) were studied for their clay mineralogy and bulk geochemistry. Both geographical areas were compared with each other, then compared with the area south of Biscay Bay (Site 398, DSDP Leg 47).

In Aptian to Paleogene sediments the clay fraction is dominated by smectite. In Biscay Bay the mineral is rich in Al-Fe and chiefly expresses the erosion of soils formed under arid-warm climatic conditions with contrasted wet and dry seasons. Two stages with fibrous clays occur in Albian (attapulgitite, palygorskite) and Paleocene/Eocene (attapulgitite, sepiolite) sediments, suggesting the existence of wet and warm periods and of nearly closed marginal basins. In the south part of the Iceland Sea the smectite is of a Fe-Mg type and mainly results from the transformation of volcanic material, probably in subaerial conditions. In post-Paleogene sediments the primary minerals (illite, chlorite, quartz, feldspars) and mixed-layers increase irregularly, expressing both periodic continental cooling, the major stages of which occurred in late Miocene and Pleistocene times, an increase in the intensity of the north/south oceanic current. In general, kaolinite and fibrous clays are less abundant, smectite more abundant, and coolings appear to have been stronger in Pleistocene time in the more northern drill sites.

The diagenetic changes are unusual. There is no modification with depth of burial and no basic chemical sedimentation. An in situ evolution in volcanic environment appears locally in Rockall sites only. The "black shales" facies does not induce any argillaceous modification in north Biscay Bay and affects only some chemical elements such as Ca, Fe, and Mn. Ionic removing and trapping can locally induce the autochthonous crystallization of cristobalite-tridymite and of some zeolites.

Site 402 of Biscay Bay, not as deep as Sites 398, 399, 400, and 401, seems to be aside from open sea circulations, which might affect especially the distribution of Mn in Albian to lower Miocene sediments and, perhaps, as well, that of fibrous clays. The chemical and mineralogical sequence observed from Site 402 to Sites 399 and 400 in Upper Cretaceous sediments suggests a deltaic paleoenvironment, which, seaward is marked by a geochemical homogenization, a decrease of the carbonaceous phase, and an increase of small-sized, highly buoyant minerals (smectite, fibrous clays). The sudden arrival of detrital primary minerals in the Campanian/Maestrichtian suggests the establishment of a deep-sea circulation perhaps related to the opening of the western North Atlantic, or to a tectonic event or a marine regression. South of Rockall Plateau during early Cenozoic time, the chemical and mineralogical environment was more pelagic than in Biscay Bay, especially at Sites 405 and 406 where the volcanoclastic influence was not as strong as at Sites 403 and 404. The ending of the major volcanic activity in mid-Eocene was followed by an increase in the pelagic supply, probably related to the widening of the eastern North Atlantic.

#### INTRODUCTION

Leg 48 of the Deep Sea Drilling Project was located in the eastern North Atlantic Ocean, partly in Biscay Bay and

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partly on the Rockall Plateau. Four holes were drilled in each area, Sites 399 to 402 and Sites 403 to 406, respectively (Figure 1); their general character is as follows (for detailed description see Site Chapters, this volume).

### Bay of Biscay

Site 399 (47°23.4'N, 09°13.3'W; 4399 m water depth; 72.5 m sub-bottom depth); located at the foot of the Meriadzek Terrace Escarpment; Pleistocene section.

Site 400 (47°22.90'N, 09°11.90'W; 4399 m water depth; 768.5 m sub-bottom depth); located near to Site 399 at the foot of the Meriadzek Terrace Escarpment; section from Pleistocene to lowermost Aptian.

Site 401 (47°25.65'N, 08°48.62'W; 2495 m water depth; 341 m sub-bottom depth); located at the edge of the Meriadzek Terrace on an elevated fault block; section from Pleistocene to Kimmeridgian, with major hiatuses between Upper Jurassic and Upper Cretaceous, and between Eocene and Pleistocene.

Site 402 (47°52.48'N, 08°50.44'W; 2339.5 m water depth; 469.5 m sub-bottom depth); located in a canyon cutting a spur on the Armorican slope; section from Pleistocene to Aptian with a major hiatus between Albian and middle Eocene.

### Rockall Plateau

Four sites were drilled in two sectors: Sites 403 and 404 lie in the southwest margin of the plateau in 2317 to 2322

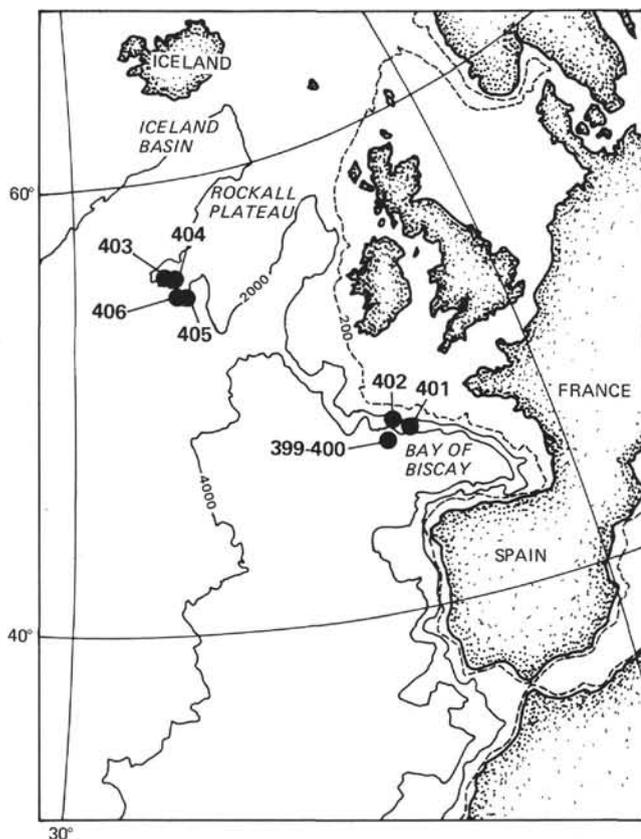


Figure 1. Location map.

meters water depths, at 56°08.13'N-23°17.64'W and 56°03.13'N-23°14.95'W, respectively. The sub-bottom depths of the holes were 489 meters and 389 meters, respectively, the oldest sediment cored being upper Paleocene in both cases. A major gap exists from middle Eocene to upper Miocene, except at Site 403 where a thin interval of Oligocene sediments is present.

Sites 405 and 406 lie south of the east-west scarp forming part of the southwest margin of the plateau in 2958 meter and 2907 meter water depths at 55°20.18'N-22°03.49'W and 55°15.50'N-22°05.41'W, respectively. Sub-bottom depths are 407 meters and 831.5 meters, respectively, the bottom sediments at each site being of early Eocene age. Site 405 shows a major hiatus between lower Eocene and upper Miocene. At Site 406 only middle Eocene and lower Oligocene are missing.

About 130 samples from the eight sites were studied for the purpose of comparing the clay mineralogy, bulk mineralogy (locally), and the bulk geochemistry. Results are presented on Figures 2 to 8 and will be commented briefly upon in stratigraphical order. Comparison first is made among all sites of each area, then between Biscay Bay, Rockall Plateau, and the Vigo Seamounts south of Biscay Bay (DSDP Leg 47B, Chamley et al., in press). Note that complementary data and comments on mineralogy are given about Biscay Bay by Cassat (this volume) and about Rockall Plateau by Latouche (this volume).

## METHODS OF INVESTIGATION

### Clay Mineralogy

All of the samples were submitted to X-ray diffraction analysis on  $<2 \mu\text{m}$  decalcified particles. We examined some of  $<8 \mu\text{m}$  non-calcareous fractions by transmission electromicroscopy. Differential thermal analyses were made on  $<2 \mu\text{m}$  non-calcareous fractions of selected samples originating chiefly from sites of Rockall Plateau. In the X-ray diffraction method, the samples were dissociated in water then decarbonized in  $N5$  hydrochloric acid; the excess acid was removed by successive centrifugations. A microhomogenization led to deflocculation. The  $<2 \mu\text{m}$  fraction was collected by decantation (Stokes law), then oriented aggregates were made on glass slides. A CGR  $\Theta 60$  diffractometer (copper radiation focused by a quartz curved-crystal monochromator) was used to run the X-ray diffraction scans at  $1^\circ 2 \Theta/\text{mn}$ . A receiving slit of 1.25 mm allowed a better determination of mixed-layer minerals. Four passages are carried out as follows: (a) from  $1^\circ$  to  $15^\circ \Theta$  on natural sample; (b) from  $1^\circ$  to  $7^\circ \Theta$  on glycolated sample; (c) from  $1^\circ$  to  $7^\circ \Theta$  on sample heated for two hours at  $490^\circ\text{C}$ ; (d) from  $12^\circ$  to  $14^\circ \Theta$  on hydrazine-hydrated sample.

Semi-quantitative evaluations were based on the peak heights and areas (Chamley, 1971). The height of 001 illite and chlorite peaks (diagram of glycolated sample) were taken as references. Compared to these values, smectite, attapulgite, and irregular mixed-layers were corrected in addition to peak heights whereas well crystallized kaolinite was corrected in diminution. The balance between chlorite and kaolinite results from peak heights ratio (respectively  $3.54 \text{ \AA}$  and  $3.58 \text{ \AA}$ ): when this ratio is 1, the amount of

chlorite is assumed to be twice as much as that of kaolinite. Final data are given in percentages, the relative error being  $\pm 5$  per cent.

### GEOCHEMISTRY

The samples were dried at 105°C, then ground and homogenized; 0.2 g was submitted to alkaline fusion, then solubilized by HCl, and diluted to 100 ml. The treatment allows gravimetric determination of SiO<sub>2</sub>, colorimetric determination of P<sub>2</sub>O<sub>5</sub>, and spectrophotometric determination of Fe, CaO, MgO, Al<sub>2</sub>O<sub>3</sub> (by atomic absorption). Another 2 g of each sample were submitted to fluoroperchloric treatment, then solubilized by HCl and diluted to 100 ml. The dilution is used for the colorimetric analysis of TiO<sub>2</sub>, the spectrophotometric analysis of Na<sub>2</sub>O and K<sub>2</sub>O (by emission) and also for traces Mn, Zn, Li, Ni, Cr, Sr, Co, Cu, Pb, V (by atomic absorption).

The emission and atomic absorption apparatus was a Type 503 Perkin-Elmer spectrophotometer using the following methods—base solution for major elements or complex synthetic solution for trace elements to which 5 per cent of lanthane in hydrochloric solution is added.

### BISCAY BAY—RESULTS

#### Sites 399 and 400; Figure 2; Table 1

##### Aptian

Aptian and Albian sediments are carbonaceous mudstone, marly nannofossil chalk, and calcareous claystone (lithologic Unit 4). In some levels smectite is nearly exclusive, accompanied by rather high contents of Fe and Mn rather than K. Particular levels locally exist which show reduction (400A-74-1, 45 cm: siderite, rhodochrosite) or oxidation (400A-68-2, 49 cm): irregular mixed-layers illite-smectite and chlorite-smectite, goethite, subamorphous iron oxides); both types show an antagonism between SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>/K<sub>2</sub>O ratios.

##### Albian

Smectite is the main clay mineral, as it is in all sediments up to those of the Miocene at least. Associate minerals are chlorite, illite, kaolinite, attapulgite (Plate 1; Figures 1, 2), quartz, feldspars, zeolites (clinoptilolite). Mn and Ca increase whereas the Sr/CaO ratio is variable.

##### Campanian/Maestrichtian

Four levels (-61-3, 136 cm, -61-1, 26 cm, -60-3, 11 cm, -60-1, 4 cm) studied for clay mineralogy in the nannofossil chalk of Unit 3 show the presence, besides smectite, of 10 to 35 per cent illite, and a large amount of quartz and feldspars. Chlorite is more abundant than below and above; amphiboles are locally present in the  $< 2 \mu\text{m}$  fraction.

##### Upper Paleocene, Eocene

Siliceous mudstone, calcareous claystone, and marly chalk from the base of lithologic Unit 2 contain a large amount of smectite. Kaolinite increases upwards as well as the Al<sub>2</sub>O<sub>3</sub>/K<sub>2</sub>O ratio, whereas CaO decreases. Attapulgite and/or sepiolite are present, especially in middle Eocene sediments. Zeolites occur rarely, then disappear in the

middle Eocene interval. MgO/K<sub>2</sub>O and Sr/CaO ratios increase, with a maximum at the Eocene/Oligocene boundary.

##### Oligocene, Lower Miocene

The siliceous marly nannofossil chalk and mudstone of the upper part of Unit 2 show several trends upwards from the Eocene/Oligocene boundary: stabilization of Sr/CaO ratio; increase of Ca, Mn, illite, and kaolinite; appearance, then development of chlorite; disappearance of fibrous clays on X-ray diagrams, fibers subsisting on electromicrographs in small quantities only (Plate 1; Figure 5); in middle Miocene, end of metallization.

##### Upper Miocene to Pleistocene

Lithologic Unit 1, nannofossil and marly nannofossil ooze, and calcareous mud, is marked by an irregular decrease of smectite and increase in the abundance of illite, chlorite, followed in turn by irregular mixed-layers, quartz, feldspars, amphiboles, and goethite. Attapulgite appears in small quantities on micrographs. At the base of the zone is a geochemical break manifested by increase of Ca and Sr, and decrease of Mn, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>/K<sub>2</sub>O. The Pleistocene is marked by an increase in SiO<sub>2</sub>, Ti, Cr, V, and Zn contents.

#### Site 401; Figure 3; Table 2

##### Kimmeridgian

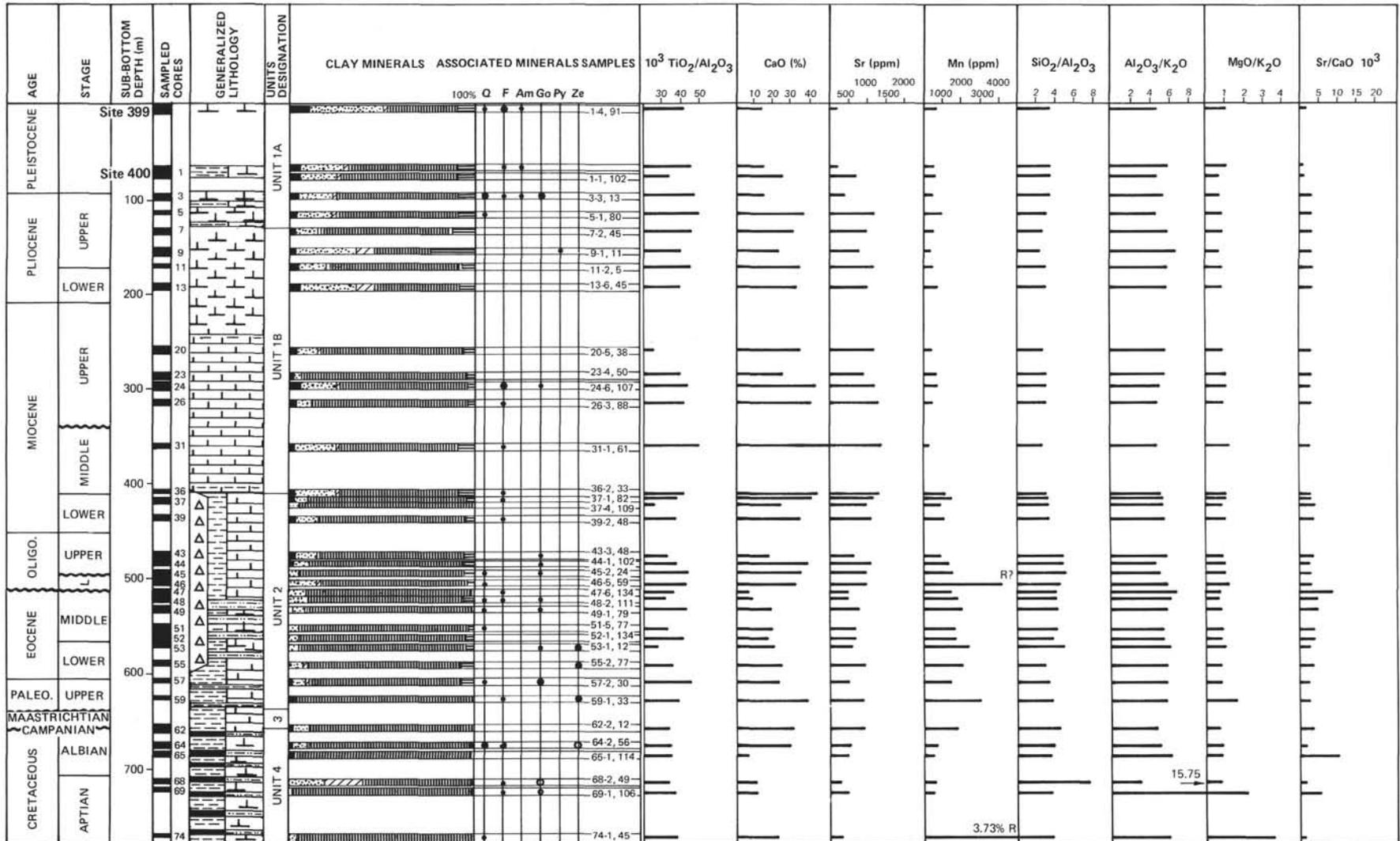
The Upper Jurassic limestone (Unit 4) is poor in clay fraction; it could not be extracted in sufficient amounts for X-ray analysis. The richness of Ca is followed by high MgO/K<sub>2</sub>O ratios, low Sr/CaO ratios.

##### Campanian

Illite and chlorite constitute more than half of the clay fraction (19-1, 125 cm) and are marked by relative high contents of Al and K. CaCO<sub>3</sub> is abundant; Sr/CaO ratio continues to be low. Phosphates are locally individualized. A resampling and study of Cores 18 and 19 (Campanian and Maestrichtian: -18-1, 50 cm, -18-2, 49 cm, -18-2, 88 cm, -19-1, 8 cm, -19-1, 50 cm, -19-1, 90 cm) lead to the following average clay mineralogy: chlorite 5 per cent, illite 35 per cent, irregular mixed-layers illite-smectite and chlorite-smectite 5 per cent, smectite 45 per cent, kaolinite 5 per cent, attapulgite 5 per cent, sepiolite traces; associate minerals are abundant quartz, feldspars and, locally, amphiboles. Illite and chlorite particles are often large sized and well edged (Plate 1; Figure 3).

##### Paleocene, Eocene

The nannofossil, marly or calcareous chinks of lithologic Units 3 and 2 are marked by abundant smectite, with locally rather abundant attapulgite, sepiolite, and clinoptilolite (resample of -17-1, 50 cm, Plate 1, Figure 4). Illite, chlorite, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, and Sr/CaO ratios increase more or less progressively towards upper Eocene. In lower Paleocene a large increase of Sr and Mn occurs, the latter element showing a maximum in middle Eocene where sepiolite content is the larger.



CLAY MINERALS: C CHLORITE K KAOLINITE  
 I ILLITE R ROUGH VALUE  
 ML MIXED LAYERS A ATTAPULGITE (Low or very low clay content)  
 SM SMECTITE S SEPIOLITE

ASSOCIATED MINERALS:  
 Q = Quartz  
 Am = Amphiboles  
 Py = Pyrite  
 F = Feldspars  
 Go = Goethite  
 Ze = Zeolite  
 ● very rare  
 ○ abundant  
 ● rare  
 ○ very abundant

Figure 2. Sites 399 and 400, clay mineralogy and bulk geochemistry.

TABLE 1  
Geochemical Data, Sites 339 and 400

Sample (Interval in cm)	%									ppm									
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Fe	Mn	Zn	Li	Ni	Cr	Sr	Co	Cu	Pb	V
<b>Site 339</b>																			
1-4, 95	48.35	13.74	14.10	2.86	1.65	2.71	0.58	n.d.	3.40	740	150	37	35	96	200	15	22	22	95
2-2, 68	46.55	13.98	13.82	2.61	1.35	2.35	0.63	n.d.	4.00	560	160	36	34	110	180	13	18	23	110
<b>Site 400</b>																			
1-1, 102	34.80	9.63	24.70	1.67	1.30	2.01	0.33	n.d.	2.43	570	200	31	27	68	750	11	33	27	89
3-3, 13	45.90	13.10	14.42	2.00	1.33	2.38	0.63	n.d.	3.00	400	94	38	28	100	430	14	36	28	120
5-1, 80	19.85	6.38	37.15	1.18	1.10	1.35	0.32	n.d.	1.55	1030	180	21	22	42	1210	11	28	26	58
7-2, 45	26.50	9.56	29.54	1.42	1.10	1.55	0.44	n.d.	2.08	510	75	31	26	38	930	12	47	37	66
9-1, 11	34.40	13.79	22.95	1.35	1.30	2.01	0.55	n.d.	2.03	275	110	41	32	80	790	9	48	33	100
11-2, 5	21.25	6.61	34.48	1.31	1.00	1.28	0.30	n.d.	1.87	390	126	24	34	36	1150	16	63	39	49
13-6, 45	24.15	7.51	33.13	1.37	1.38	1.50	0.30	n.d.	1.85	650	130	27	29	57	1010	13	40	20	63
20-5, 38	24.30	8.78	33.69	1.34	1.00	1.50	0.22	n.d.	1.75	400	170	30	31	61	1140	13	28	23	58
23-4, 50	29.75	9.91	25.38	1.78	1.30	1.68	0.40	n.d.	2.20	600	88	33	34	45	900	13	48	34	59
24-6, 107	13.65	4.04	42.18	0.91	0.68	0.78	0.18	n.d.	1.03	680	49	15	24	41	1200	12	21	24	23
26-3, 88	15.55	4.98	39.73	1.01	0.73	0.99	0.21	n.d.	1.17	400	62	19	32	51	1300	13	23	31	24
31-1, 61	4.50	1.59	49.18	0.44	0.65	0.31	0.08	n.d.	0.36	280	40	7	19	35	1370	7	17	39	5
36-2, 33	13.10	4.01	43.05	0.90	0.58	0.76	0.17	n.d.	1.07	1200	53	14	31	34	1300	14	35	32	23
37-1, 82	17.00	5.19	39.20	1.12	0.65	0.93	0.19	n.d.	1.14	1450	61	17	37	50	1150	17	54	39	36
37-4, 109	37.05	11.05	23.06	1.77	1.08	1.93	0.28	n.d.	2.23	780	160	34	83	64	970	26	37	26	63
39-2, 48	24.45	6.99	33.18	1.36	0.70	1.21	0.27	n.d.	1.45	1100	60	21	38	54	1100	13	31	24	48
43-3, 48	47.10	9.56	15.93	1.68	1.15	1.61	0.31	n.d.	2.47	750	94	34	61	49	600	21	35	29	60
44-1, 102	22.95	4.16	37.92	0.90	0.65	0.83	0.15	n.d.	0.93	1340	165	16	47	33	1060	19	16	23	16
45-2, 24	25.90	4.96	33.78	0.99	0.73	0.95	0.21	n.d.	1.19	1470	73	17	44	40	930	16	35	32	32
46-5, 59	26.25	5.94	31.15	1.29	0.75	1.01	0.25	n.d.	1.90	4100	87	21	58	18	950	31	97	47	37
47-6, 34	57.65	13.05	5.60	1.54	1.28	1.88	0.47	n.d.	3.28	1450	156	32	67	92	470	24	67	18	63
48-2, 111	58.25	14.64	9.09	1.67	1.30	2.28	0.46	n.d.	3.33	1720	95	35	50	61	410	17	53	12	89
49-1, 79	44.35	10.00	17.33	1.54	1.03	1.74	1.43	n.d.	2.38	2050	99	24	47	84	720	25	26	33	94
51-5, 74	46.65	10.86	18.82	1.59	1.18	2.01	0.35	n.d.	2.85	1680	170	25	51	69	650	19	63	18	68
52-1, 134	42.65	11.09	16.35	1.78	1.13	2.03	0.45	n.d.	3.00	1650	130	26	66	71	670	30	22	35	84
53-1, 12	53.50	10.58	18.57	1.68	1.30	1.74	0.30	n.d.	2.45	2250	170	33	53	47	530	20	40	21	53
55-2, 77	30.25	9.92	23.65	1.31	1.15	1.70	0.35	n.d.	2.60	1950	200	21	57	47	900	24	49	45	37
57-2, 30	42.10	12.75	22.21	1.65	1.15	2.13	0.57	n.d.	3.60	1350	170	32	48	98	460	18	18	26	95
59-1, 33	18.45	4.48	36.75	1.26	0.73	0.78	0.17	n.d.	1.53	3050	63	14	58	33	910	26	68	28	17
62-2, 12	28.65	6.50	28.61	0.95	1.18	1.38	0.22	n.d.	1.17	1750	154	11	36	42	840	9	92	26	53
64-2, 56	37.15	9.63	28.47	1.62	1.15	1.89	0.33	n.d.	2.01	630	140	19	66	68	500	13	77	16	53
65-1, 144	56.05	15.71	4.82	2.03	1.73	2.50	0.54	n.d.	5.05	380	102	24	150	110	460	32	68	26	105
68-2, 49	46.10	6.14	10.46	1.56	1.35	2.08	0.20	n.d.	19.70	500	120	10	44	46	190	6	8	32	210
69-1, 106	46.95	13.23	9.76	1.79	1.54	0.84	0.47	n.d.	3.00	370	83	18	29	52	470	5	23	46	63
74-1, 45	20.55	5.76	20.64	3.44	0.73	0.99	0.21	n.d.	14.03	3.73 <sup>a</sup>	280	12	31	43	270	19	72	39	37

<sup>a</sup>Data in %; rhodocrosite is present.

### Pleistocene

The marly calcareous ooze of Unit 1 contains illite, chlorite, irregular mixed-layers, relatively abundant associate primary minerals, accompanied by high values of SiO<sub>2</sub>, K<sub>2</sub>O, Ti, Cr, and low contents of Sr and Mn.

### Site 402; Figure 4; Table 2

#### Aptian, Albian

In the carbonaceous sediments of lithologic Units 3 and 2, smectite is abundant and well crystallized, followed by illite and kaolinite. Clinoptilolite occurs in Albian only, as at Site 400. The silty samples show an increase of illite and kaolinite content. Ca is high and variable. Pyrite is present especially in the lower Albian "black shales." Geochemical changes occur in upper Albian, where smectite is very abundant, manifested by stabilization of Al<sub>2</sub>O<sub>3</sub>/K<sub>2</sub>O ratio, low content of transition elements (Mn, Co, Cu), and local augmentation of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios.

#### Cenomanian

At level 9A-1, 40 cm, where the Albian/Cenomanian transition is located, clay minerals are rare; silicates

(cristobalite) are abundant, accompanied by relative high values of Co and MgO/K<sub>2</sub>O. Minimal values occur in Fe, Ni, Cu, Pb and V contents.

#### Middle Eocene

In the nannofossil chalk to siliceous marly nannofossil chalk of Sub-unit 1B, an increase of illite occurs upwards, whereas chlorite, irregular mixed-layers, kaolinite, quartz, and feldspars appear in the clay fraction. Ca and Mn increase; Al<sub>2</sub>O<sub>3</sub> is little present. Zeolites are absent and fibrous clays are absent or rare.

#### Pliocene, Pleistocene

The marly calcareous ooze of Sub-unit 1A, as at other sites, shows decreased smectite whereas primary or little weathered minerals such as illite, chlorite, mixed-layers, quartz, and feldspars increase.

## DISCUSSION

### General Mineralogical and Geochemical Evolution

No progressive and continuous change is observed along the mineral and chemical assemblages of the sediments

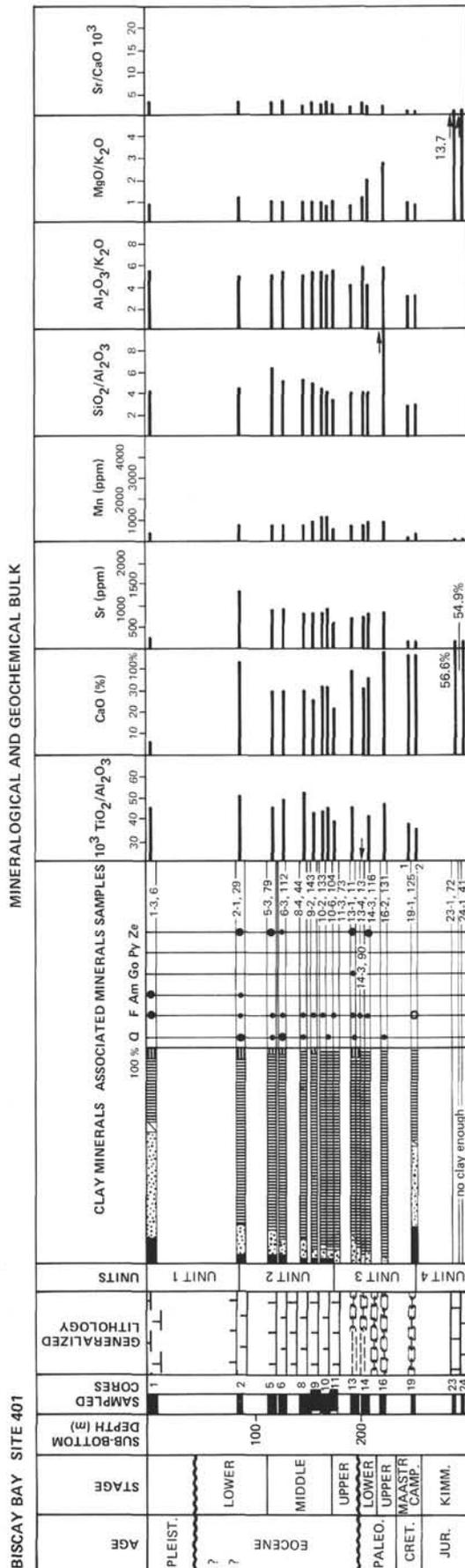


Figure 3. Site 401, clay mineralogy and bulk geochemistry.

from Upper Jurassic to Pleistocene recovered from Sites 399, 400, 401 and 402. This demonstrates the absence of diagenetic evolution associated with depth of burial and confirms the results obtained from other sites in the North Atlantic margins (von Rad and Rösch, 1972; Chamley and Giroud d'Argoud, in press; Chamley et al., in press; Pastouret et al., 1978, etc.).

From Cretaceous to upper Eocene the sediments are marked by an abundant smectite mineral phase associated with Al, Fe, Ti, V, Ca, Li. That phase is virtually independent of lithology, and is not related to volcanic materials or chemical sediments. An essentially detrital origin must be envisaged, which must have been derived either from ancient continental rocks subjected to erosion or newly formed continental soils. Both sources could have provided the sediment, but soils would most likely have been the principal one on account of the vulnerability of superficial formations and of the broad development of soils in Cretaceous depressed landscapes.

Such a mainly pedological origin of the smectites deposited in Biscay Bay suggests that the continental climate was warm and arid with alternating dry and wet seasons (Paquet, 1969). The detrital origin of smectite is supported by the data of accompanying rare earth elements of typical continental assemblage (analysis of C. Courtois, Paris).

From upper Eocene to Pleistocene the sediments show irregular but continuous increase in primary clayey minerals (illite, chlorite associated with  $Al_2O_3$  and  $K_2O$ ), together with irregular mixed-layers of low degradation and non-argillaceous detrital minerals (quartz, feldspars, and, in places, amphiboles). This change, which is particularly marked from upper Miocene into Pleistocene, suggests a general trend to climatic cooling which disfavors soil development and favors direct erosion of rocks. This conclusion agrees with the isotopic data of calcareous organisms for the Leg 48 sites (Létolle and Vergnaud-Grazzini, this volume). Another cause may have been the effect of Atlantic widening accompanied by development of meridian currents and the rejuvenation of European reliefs in the Paleogene with consequent increased continental erosion.

Marked geochemical changes occur at various boundaries such as between Aptian/Albian (Site 402), and Albian/Paleocene, Eocene/Oligocene, and lower-middle Miocene (Site 400). The changes vary in nature, but are not accompanied by dolomitization or phosphatization. In the hypothesis of a warm and wet climate, proposed on mineralogical grounds, margin tectonism should provoke organic or inorganic precipitation of phosphate in association with upwelling currents on the outer edge of continental shelf (Krauskopft, 1967). Phosphate being absent, the geochemical changes may be due to a climatic or current control.

Fibrous clay stages occur in the Albian (attapulgitite = palygorskite) as well as at Paleocene/Eocene boundary (attapulgitite, sepiolite) in the two deeper Sites, 400 and 401. Those minerals with short broken fibers, widely spread among detrital minerals in various reworked sediments, have a detrital origin. Their development is favored by a particularly warm, wet climate favoring ionic mobilization

TABLE 2  
Geochemical Data, Sites 401 and 402

Sample (Interval in cm)	%									ppm									
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Fe	Mn	Zn	Li	Ni	Cr	Sr	Co	Cr	Pb	V
<b>Site 401</b>																			
1-3, 6	54.00	13.17	7.31	2.03	1.60	2.36	0.59	n.d.	3.25	440	95	28	27	110	230	11	13	24	68
2-1, 29	13.00	3.03	43.38	0.78	0.80	0.63	0.15	n.d.	0.85	660	120	8	24	27	1350	10	12	31	63
5-3, 79	28.25	4.52	30.33	0.99	0.98	0.95	0.20	n.d.	1.21	760	210	11	24	41	920	7	24	23	68
6-3, 112	29.10	5.85	29.38	1.01	0.98	1.06	0.28	n.d.	1.49	780	110	11	25	56	900	7	15	15	84
8-4, 44	31.80	6.02	30.45	1.14	0.90	1.25	0.31	n.d.	1.70	670	71	12	32	31	810	14	16	26	42
9-2, 143	32.80	6.61	26.34	1.01	1.03	1.23	0.28	n.d.	1.65	1050	140	12	38	43	800	16	58	18	95
10-2, 133	24.70	5.73	31.76	0.94	0.80	1.10	0.24	n.d.	1.43	1100	100	9	53	44	870	52	170	25	115
10-6, 104	25.95	6.20	31.17	1.00	0.88	1.23	0.28	n.d.	1.45	1200	160	10	33	33	950	13	19	21	100
11-3, 73	34.50	10.51	22.35	1.65	1.35	1.91	0.40	n.d.	2.71	460	225	20	36	56	580	18	26	38	37
13-1, 71	16.25	4.12	38.83	0.82	0.80	1.03	0.18	n.d.	1.21	750	207	8	29	53	710	8	45	29	42
14-3, 90	32.30	8.44	30.92	1.65	0.94	1.48	0.05	n.d.	2.09	720	260	15	34	61	730	13	30	19	95
14-3, 116	20.35	5.19	36.05	2.65	0.96	1.29	0.21	n.d.	1.40	990	127	9	46	32	780	11	34	25	130
16-2, 131	14.85	1.51	48.97	0.72	0.70	0.26	0.07	n.d.	0.48	950	85	6	27	16	840	9	29	28	63
19-1, 125.1 <sup>a</sup>	7.10	2.72	46.17	0.86	0.39	0.94	0.10	n.d.	0.63	79	250	8	20	38	140	6	15	33	37
19-1, 125.2 <sup>d</sup>	9.45	3.50	45.82	0.86	0.50	1.13	0.12	0.83	1.35	300	140	11	26	31	160	6	28	32	53
23-1, 72	n.d.	n.d.	54.57	0.41	0.16	0.03	n.d.	n.d.	n.d.	16	72	n.d.	11	13	150	24	8	33	n.d.
24-1, 41	n.d.	n.d.	54.92	0.51	0.14	0.03	n.d.	n.d.	n.d.	16	82	n.d.	9	13	160	15	6	32	n.d.
<b>Site 402</b>																			
1-2, 12	54.55	9.33	10.18	1.85	1.48	2.10	0.41	n.d.	2.40	340	140	23	14	89	350	5	13	79	53
W1b	31.15	4.49	28.58	1.27	0.94	1.05	0.25	n.d.	1.25	140	93	17	12	56	920	2	20	21	53
W2b	13.95	2.68	41.28	0.91	0.84	0.61	0.14	n.d.	0.65	130	87	11	15	48	1420	7	16	28	37
3-1, 143	33.75	4.43	34.71	0.89	1.20	1.04	0.25	n.d.	1.19	150	72	15	13	57	720	4	13	240	47
5-1, 16	23.60	4.09	38.83	1.13	1.15	0.98	0.16	n.d.	1.13	860	76	19	25	54	1020	8	10	25	58
1-4, 118	32.90	5.90	32.39	1.16	0.98	1.18	0.27	n.d.	1.55	280	120	20	16	33	920	4	12	25	95
3-2, 129	37.85	4.70	30.68	1.08	1.05	0.96	0.20	n.d.	1.31	260	115	15	14	56	680	2	11	16	89
4-2, 81	46.50	6.09	23.19	1.19	1.20	1.28	0.23	n.d.	1.55	360	93	18	11	69	670	6	7	26	16
4-3, 12	45.10	7.97	23.93	1.24	1.23	1.35	0.28	n.d.	1.64	420	130	20	13	68	610	7	7	27	37
9-1, 38	51.15	1.06	29.64	0.57	0.35	0.29	0.07	n.d.	0.27	80	29	5	9	39	670	24	5	7	21
11-3, 140	48.45	8.86	22.26	1.25	1.24	1.43	0.33	n.d.	1.42	90	113	119	15	68	1340	5	8	31	63
13-2, 101	31.10	9.09	28.32	1.73	1.25	1.40	0.36	n.d.	2.19	170	97	26	31	53	1370	6	12	31	84
15-5, 75	46.25	11.10	20.50	1.17	1.04	1.68	0.46	n.d.	1.71	69	130	35	31	89	1220	6	13	32	95
19-4, 109	48.15	9.09	22.04	1.05	1.04	1.40	0.35	n.d.	2.50	112	118	31	32	79	1180	6	10	31	89
21-1, 90	45.85	14.70	18.70	1.20	1.04	1.61	0.50	n.d.	2.29	96	160	59	70	140	830	12	19	28	130
23-1, 90	29.65	4.02	35.92	0.96	0.68	0.93	0.15	n.d.	2.02	360	67	12	21	49	670	3	9	21	53
24-3, 94	40.20	11.69	21.19	1.26	1.10	1.45	0.46	n.d.	3.75	100	130	49	100	135	960	17	22	38	130
25-1, 125	37.65	12.52	26.08	1.35	1.08	1.35	0.47	n.d.	1.70	160	140	53	46	95	1180	5	19	37	130
30-2, 20	38.65	11.10	25.05	1.22	0.98	1.73	0.48	n.d.	2.48	130	130	41	33	84	960	n.d.	25	33	120
31-6, 78	43.00	16.24	21.20	1.18	0.95	1.80	0.68	0.20	2.22	250	110	73	54	125	690	12	23	37	130
32-4, 47	36.70	13.23	26.45	1.17	0.90	1.50	0.57	n.d.	2.13	420	130	64	43	97	880	10	22	39	120
33-4, 62	17.50	3.78	43.05	1.11	0.48	0.70	0.16	n.d.	1.10	570	120	11	34	28	460	22	11	33	42
35-5, 21	20.40	7.20	35.99	1.75	0.48	1.38	0.29	n.d.	1.94	320	120	42	34	49	670	21	16	32	79

during hydrolysis and crystallization in a basic chemical environment (Millot, 1964). An enrichment in Mn occurs from the first appearance of fibrous clays in Albian sediments to their quasi-disappearance after Oligocene time. The increase in Mn does not affect Site 402 which contains few or no fibrous clays. The Mn/fibrous clays relation, however, is not a direct one, because the sediments other than Albian and Paleocene/Eocene, poor in fibrous clays, are marked by manganese flow. It is, however, a deep water phenomenon because it is not encountered in the shallower Site 402.

### Local Diagenesis

Although the argillaceous and chemical mineral components do not show any geochemical evolution with the depth of burial, there is suggestion of local and temporary diagenetic manifestations in the sedimentary sequences of Sites 399 to 402.

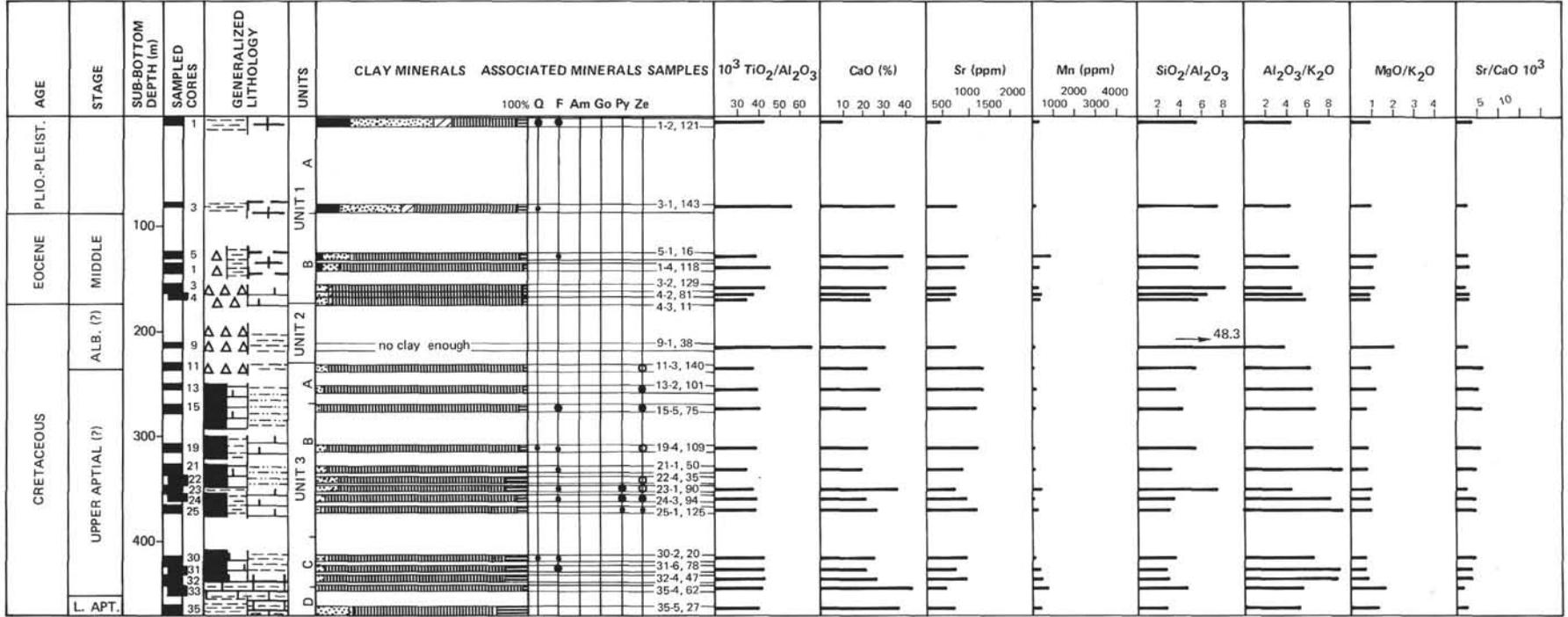
The black shales facies of Aptian and Albian age is not characterized by a clayey assemblage distinct from more oxidized facies such as the ones from Paleocene to Eocene. Smectite, in particular, which is often fragile in an organic medium (Sigl et al., 1978) is as abundant and well

crystallized in them as it is in other facies; irregular mixed-layers are rare or absent. There is consequently no perceptible modification of the argillaceous sequence in organic-rich surroundings which, themselves, show little change (Tissot et al., this volume). However, ionic mobilizations affect certain chemical elements such as Fe, Mn, and Ca, occurring in diffused concentrations, notably as carbonates (siderite, rhodochrosite, calcite, i.e., 400A-74-1, 95 cm). It is consequently probable that the black shales facies, which has no effect on clay mineralogy, has a minor diagenetic influence on the dissolution, diffusion, and re-precipitation of carbonates and of some other minerals. Organic acids and decrease of the redox potential in specific zones (i.e., immediately in the neighborhood of black shales) favor Fe and Mn dissolution in bivalent state, and their precipitation in carbonate state when the precedent effects disappear.

No evidence of *in-situ* modification of minerals from volcanic origin exists in northern Biscay Bay. Although smectite and fibrous clays are independent of lithology and petrography, the zeolites and cristobalite encountered may have resulted from such an evolution. There is, however, no evidence that they are not associated with typically volcanic or hydrothermal mineral/geochemical components.

BISCA Y BAY SITES 402 AND 402A

CLAY MINERALOGY AND BULK GEOCHEMISTRY



When the ratio is superior to the limit, this numerical value is indicated.

CLAY MINERALS: C CHLORITE K KAOLINITE  
 I ILLITE ROUGH VALUE (Low or very low clay content)  
 ML MIXED LAYERS ATTAPULGITE  
 SM SMECTITE SEPIOLITE

ASSOCIATED MINERALS:  
 Q = Quartz ● very rare  
 Am = Amphiboles ● abundant  
 Py = Pyrite ● rare  
 F = Feldspars ○ very abundant  
 Go = Goethite  
 Ze = Zeolite

GEOCHEMICAL ANALYSES: 1/2: Two analyses for the same sample

Figure 4. Site 402, clay mineralogy and bulk geochemistry.

The fibrous clays, having a detrital aspect, probably originated in a chemically basic environment (Millot, 1964) in semiclosed marginal basins in Albian and Paleocene/Eocene times. Sediments formed in such basins were partially reworked owing to the instability of the subsident margins and thence deposited in the open oceanic environment. Some of the clinoptilolite and cristobalite may have had a similar origin because they too can form in basic and confined sedimentary environments and under conditions like those governing the formation of some smectites, attapulgites, and sepiolites (Sommer, 1972; Weaver and Beck, 1977). The increase in zeolites in Site 402, which is the innermost and the least deep on the European margin, seems to favor this possibility. It is probable, however, that some of the zeolites and cristobalite originated *in situ* under conditions of dissolution and recrystallization of free silica and associated cations by local diagenesis (Wise and Kelts, 1972; Stonecipher, 1976; Mitsui and Taguchi, 1977; Kagami, this volume).

#### Comparison Between the Three Sites of North Biscay Bay

From the shallowest Site 402 to the deepest Sites 399 and 400 an increase occurs in relatively small sized minerals of high buoyancy potential (smectite, fibrous clays) to the detriment of more rapidly deposited minerals (illite, chlorite, kaolinite, feldspars) (Figure 5). This indicates a differential settling offshore evoking a deltaic environment *s. l.* (Millot, 1964; Chamley, 1971; Gibbs, 1977), which is in agreement with other sedimentological observations (Auffret, this volume). Another cause of the scarcity of fibrous clay minerals at Site 402 could be a supply by relatively deep meridian currents originating from lower latitudes where these minerals are abundant on continents (Millot, 1964; Chamley, 1971; Chamley et al., in press). The difficulty to supply these minerals from the adjacent land masses must also be envisaged: fibrous minerals are poorly represented in the Armorican basins (Estéoule-Choux, 1967), and the flat morphology of the large Basin of Paris where they are frequent (Sommer, 1969; Trauth et al., 1969; Trauth, 1974) does not favor their erosion and their transport toward the open sea.

From Site 402 to Site 400, the differentiation between the three sites also manifests itself from a chemical point of view by decrease of carbonates and increase of transition elements (Mn).

### ROCKALL PLATEAU — RESULTS

#### Site 403; Figure 6; Table 3

##### Upper Paleocene (?), Lower and Middle Eocene

Lithologic Units 3 and 2 consist of arkosic sandstone, lapilli tuff and conglomerate, tuffaceous mudstone, and siliceous nannochalk. Smectite is predominant and well crystallized. Illite and kaolinite locally occur in traces. The geochemistry is characterized by the predominance of the siliceous phase (Si, Al, Fe, Mg, Ti) in contrast with the calcitic one (Ca, Sr). An exception exists in -40-1, 5 cm where Ca is present in noticeable amounts, associated with Mn and  $P_2O_5$ . The ratios are as follows:  $SiO_2/Al_2O_3$  low,  $MgO/K_2O$  and  $TiO_2/Al_2O_3$  high, Sr/CaO unstable. The lower Eocene sediments are rich in Mg, Fe, V, and Cr.

Alkaline and reducing sediments are suggested by the presence of rhodochrosite, carbonate-apatite, calcite, siderite, and glauconite.

#### Oligocene

In the upper part of lithologic Unit 2 the clay fraction is poor; slight increase in illite and kaolinite and the appearance of chlorite, zeolite, and irregular mixed-layers occur. Mn and  $Al_2O_3/K_2O$  and  $TiO_2/Al_2O_3$  ratios decrease, whereas that of  $SiO_2/Al_2O_3$  increases; Sr carbonate and minor phosphate appear.

#### Upper Miocene

The base of Unit 1 (nannofossil ooze, marly ooze, calcareous mud) is poor in the clay fraction, and consists chiefly of smectite. The chemical composition is marked by high contents of Ca and Sr, and a decrease of the Si phase and Mg. A major change occurs between -9-5, 80 cm and -9-4, 129 cm, with abrupt decrease of  $Al_2O_3$ , Si, Na, and quartz contents.

#### Pliocene, Pleistocene

In the upper part of Unit 1, a marly foram nannofossil ooze, the clay fraction becomes abundant and is marked by a steady upward increase in illite, chlorite, irregular mixed-layers, quartz, feldspars, amphiboles.  $SiO_2$  also increases, whereas a general decrease affects CaO, Sr,  $SiO_2/Al_2O_3$ ,  $TiO_2/Al_2O_3$ , and  $MgO/K_2O$ .

#### Site 404; Figure 7; Table 3

The same mineralogical and geochemical successions occur as in Site 403. A local enrichment in Mn (rhodochrosite) and  $P_2O_5$  (apatite) contents is noted in Eocene sediments.

#### Site 405; Figure 8; Table 4

Although sparsely sampled, the site shows results close to those obtained for Site 406. Sediments of lower Eocene are peculiarly rich in  $SiO_2$  and also contain fairly high amounts of Mn.

#### Site 406; Figure 9; Table 4

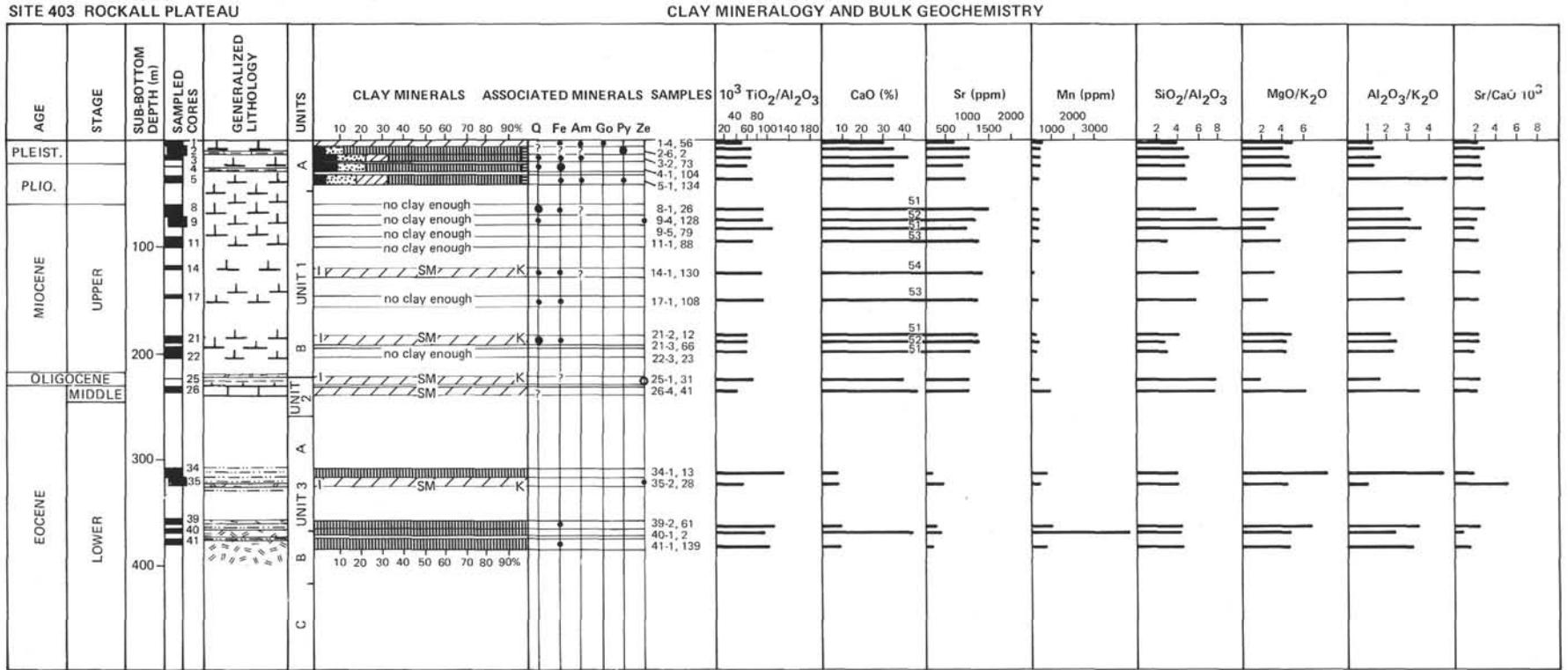
#### Eocene

Calcareous claystone, followed upward by marly limestone and siliceous and/or calcareous chalk, constitutes Unit 5 and the base of Unit 4.

The clay mineral is nearly exclusively smectite, and is often accompanied by cristobalite. A geochemical break occurs between lower Eocene and middle/upper Eocene sediments (Cores 45 to 42); the lower Eocene has (1) high values of Si, Sr/CaO,  $Al_2O_3/K_2O$ ,  $TiO_2/Al_2O_3$ , (2) moderate to low Ca content, (3) locally, simultaneous abundance of Fe and Mg (presence of hypersthene in -43-6, 47 cm). Middle/upper Eocene sediments are high in carbonates, show a decrease of the above-mentioned ratios, an end to Mn metallization, and simultaneous disappearance of high Fe and Mg values.

#### Oligocene, Early Miocene

In the calcareous chalk of the top of Unit 4 and in the siliceous calcareous chalk and calcareous diatomite of Unit



When the ratio is superior to the limit, this numerical value is indicated.

CLAY MINERALS:

- C ■ CHLORITE
- I ■ ILLITE
- ML ■ MIXED LAYERS
- SM ■ SMECTITE
- K ■ KAOLINITE
- ROUGH VALUE (Low or very low clay content)

ASSOCIATED MINERALS:

- Q = Quartz
- Am = Amphiboles
- Py = Pyrite
- Go = Goethite
- Ze = Zeolite
- F = Feldspars
- very rare
- abundant
- rare
- very abundant

1: Two analyses for the same sample.

Figure 5. Site 403, clay mineralogy and bulk geochemistry.

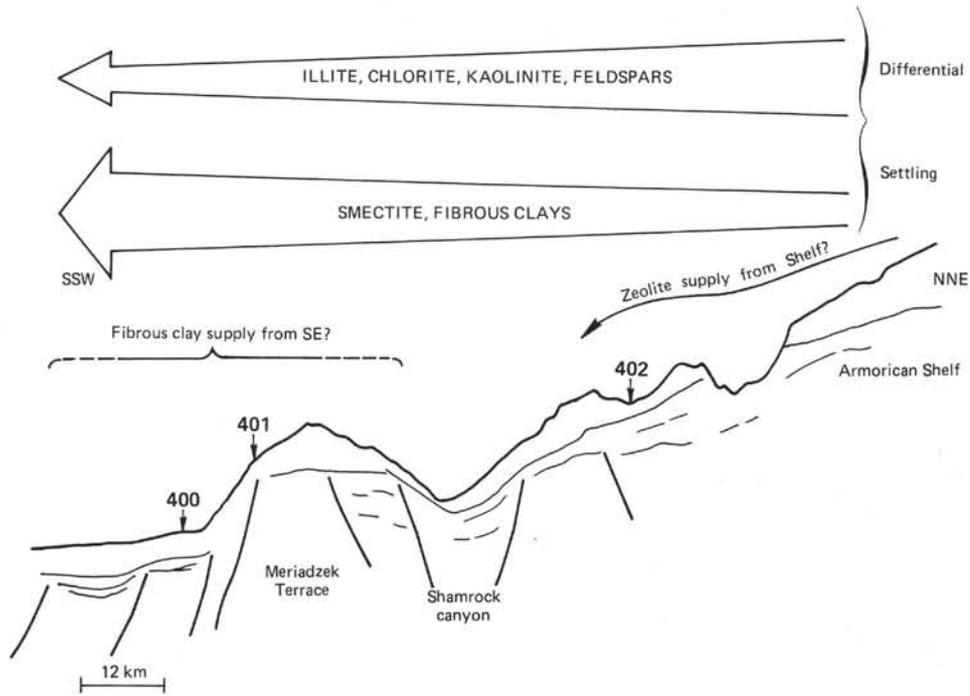


Figure 6. Origin and distribution of clay fraction components on the north of Biscay Bay margin.

TABLE 3  
Geochemical Data, Sites 403 and 404

Sample (Interval in cm)	%										ppm									
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Fe	Mn	Zn	Li	Ni	Cr	Sr	Co	Cu	Pb	V	
<b>Site 403</b>																				
1-4, 67	29.15	7.32	30.85	1.78	3.18	1.50	0.36	n.d.	2.09	560	110	16	34	65	720	14	38	23	89	
2-6, 3	22.90	4.96	34.67	1.61	2.18	1.28	0.35	n.d.	2.22	450	75	14	29	46	1030	19	48	46	79	
3-2, 74	14.30	2.78	41.83	0.98	1.53	0.60	0.19	n.d.	0.94	510	54	5	18	30	1050	11	22	26	30	
4-1, 105	22.60	4.80	34.65	1.28	1.73	1.00	0.28	n.d.	1.45	380	54	10	25	26	900	12	24	21	45	
5-1, 135	20.75	4.38	35.00	1.31	1.65	0.93	0.29	n.d.	1.62	430	66	9	26	38	970	16	25	27	51	
8-1, 27	3.25	0.58	50.58	0.43	1.00	0.16	0.05	n.d.	0.29	330	33	2	19	25	1500	13	14	41	11	
9-4, 129	3.55	0.46	52.15	0.45	0.90	0.15	0.04	n.d.	0.28	460	53	3	27	24	1220	15	14	31	5	
9-5, 80	3.70	0.35	50.58	0.52	1.08	0.15	0.04	n.d.	0.36	390	42	3	26	25	1020	14	13	32	9	
11-1, 89	1.70	0.59	53.38	0.45	0.93	0.16	0.04	n.d.	0.31	400	34	3	21	19	1300	16	14	32	9	
14-1, 131	2.60	0.44	53.90	0.37	0.93	0.14	0.04	n.d.	0.18	210	30	2	15	16	1350	11	14	32	8	
17-1, 109	1.90	0.33	52.85	0.35	0.90	0.13	0.03	n.d.	0.15	360	37	1	16	27	1230	11	12	41	11	
21-2, 13	3.75	0.90	51.45	0.40	0.98	0.19	0.05	n.d.	0.31	280	47	3	25	23	1240	15	8	36	13	
21-3, 67	1.90	0.65	51.98	0.36	0.75	0.15	0.04	n.d.	0.25	400	46	2	18	27	1300	11	13	37	15	
22-3, 24	3.05	0.99	50.75	0.50	0.94	0.23	0.06	n.d.	0.37	280	34	3	24	29	1030	15	24	33	9	
25-1, 32	16.35	2.13	40.36	1.74	1.50	1.11	0.14	0.89	2.48	380	140	20	89	52	1030	35	28	33	79	
26-4, 43	8.95	1.18	45.50	0.65	1.25	0.19	0.05	n.d.	0.61	960	46	8	31	15	1050	13	16	44	4	
34-1, 15	48.50	48.50	7.82	6.70	3.55	1.50	1.55	n.d.	7.80	800	99	22	63	140	160	52	100	4	320	
35-2, 28	56.80	14.29	8.93	3.32	3.68	3.25	0.65	n.d.	4.33	470	71	33	38	130	460	21	28	9	120	
39-2, 63	49.50	11.57	10.00	5.75	2.95	1.73	1.30	n.d.	7.00	1010	120	27	47	110	240	36	61	7	270	
40-1, 5	12.75	3.07	42.64	1.48	0.88	0.65	0.28	n.d.	2.14	4750	86	8	24	26	330	18	17	26	68	
41-4, 140	47.45	10.75	8.85	7.31	4.45	2.38	1.04	n.d.	9.68	750	110	7	56	110	140	44	94	7	300	
<b>Site 404</b>																				
11-2, 76	7.40	1.32	46.20	0.59	1.45	0.34	0.10	n.d.	0.47	410	34	2	17	33	1120	10	18	39	12	
4-2, 102	1.80	0.63	52.85	0.42	0.93	0.14	0.04	n.d.	0.25	400	36	3	21	23	1190	12	18	33	12	
7-1, 20	57.50	4.96	16.42	1.78	2.60	0.65	0.64	n.d.	2.88	450	84	24	45	79	330	16	35	20	170	
10-1, 65	47.40	6.61	21.67	3.66	2.30	0.43	1.05	n.d.	3.70	950	79	18	52	91	450	33	44	14	190	
16-1, 115	43.20	8.27	20.61	4.70	2.28	1.30	0.63	n.d.	4.55	670	170	17	89	130	460	35	47	17	195	
17-5, 18	31.15	6.38	27.11	3.83	1.58	1.00	0.19	1.13	5.00	9250	116	15	36	57	180	29	65	11	190	
21-2, 132	25.25	4.72	32.51	3.66	1.73	1.08	0.15	3.72	3.80	7300	91	15	44	71	310	32	34	18	130	

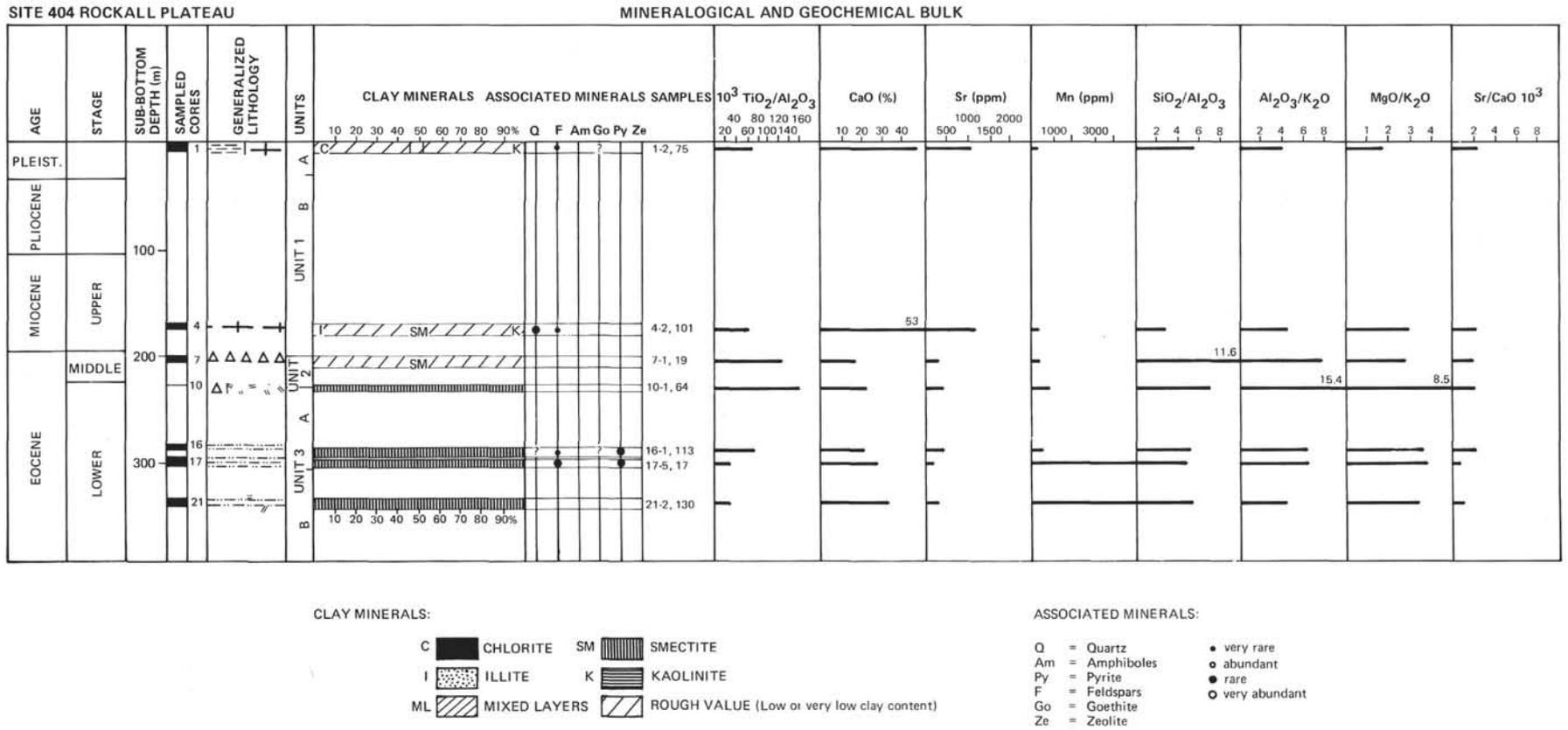
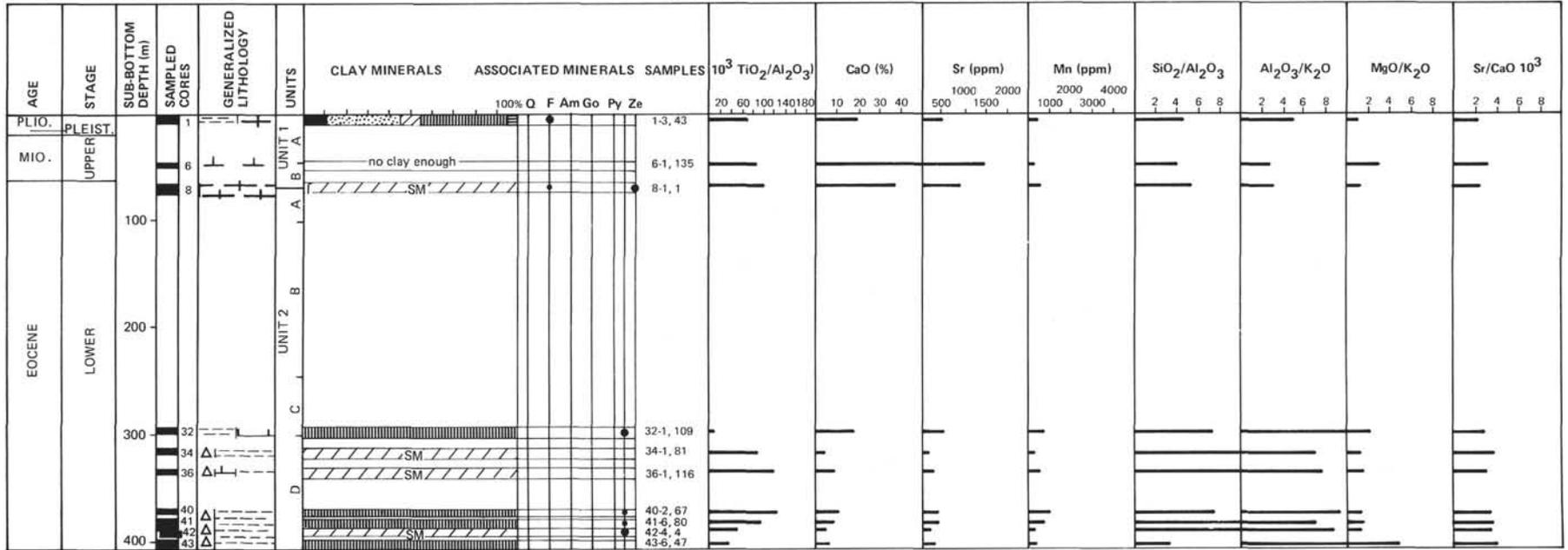


Figure 7. Site 404, clay mineralogy and bulk geochemistry.

SITE 405 ROCKALL PLATEAU

CLAY MINERALOGY AND BULK GEOCHEMISTRY



CLAY MINERALS:

- C ■ CHLORITE
- I ■ ILLITE
- ML ▨ MIXED LAYERS
- SM ▨ SMECTITE
- K ▨ KAOLINITE
- ▨ ROUGH VALUE (Low or very low clay content)

ASSOCIATED MINERALS:

- Q = Quartz
- Am = Amphiboles
- Py = Pyrite
- F = Feldspars
- Go = Goethite
- Ze = Zeolite
- very rare
- abundant
- rare
- very abundant

Figure 8. Site 405, clay mineralogy and bulk geochemistry.

TABLE 4  
Geochemical Data, Sites 405 and 406

Sample (Interval in cm)	%									ppm									
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Fe	Mn	Zn	Li	Ni	Cr	Sr	Co	Cu	Pb	V
<b>Site 405</b>																			
1-3, 43	39.55	8.50	19.32	1.87	2.48	1.73	0.45	n.d.	2.26	480	42	15	33	73	450	15	23	33	58
6-1, 139	1.40	0.35	49.70	0.37	0.68	0.13	0.03	n.d.	0.20	270	5	2	40	35	1470	16	6	35	n.d.
8-1, 1	14.70	2.68	37.63	1.12	1.48	0.85	0.28	n.d.	2.57	600	52	9	51	53	900	16	18	31	29
32-1, 109	53.15	7.32	18.33	1.74	1.85	0.75	0.09	n.d.	3.50	770	180	7	45	48	510	39	72	6	120
34-1, 81	78.70	2.78	4.55	0.54	0.75	0.40	0.25	n.d.	1.35	270	n.d.	2	79	61	170	52	4	6	21
36-1, 116	70.40	3.56	8.68	0.75	1.03	0.46	0.43	n.d.	2.06	540	160	4	49	64	260	12	16	27	63
40-2, 67	55.60	7.44	11.03	1.45	1.73	0.79	0.94	n.d.	4.00	1080	47	9	41	73	380	12	36	17	280
41-6, 80	67.45	4.37	8.40	1.01	1.73	0.62	0.42	n.d.	2.66	730	34	5	59	62	310	21	46	13	47
42-4, 4	80.45	2.56	4.62	0.67	0.86	0.50	0.23	n.d.	1.87	290	160	4	280	57	160	49	29	30	32
43-6, 47	50.60	15.12	6.82	2.98	2.45	0.60	0.55	n.d.	4.95	340	16	17	61	55	270	n.d.	35	10	100
<b>Site 406</b>																			
1-1, 32	41.65	12.99	12.71	2.53	2.49	2.58	0.75	n.d.	3.57	510	74	29	38	96	320	20	25	29	130
2-4, 125	54.75	14.23	5.43	2.20	2.49	2.73	0.75	n.d.	4.31	360	49	32	59	91	290	19	20	21	150
4-1, 70	1.10	0.32	52.50	0.31	0.76	0.13	0.03	n.d.	0.17	320	15	1	44	34	1480	12	6	33	11
7-1, 30	4.20	1.15	49.70	0.41	0.70	0.28	0.07	n.d.	0.39	540	7	4	46	42	1500	14	4	35	16
8-5, 56	3.90	1.02	48.37	0.37	0.70	0.24	0.06	n.d.	0.40	600	14	4	50	49	1420	17	12	35	n.d.
10-1, 24	2.45	0.60	49.70	0.33	0.65	0.16	0.04	n.d.	0.24	510	6	3	49	17	1430	15	8	63	11
13-2, 71	3.15	0.91	48.65	0.36	0.63	0.19	0.04	n.d.	0.30	550	6	4	51	48	1480	14	11	36	n.d.
14-1, 117	6.05	1.56	45.33	0.46	0.64	0.34	0.08	n.d.	0.50	490	6	6	55	39	1530	16	7	33	16
16-1, 85	2.50	0.58	50.58	0.32	0.63	0.16	0.03	n.d.	0.24	420	6	3	42	25	1450	14	7	34	5
22-1, 25	6.40	1.07	46.55	0.41	0.81	0.24	0.06	n.d.	0.49	1200	35	4	55	38	1490	13	9	34	5
23-2, 130	12.35	2.31	41.65	0.62	0.84	0.46	0.11	n.d.	0.83	1000	62	9	63	48	1540	18	30	32	16
24-1, 95	26.50	5.16	28.60	1.20	1.11	1.04	0.28	0.30	1.85	280	150	26	95	58	1200	32	25	26	63
27-1, 20	48.45	0.89	23.00	0.29	1.11	0.20	0.04	n.d.	0.30	68	8	2	15	26	830	4	1	25	n.d.
28-2, 7	41.35	0.92	27.13	0.32	1.91	0.20	0.04	n.d.	0.31	97	23	3	19	48	900	4	6	18	n.d.
29-4, 130.1 <sup>a</sup>	27.50	1.75	34.65	0.53	0.98	0.38	0.08	n.d.	0.67	270	120	9	36	27	1080	7	20	48	32
29-4, 130.2 <sup>a</sup>	32.95	2.60	29.22	0.65	1.28	0.49	0.12	n.d.	0.92	210	110	5	55	47	1230	9	26	32	37
30-2, 14	13.70	1.42	43.05	0.47	0.86	0.31	0.08	n.d.	0.48	310	73	5	44	29	1090	9	4	26	16
31-3, 55	11.30	1.60	43.75	0.56	0.78	0.30	0.08	n.d.	0.57	570	116	5	66	27	1110	12	35	33	16
32-4, 70	19.00	2.24	35.70	0.66	1.05	0.40	0.13	n.d.	0.86	600	45	9	37	35	1050	9	10	25	16
33-4, 67	13.50	2.92	39.55	0.85	0.63	0.46	0.15	n.d.	1.12	610	19	8	52	47	1100	13	18	28	21
35-2, 30	5.50	0.93	49.00	0.41	0.46	0.19	0.05	n.d.	0.45	680	16	3	49	21	1270	13	2	33	5
36-2, 53	18.25	3.32	36.93	1.09	0.79	0.68	0.19	n.d.	2.29	520	67	8	88	55	890	21	6	27	42
37-3, 137	5.70	0.96	47.95	0.46	0.40	0.21	0.04	n.d.	0.52	660	65	66	32	24	1030	11	8	32	16
38-3, 77	12.35	0.83	43.58	0.50	0.40	0.14	0.05	n.d.	0.45	570	8	4	32	40	710	11	9	28	n.d.
39-4, 13	32.85	4.13	29.61	1.04	0.71	0.56	0.18	0.17	1.11	380	130	130	110	47	770	17	52	22	42
40-3, 33	13.85	1.75	42.80	0.58	0.43	0.24	0.07	n.d.	0.60	540	92	68	43	28	920	8	16	32	21
41-4, 80	8.15	1.50	46.37	0.53	0.38	0.23	0.07	n.d.	0.60	630	123	3	45	25	1130	12	14	25	21
42-3, 101	9.45	1.00	45.50	0.41	0.46	0.15	0.06	n.d.	0.42	740	42	2	34	24	1090	12	11	32	5
45-4, 38	7.65	1.06	46.37	0.41	0.50	0.16	0.05	n.d.	0.28	3500	62	2	46	14	1210	9	18	140	16
46-1, 8	40.30	8.27	14.88	2.49	1.73	1.23	0.64	n.d.	7.14	930	74	27	68	58	1000	26	34	23	205
47-1, 63	39.20	9.21	19.43	1.82	1.45	0.78	0.71	n.d.	3.60	1400	48	12	70	91	940	31	68	25	170
48-1, 40	39.80	8.74	17.50	1.64	1.39	0.70	0.71	n.d.	3.62	1500	86	7	58	97	930	25	82	25	130
49-1, 75	37.05	8.26	22.33	1.76	1.23	0.61	0.48	n.d.	3.50	1600	135	6	76	91	980	35	86	64	120
49-2, 31	37.95	7.32	21.18	1.45	1.19	0.63	0.67	n.d.	3.29	3400	64	5	63	42	930	23	53	28	97

<sup>a</sup> Heterogeneous sample, two analyses.

3, clay is rare and is characterized by smectite, locally accompanied by traces of illite and kaolinite. The geochemistry is heterogeneous, with a high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio due to free silica (diatoms); transition elements disappear.

#### Middle and Upper Miocene

The nannofossil chalk and nannofossil ooze of Unit 2 contain few clay minerals. Smectite is in excess of chlorite and illite, but the latter minerals increase upwards. The rather homogeneous chemical composition is marked by little SiO<sub>2</sub> and Mn, and much carbonate. A local phosphate occurrence and an increase of Mn content occurs at the early/middle Miocene boundary.

#### Pliocene, Pleistocene

In the marly foraminiferous nannofossil ooze of Unit 1 the clay assemblage becomes diversified and includes chlorite, illite, irregular mixed-layers (chiefly illite-

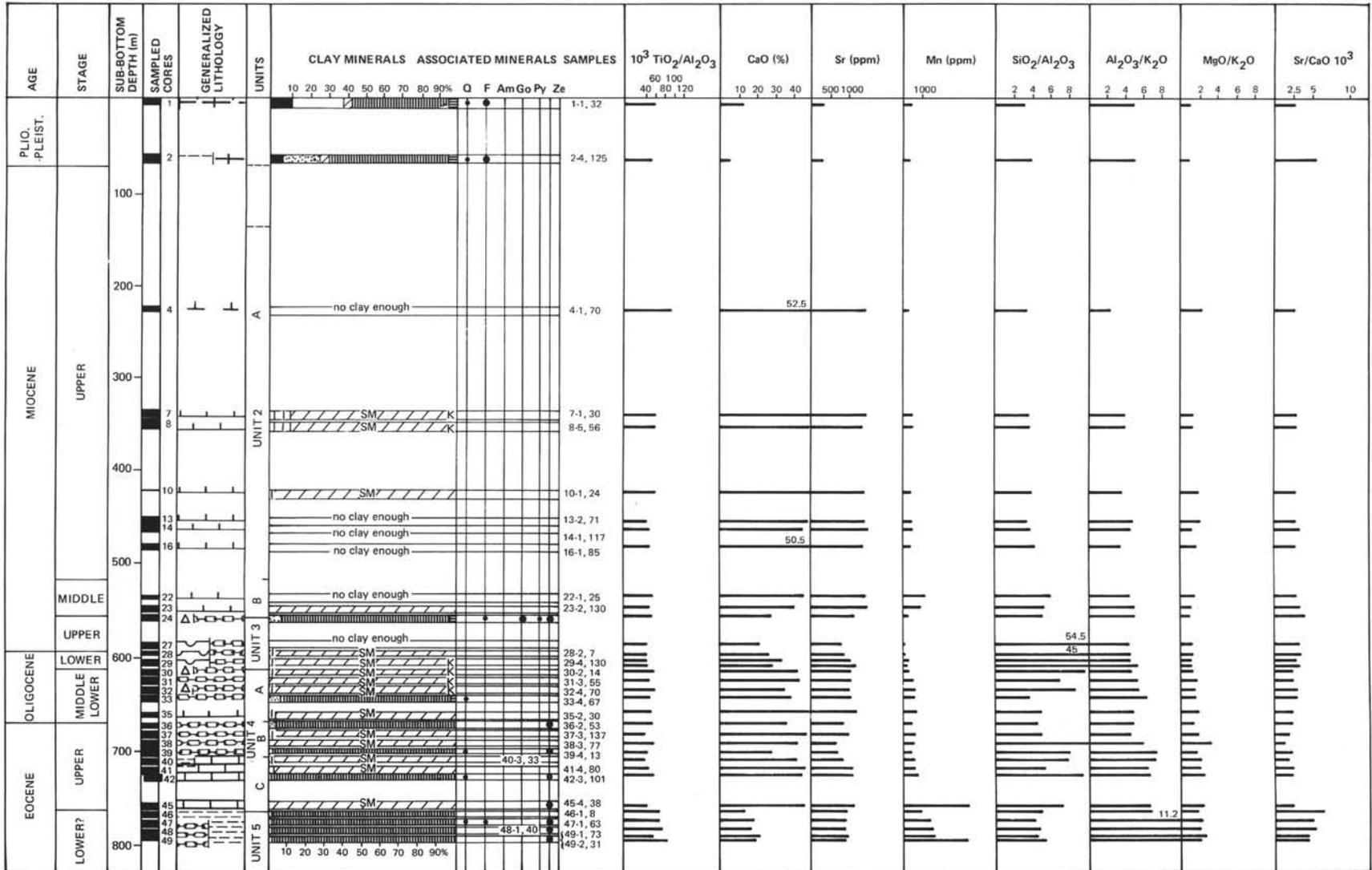
smectite, little chlorite-smectite), smectite (fairly well crystallized), kaolinite, accompanied by quartz and feldspars. SiO<sub>2</sub> increases whereas CaO decreases.

#### DISCUSSION

Because of the limited sampling of Sites 404 and 405, the following discussion is based mainly on data from Sites 403 and 406.

#### Origin of the Principal Mineral and Chemical Phases

In the sediments deposited from Paleocene to lower Miocene time nearly all of the clay is usually well-crystallized smectite. Fe and Mg are relatively abundant and are commonly associated with cristobalite/tridymite and sometimes zeolites which suggest a source rich in the vitreous and mineral elements of volcanic origin (Harrison et al., this volume; Harding, this volume; Latouche, this volume; see also Site Chapters, this volume). Fe and Mg do not generally occur as oxides, sulfides,



CLAY MINERALS:

- C CHLORITE
- I ILLITE
- ML MIXED LAYERS
- S SMECTITE
- K KAOLINITE
- ROUGH VALUE (Low or very low clay content)

ASSOCIATED MINERALS:

- Q = Quartz
- Am = Amphiboles
- Py = Pyrite
- F = Feldspars
- Go = Goethite
- Ze = Zeolite
- very rare
- abundant
- rare
- very abundant

GEOCHEMICAL ANALYSES: 1/2: Two analyses for the same sample

Figure 9. Site 406, clay mineralogy and bulk geochemistry.

carbonates, or ferromagnesian sandy minerals and consequently are incorporated mainly in the smectite lattice as shown by differential thermal analysis curves. Such smectites suggest, at least partially, a volcanic origin. Such a hypothesis is supported by titanium enrichment (Rankama and Sahama, 1950), especially in the Eocene sediments of the Rockall area (Figure 10). Furthermore, the rare-earth elements examined by C. Courtois (University of Paris XI) are marked by a noticeable poverty in light elements (lanthanum, cerium, neodyme, samarium) in comparison to heavy elements (europium, terbium, ytterbium, lutetium). Such a composition, which is not in equilibrium with that of seawater and cannot be of purely sedimentary origin, is close to the composition of a tholeiitic basalt. It is therefore highly probable that the smectite and other associated chemical elements resulted from the transformation of volcanic ash and glass rather than being derived as detritus from the weathering of sedimentary rocks.

An indeterminable part of the smectite, however, may be of remote origin, either pedologic or sedimentary, as shown by the occasional presence of detrital minerals such as kaolinite, illite, and chlorite. A non-volcanic origin is probable in those Eocene and Oligocene levels that are marked by a decrease in Fe, Mg, Ti (Table 4).

Whether the smectite formed in a submarine or subaerial environment is questionable. The composition of the rare-earth elements (in Sample 405-43-6, 47 cm) is not in equilibrium with that of typical seawater which does not favor a submarine genesis. The active volcanism during the Paleogene, and particularly in the Eocene, probably

produced volcanic areas exposed to subaerial alteration. The authors are inclined to favor a subaerial genesis for the smectite, followed by its erosion and deposition in the sea along with the other components, including pelagic carbonates, silica, and/or volcanoclastics.

Sites 405 and 406 are marked generally by more carbonates, less clay, and larger amounts of smectite and cristobalite/tridymite than at Sites 403 and 404. This suggests that sedimentation was generally more pelagic in the Paleogene in the Site 405-406 area than at Sites 403 and 404. In Figure 11 the mean compositions for Sites 403 and 404 are more closely related to the MgO and F<sub>2</sub>O<sub>3</sub> poles than are those of Sites 405 and 406; this suggests closer proximity of Sites 403 and 404 to volcanic sources which is the sign of a strong volcanic influence.

**Climates and Currents**

Mineralogical and chemical changes, announced in Oligocene time, develop in the Miocene and particularly in the Pleistocene: primary detrital minerals or those from moderate continental alteration (mixed-layers) gradually replace smectite whereas carbonates and associate chemical elements increase. That change indicates a decrease in volcanic activity accompanied by a general modification of climatic conditions. The step-by-step cooling took place from late Paleogene onwards (see also Létolle and Vergnaud-Grazzini, this volume) and favors direct continental erosion of rocks, and the development of large meridian currents and calcareous planktonic communities. Pelagic sedimentation developed after the sinking of

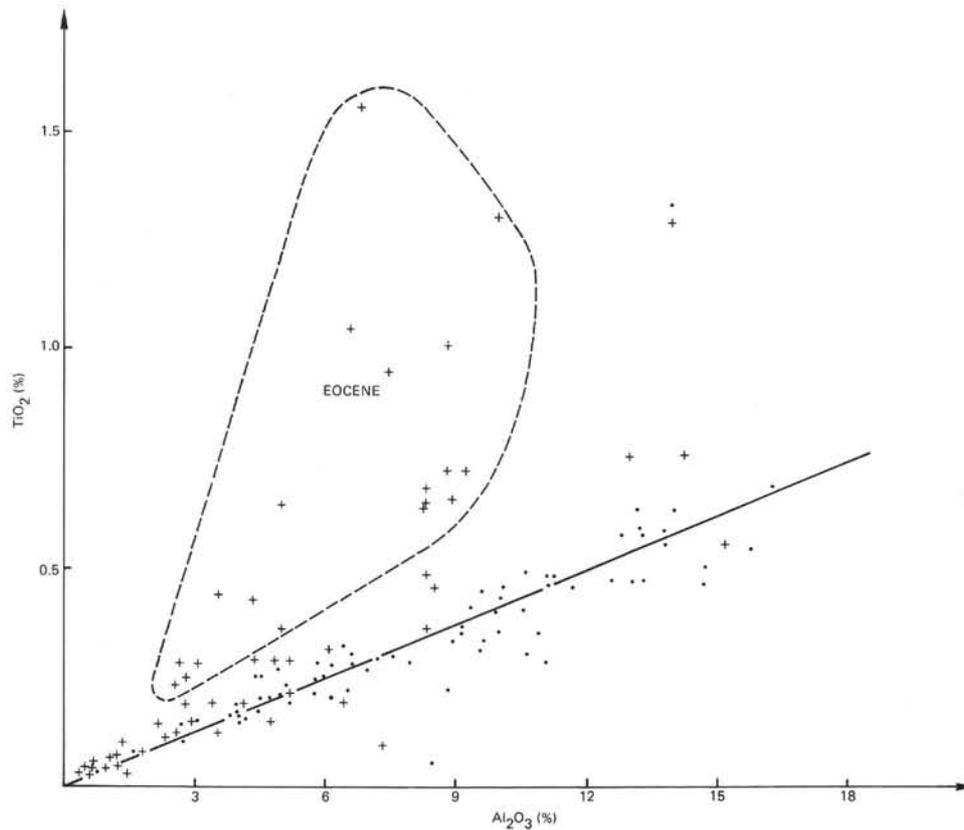


Figure 10. Rockall Plateau and Biscay Bay:  $TiO_2 = f(Al_2O_3)$ .

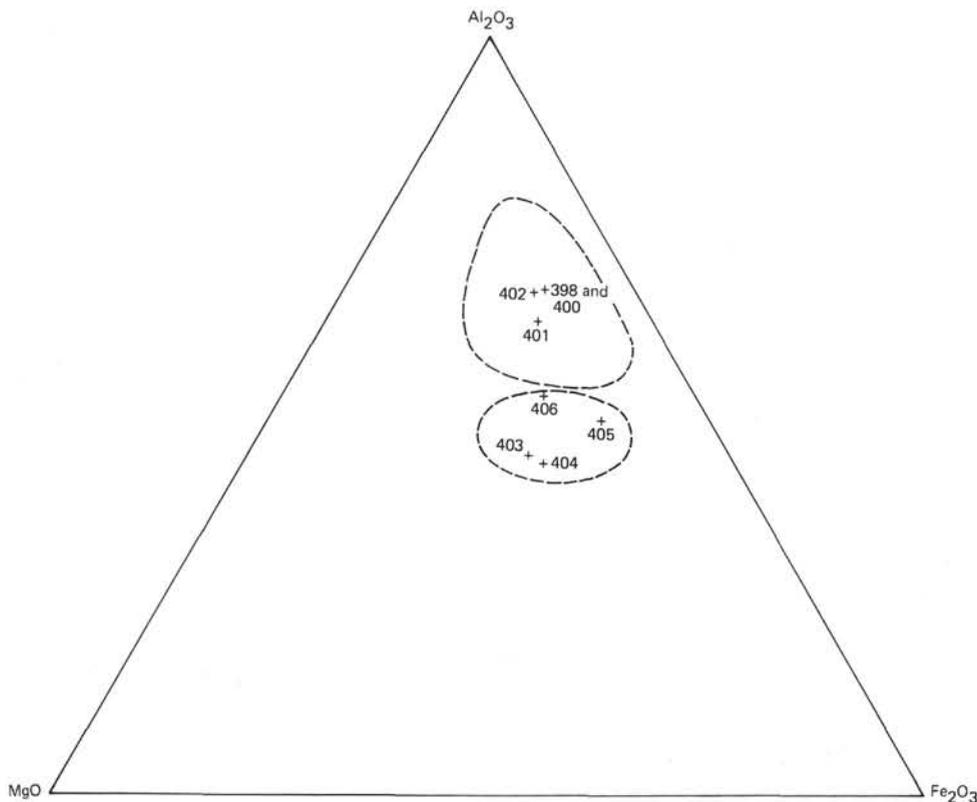


Figure 11. Geochemical average data of each Leg 48 site.

emerged volcanic areas located between Greenland and Europe, which followed the major phase of the opening of Northeast Atlantic (Laughton, Berggren et al., 1972). In the Pleistocene the spread of glaciers provoked an increase in terrigenous supplies which diluted the planktonic carbonates.

### GEOGRAPHICAL COMPARISONS—CONCLUSIONS

**Comparison Between North and South Biscay Bay (Leg 48, Sites 399, 400, 401, 402; Leg 47B, Site 398, Chamley et al., 1978)**

#### Common Characteristics

1) Late Cretaceous to Paleogene sediments in both areas contain abundant crystallized aluminiferous smectite with isochronous quantitative variations. The smectite was probably derived from a deeply weathered continental source subject to a warm and arid climate with alternating wet and dry seasons.

2) Two intervals of fibrous clay with associated Mn deposition occur in both areas in Albian time (attapulgite = palygorskite) and at the Paleogene/Eocene boundary (attapulgite, sepiolite). Derivation was probably from a chemically basic setting (Millot et al., 1957; Millot, 1964) established on the continental margin under hydrolysing climates. Simultaneous development of fibrous clays is known from the South Atlantic (Chamley, unpublished data, DSDP Leg 40). Fibrous clays in all these DSDP sites are detrital and reworked due to the marginal instability.

3) Abrupt mineralogical change occurs in the Campanian/Maestrichtian period, manifested by a sudden increase in the quantity of primary minerals. The cause could be a major stage in the North Atlantic widening (Laughton, Berggren et al., 1972; Berggren and Hollister, 1974), favoring the mineralogical supply from high latitudes. Additional causes could be a pre-alpine rejuvenation and/or a continental cooling.

4) Irregular increase in primary minerals and irregular mixed-layers from Oligocene upwards, in relation with a world cooling the major stages of which occur in the upper Miocene and in the Pleistocene (see also Pastouret et al., 1978; Chamley and Giroud d'Argoud, in press). At the same time the marine circulation increased, leading to the development of calcareous plankton and carbonated sediments. In the Pleistocene the Glacial/Interglacial alternation determined an increase in erosion of northern continental rocks, rich in silicated components.

5) The chemical composition of the sediments at Sites 398 and 400 are comparable (Figure 12). This is particularly well demonstrated in the mean compositions (Figure 11) and indicates a common origin for the detrital minerals. The chemical successions with time also follow one another in the same manner at the two sites.

6) Study of geochemical relations confirm the analogies between Sites 400 and 398. In both cases the siliceous phase, well defined by close linkages between  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{K}_2\text{O}$ , is marked by the same group of traces (Ti, V, Cr, Li). This fact defines not only identical detrital contributions but also identical sources for these contributions. Moreover in these two sites there exists an

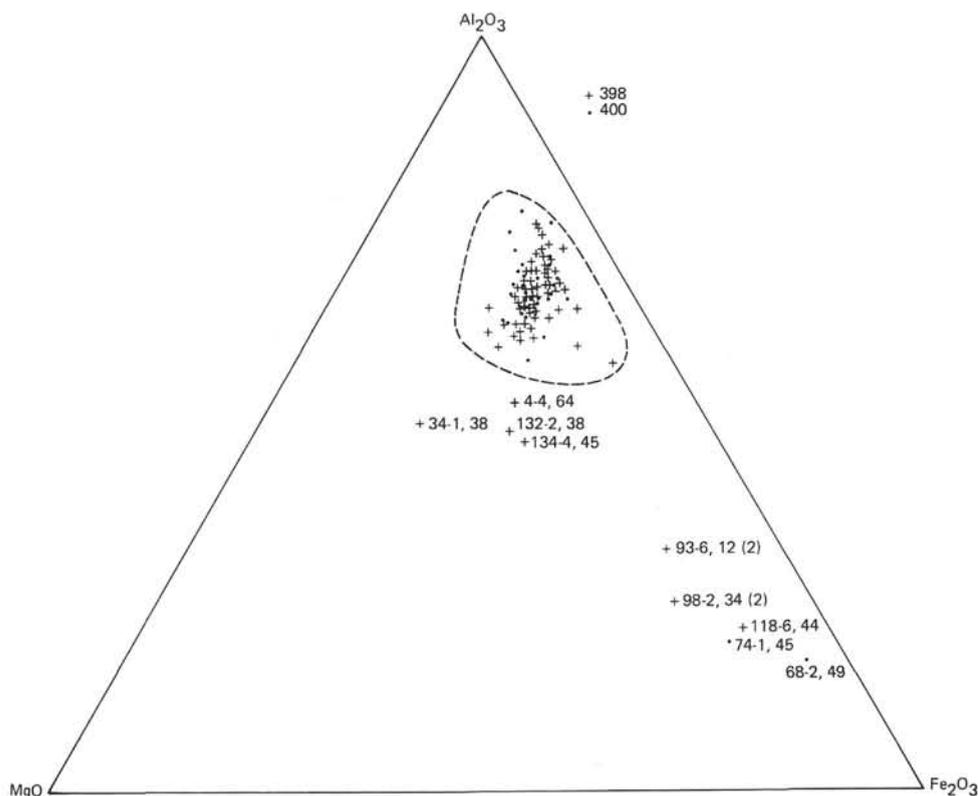


Figure 12. *Triangular diagram,  $Al_2O_3$  -  $Fe_2O_3$  -  $MgO$ . Comparison between south and north of Biscay Bay (Sites 399 and 400 and Site 398).*

independent metalliferous phase, characterized by transition elements (Mn, Ni, Co). This third phase begins and disappears at the same time as the fibrous clays, that is, it persists from Albian to Oligo-Miocene.

#### Unique Characteristics

1) The sediments of the north Biscay Bay sites contain less kaolinite and fibrous clays than those in the south. This evokes the climatic zonation of sedimentary rocks and soils on land masses, favoring kaolinite and fibrous clays in lower latitudes. The occurrence of terrestrial paleoclimatic belts seems to be reflected in sediments as today (Griffin et al., 1968; Pédro, 1968), with major influence of supplies from adjacent continents.

2) Smectite and MgO increase northward, probably in relation with soil and sediment supplies from the Paris Basin rather than with submarine volcanic activity.

3) More primary minerals (and, consequently, associated chemical elements) occur in the Neogene and Pleistocene sediments in the north than in the south. Probably this points to a manifestation of lower temperatures in the source area that supplied the northern sites, as is the case today (Griffin et al., 1968).

4) In the Albo-Aptian "black shales" in the north diagenesis of organic matter is less marked and concerns mobile chemical elements only (Mn, Fe, Ca), showing the variability of mineral and organic components in this lithological facies (Ryan and Cita, 1977a,b; Deroo et al., 1978; Deroo and Herbin, in press; Tissot et al., this volume).

#### Comparison Between North Biscay Bay and Rockall Plateau (Sites 399 and 400 to 402 and Sites 403 to 406)

##### Common Characteristics

The main similarity between the two areas drilled during Leg 48, and which is equally common to the area located off the Iberian peninsula, invokes the unsteady increase of primary minerals and the occurrence of mixed-layers from late Paleogene onwards and particularly during Neogene and Pleistocene time. That change is illustrated in particular by the decrease of the smectite-Mg couple and the increase of the illite- $SiO_2$  couple. It is a product of general cooling in Middle and Upper Cenozoic, influencing the conditions of erosion, continental pedogenesis, and oceanic circulation.

##### Unique Characteristics

1) The geochemistry of the sediments of Paleocene, Eocene, and Oligocene age in the Rockall area are distinctly ferromagnesian and titaniferous (Figures 10, 11, and 13). Figure 11 demonstrates that, for the Rockall sites, the cloud of points is close to the MgO and  $Fe_2O_3$  poles and the dispersion is greater than for the Biscay Bay sites.

2) The analysis shows, for Biscay Bay, there is a close relation in the  $Al_2O_3/TiO_2$  bond (due to Ti in the smectites); the relationship is linear (Figure 10). For the Rockall area a similar relationship occurs, but differs in that 80 per cent of the points fall above the line. This is particularly true for the Eocene section of the Rockall sites. The Ti is concentrated

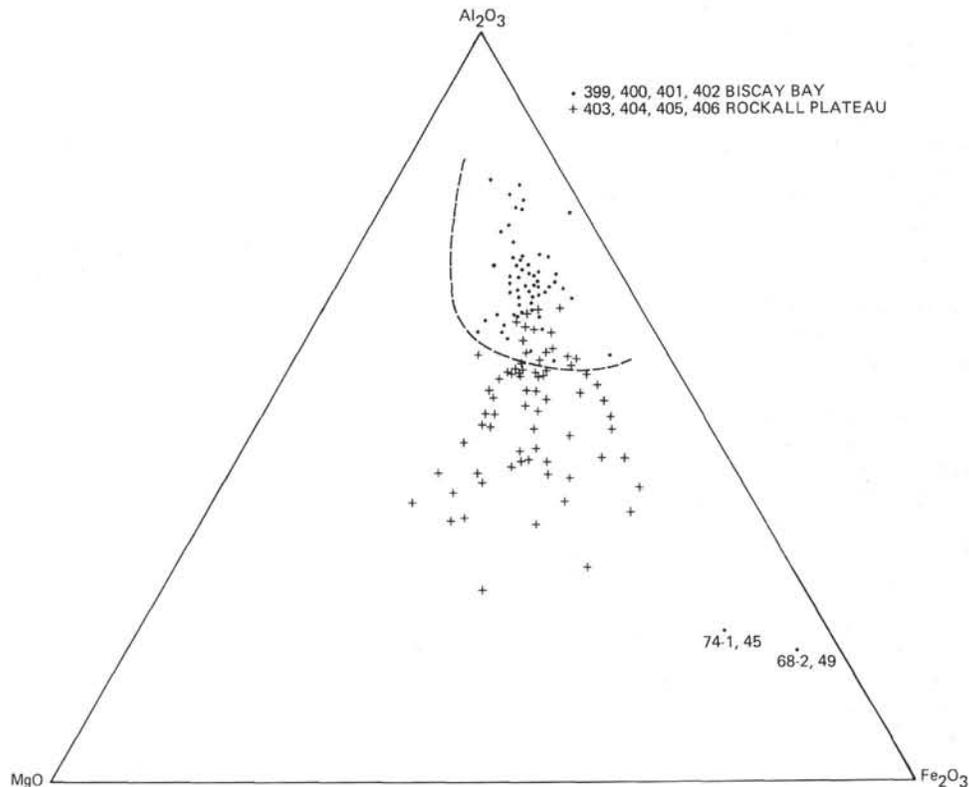


Figure 13. *Triangular diagram,  $Al_2O_3 - Fe_2O_3 - MgO$ . Comparison between Biscay Bay and Rockall Plateau.*

in the Fe- and Mg-rich smectites (Caillère and Henin, 1963; Deer et al., 1962), and suggests, together with rare earth and V, Cr, Co data, that the smectite chiefly originated from basic volcanic material.

3) In the Rockall sites, Mn is not present consistently as a metalliferous phase. We find it in the Eocene as rhodochrosite, associated with other minerals (siderite, glauconite, phosphate; see also Odin, this volume). This suggests an environment reduced by an anaerobic decay of organic material of animal origin (Rivière, 1941). In the sites of the Bay of Biscay, rhodochrosite does not appear after the Albian and especially is not associated with phosphorous. Effectively the reduced conditions are induced by decay of vegetable organic material of detrital origin, suggesting a very different environment.

4) A lesser clay fraction and more abundant carbonate, siliceous and volcanoclastic material occurs in the north, indicating a more oceanic and volcanic environment. This trend increases from Sites 403 and 404 toward Sites 405 and 406.

5) Kaolinite and fibrous clays are less abundant in the clay fraction northward, due to remoteness from continental sources and from less hydrolyzing climatic zones (lower latitudes).

6) The cooling expressed in clay assemblage occurs later and stronger in Rockall area (increase in illite, chlorite, mixed-layers content). The principal causes are the additional influence of volcanic activity to the climatic changes in the setting up of the mineralogical composition,

and the vicinity to the cooling sources during the Pleistocene (see Moyes et al., 1974; Chamley, 1975).

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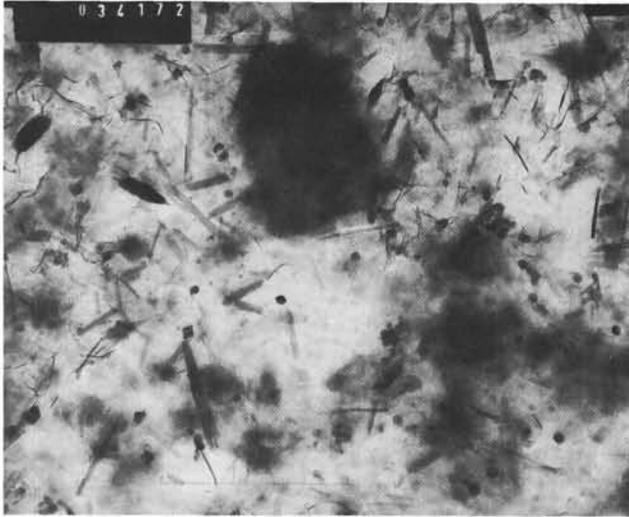
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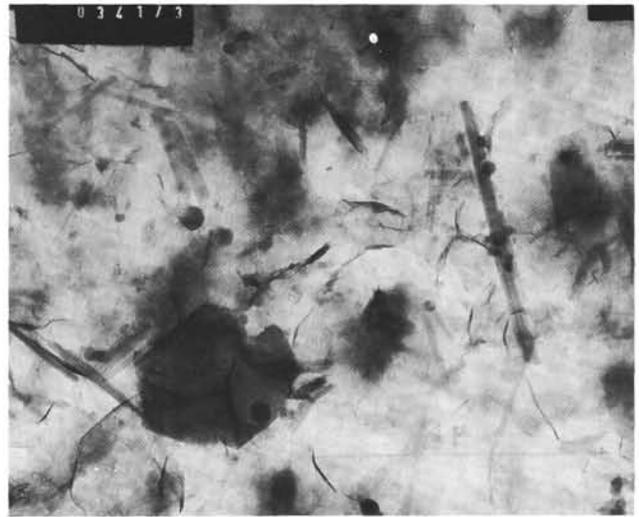
PLATE 1  
Electromicrographs

- Figure 1      Sample 400A-64-2, 56 cm ( $\times 25,000$ ). Upper Albian. Attapulgitic (=palygorskite) in short and straight fibers. Smectite in fleecy particles. Well-shaped illite.
- Figure 2      Sample 400A-64-2, 56 cm ( $\times 39,000$ ). Upper Albian. Attapulgitic, smectite, hexagonal kaolinite.
- Figure 3      Sample 401-19-1, 125 cm ( $\times 6800$ ). Lower Campanian. Large-sized and well-shaped illite and chlorite, with fleecy smectite.
- Figure 4      Sample 401-17-1, 50 cm ( $\times 20,000$ ). Early Paleocene. Local increase of straight or flexuous fibrous clays (sepiolite, attapulgitic) in a smectite-rich assemblage.
- Figure 5      Sample 400A-43-3, 148 cm ( $\times 39,000$ ). Upper Miocene. Smectite, illite, kaolinite, fairly rare attapulgitic, fragments of dissolved diatoms.
- Figure 6      Sample 400A-20-5, 38 cm ( $\times 39,000$ ). Upper Miocene. Smectite, illite, kaolinite, rare attapulgitic.

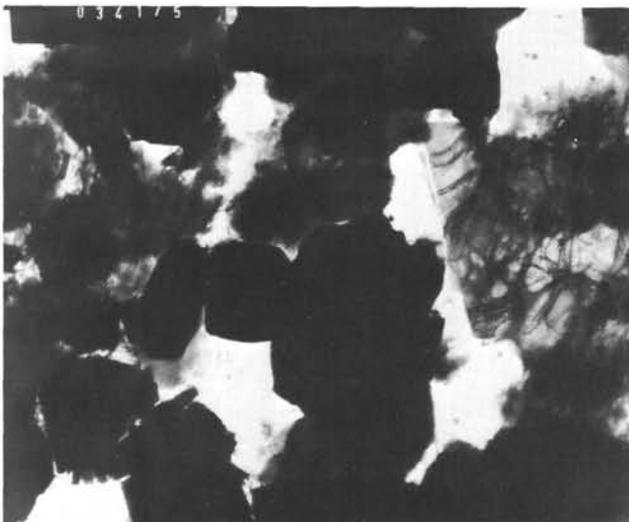
PLATE 1



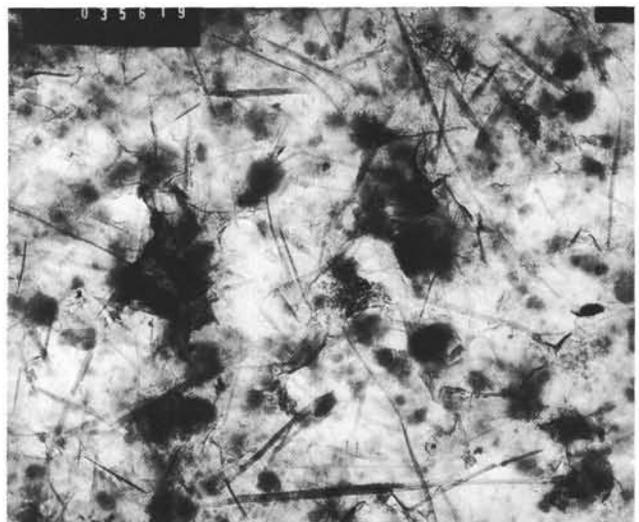
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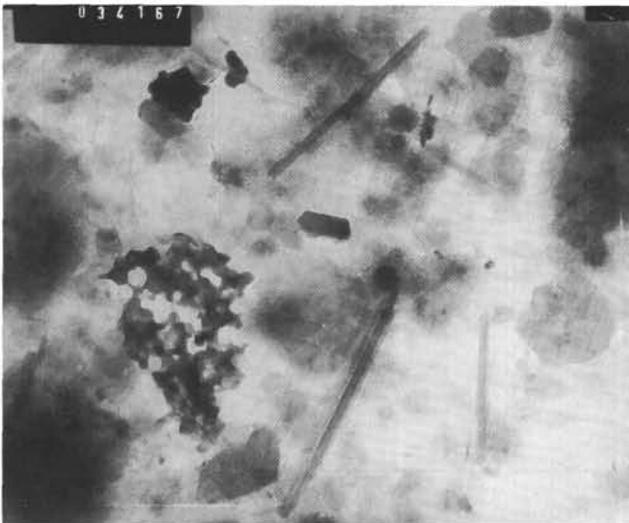
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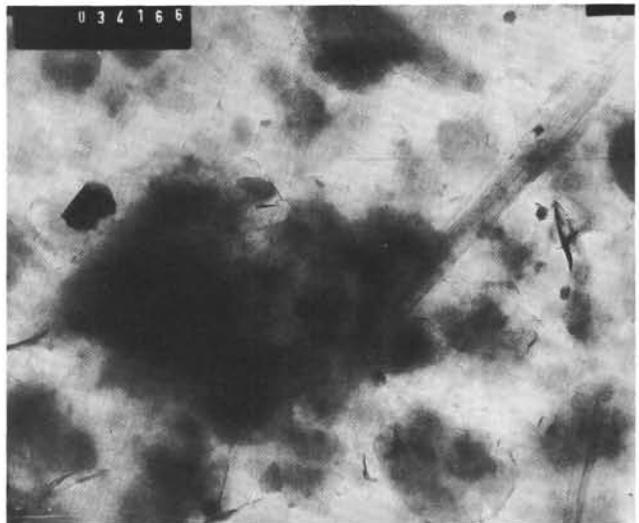
3 1 μm



4 1 μm



5 1 μm



6 1 μm