13. LEG 68: SHORE-BASED X-RAY MINERALOGY[1]

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INTRODUCTION

Eighty-four sediment samples from four holes at Site 502 and 54 samples from three holes at Site 503 were analyzed for mineral content by semiquantitative X-ray diffraction methods.

Site 502 is located in the Western Caribbean, whereas Site 503 lies in the Eastern Pacific (probably on the north flank of the Galapagos Spreading Center). Both sites were chosen to yield continuous core sections for investigations of late Neogene and Quaternary biostratigraphy and magnetostratigraphy and to study events such as the closing of the Isthmus of Panama.

Our X-ray diffraction work should provide a framework for further investigations—for example, determination of climatic changes in relationship to clay mineral composition or the influx of terrigeneous sediment components from South America before and after development of the Panama landbridge.

METHODS

We used methods similar to those described by Mann and Müller (1980). The mineralogical composition of powdered samples which had been dried at 70°C was determined by semiquantitative XRD methods using Cu_k-radiation, a monochromator, and a 1° detection slit. Conditions were as follows: 38 kV/24 mA, range 1×10^3 cps; time constant: 1. Clay samples (<2 μm) were smeared on glass mounts after disintegration with a KLN ultrasonic generator and centrifuging. Goniometer speed was 1°/min., except where peak splitting was done between $2\theta = 24°$–$25°$ for the determination of kaolinite and chlorite; in these cases we used a speed of ¼°/min. In most clay samples from Hole 503 chlorite and kaolinite could not be resolved.

Mineral "percentages" were obtained by multiplying peak heights of individual minerals present with factors (see Mann and Müller, 1980) or—for clay minerals—by the peak area method. Carbonate contents were determined by the "Carbonate-Bomb" method (Müller and Gastner, 1971).

RESULTS

Site 502

Sediments from the Columbia Basin at Site 502—foraminifer and nannofossil marl—were divided into four units (A–D). Unit A (sample numbers 1–5) consists of a yellowish brown to light brownish gray Pleistocene-age foraminifer-bearing nannofossil marl. $CaCO_3$ is abundant (see Fig. 1 and Table 1), and quartz and feldspar occur in low amounts. The clay mineral suite constitutes about 40 to 60%, of which kaolinite is the main mineral. The illite:smectite ratio is approximately 1.

The sediment of Unit B (Pleistocene to early Pliocene) is partly a foraminifer-bearing nannofossil marl whose colors range from gray to light olive gray. Average percentages of quartz and feldspar are 7 and 1.5%, respectively, as in Unit A, and calcite is dominant. The lowest value (37%) is from Core 502A-7, which can be described as "nanno zeolite-bearing foram marl"; XRD did not yield zeolite in our sample (Sample 502A-7-2, 101–103 cm). We find a negative correlation between smectite to illite, chlorite, and kaolinite ($r = -0.871$, -0.711, and 0.944, respectively). Smectite contents are also negatively correlated to quartz values ($r = -0.945$) and—quite expectedly—to carbonate. Dispersed or nodular pyrite identified during shipboard analysis could not be detected by XRD in bulk samples. We found pyrite framboids, identified microscopically as thin laminae (≤ 1 mm) in some samples (e.g., Sample 502B-14-2, 101–103 cm) or as small round aggregates (1–2 mm diameter). The lowermost samples of Unit B yielded pyrite as well, as pyritized radiolarians and forams.

Unit C (from 110 to 210 m sub-bottom) consists of gray to light gray foraminifer-bearing nannofossil marl and olive gray to green gray clay (lower sections), which bears ash and pyrite in some parts. Cores 26 to 37 are early Pliocene, Cores 38 to 65 late Miocene. Though calcite is dominant or common in these sediments, some nannofossil marls from Unit C are distinctly lower in $CaCO_3$ than those in A and B as clay becomes a major constituent. Clay mineral percentages vary between 35 and 82%; higher amounts prevail in the lowermost part of Unit C. Again, we found a negative correlation between smectite to illite, chlorite, and kaolinite (r between 0.78 and 0.95). Quartz and feldspar yield, respectively, r-numbers of -0.94 and -0.84 for carbonate, which points to their allochthonous (terrigenous) origin.

We did not find this clear-cut relationship in Unit B, although more samples were X-rayed (40 versus 21).

Dispersed and nodular pyrite could be observed microscopically as pyritized forams or framboids, sometimes as spots with a diameter of 1–2 mm.

Unit D also consists of a late Miocene calcareous sediment, rich in clay, which is interspersed with black pyritic ash beds. $CaCO_3$ varies between 4 and 35%; quartz and feldspar contents are as low as in the previous sections. We found a negative correlation between smectite and the other clay minerals. In general, smec-

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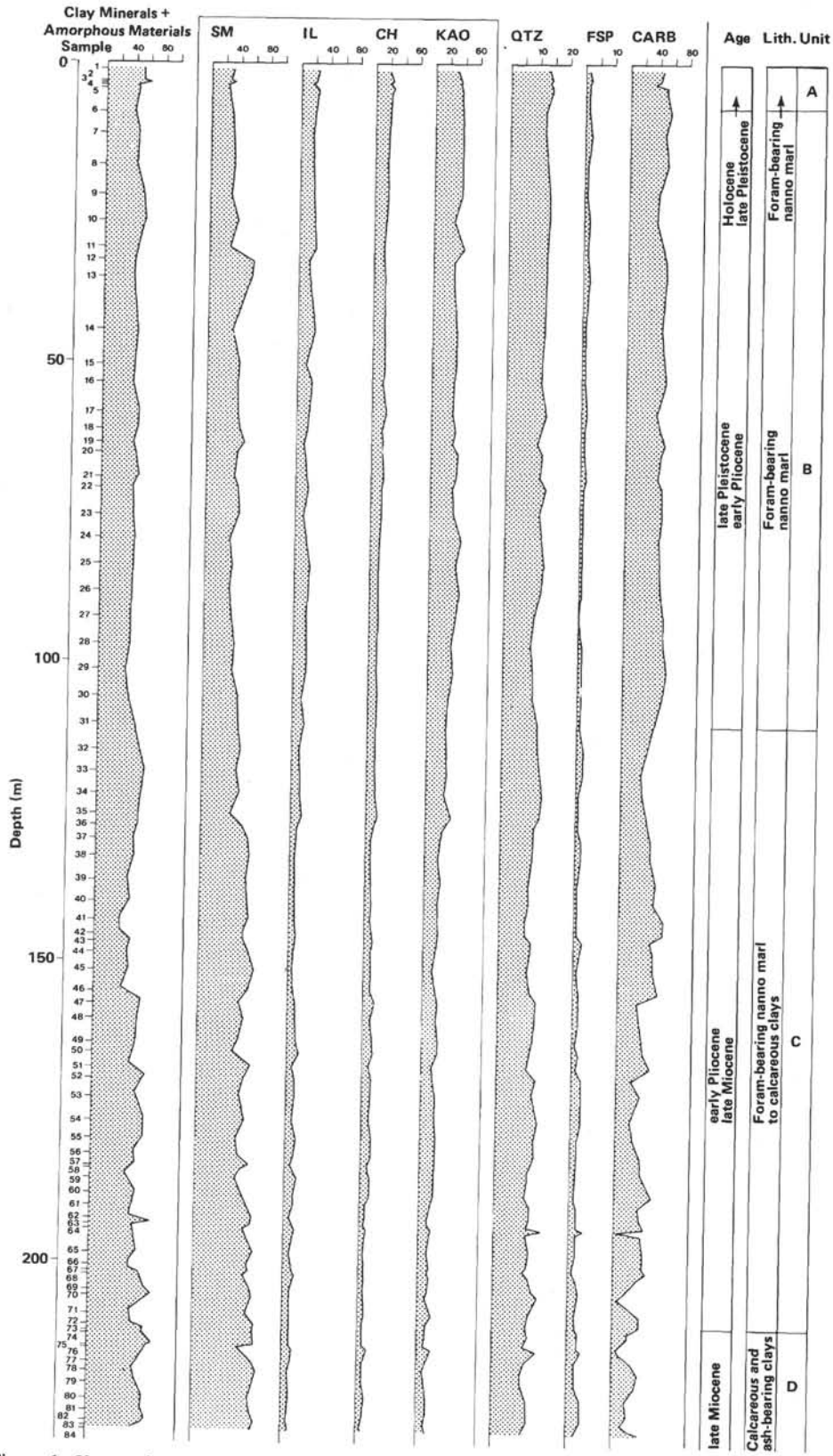

Figure 1. X-ray mineralogy of sediments from Site 502. (Abbreviations: SM = smectite, IL = illite, CH = chlorite, KAO = kaolinite, QTZ = quartz, FSP = feldspar, BAR = barite, CARB = carbonate, Dol = dolomite, Gyp = gypsum.)

Table 1. X-ray mineralogy of sediments from Site 502.

Hole	Sample (interval in cm)	Depth (m)	No.	Clay Mineralogy (100%)				Bulk Mineralogy (100%)			
				Smectite	Illite	Chlorite	Kaolinite	Clay Minerals + Amorphous	Carbonates	Quartz	Feldspar
A	1-1, 102-104	1.03	1	28	24	18	30	49	43	7	1
A	2-1, 121-123	3.12	2	24	20	21	35	50	40	8	2
	2-3, 19-20	3.19	3	30	17	19	34	58	34	7	1
	2-3, 109-110	4.10	4	21	21	24	34	41	50	8	1
A	2-2, 101-103	4.41	5	22	24	20	34	43	48	8	1
A	3-2, 52-53	8.33	6	28	19	17	36	37	56	6	1
A	4-1, 103-105	11.74	7	30	16	17	37	44	48	6	2
A	5-2, 48-50	17.09	8	31	16	16	37	40	52	7	1
A	6-2, 101-103	22.02	9	26	19	18	37	51	40	8	1
A	7-2, 101-103	26.32	10	37	20	16	27	53	37	8	2
A	8-2, 101-103	30.82	11	25	23	13	39	44	48	7	1
B	8-3, 52-53	32.82	12	48	14	11	27	40	52	7	1
B	9-2, 52-54	35.73	13	46	14	15	25	39	53	7	2
B	11-2, 51-53	44.52	14	30	23	16	31	46	46	7	1
B	12-3, 51-53	50.42	15	41	11	16	32	43	50	6	1
B	13-2, 46-48	53.27	16	39	15	18	28	40	53	6	1
B	14-2, 101-103	58.22	17	39	16	18	27	49	41	8	2
B	15-1, 101-103	61.12	18	41	14	13	32	47	46	6	1
	16-1, 131-133	63.32	19	48	10	14	28	41	53	5	1
B	16-1, 51-53	65.07	20	41	11	13	35	46	46	7	1
	17-1, 113-115	69.04	21	36	15	16	33	50	42	6	2
B	17-2, 53-55	70.94	22	41	17	14	28	42	49	8	1
B	18-2, 51-53	75.34	23	45	10	15	31	43	50	6	1
A	19-2, 103-105	79.24	24	31	16	12	41	41	46	7	1
A	20-2, 98-100	83.59	25	34	20	11	35	45	46	8	1
A	21-2, 97-99	87.98	26	31	18	11	40	43	49	7	1
A	22-2, 98-100	92.39	27	35	16	12	37	41	54	5	tr.
A	23-2, 103-105	96.84	28	41	18	11	30	42	53	4	1
A	24-2, 99-101	101.20	29	37	18	11	34	36	58	5	1
A	25-2, 103-105	105.64	30	47	12	12	29	40	54	5	1
A	26-2, 104-106	110.05	31	47	16	11	26	49	43	7	1
A	27-2, 102-104	114.43	32	52	10	11	27	57	34	7	2
A	28-2, 51-53	118.32	33	45	14	12	29	64	26	8	2
A	29-2, 103-105	121.84	34	50	12	13	25	61	29	9	1
A	30-2, 99-101	125.30	35	39	15	16	30	56	34	8	2
	31-1, 91-93	127.02	36	55	10	11	24	56	37	6	1
A	32-1, 101-103	129.32	37	64	8	8	20	51	41	6	2
A	33-1, 101-103	132.34	38	66	7	8	19	52	40	6	2
A	34-2, 48-51	136.20	39	61	8	9	22	45	49	5	1
A	35-2, 101-103	139.82	40	62	9	10	19	49	45	5	1
A	36-2, 51-53	142.82	41	66	8	8	18	35	60	4	1
A	37-2, 46-48	145.27	42	59	11	10	20	36	59	4	1
A	38-1, 101-103	146.82	43	59	10	12	19	50	41	6	3
A	39-1, 101-103	148.32	44	67	7	10	16	46	46	6	2
A	40-1, 101-103	151.32	45	73	5	10	12	48	46	5	1
A	41-2, 48-50	154.79	46	66	7	10	17	39	53	6	2
A	42-1, 101-103	156.82	47	53	11	16	20	65	25	8	2
A	43-1, 101-103	159.32	48	55	11	16	18	61	29	8	2
A	44-2, 51-53	163.32	49	53	12	14	21	59	33	7	1
A	45-1, 101-103	164.82	50	47	17	15	21	57	35	6	2
A	46-1, 101-103	167.32	51	72	6	9	13	50	44	5	1
A	47-1, 101-103	169.32	52	61	13	11	15	71	18	8	3
A	48-1, 101-103	172.32	53	57	12	12	19	59	31	7	3
A	50-1, 101-103	176.32	54	64	8	10	18	70	18	9	3
A	51-1, 101-103	179.32	55	52	14	14	20	70	20	8	2
A	52-1, 101-103	181.82	56	55	11	14	20	58	32	8	2
A	53-1, 101-103	183.82	57	69	7	9	15	60	32	6	2
	44-1, 82-84	184.13	58	58	12	20	20	54	38	6	2
A	54-1, 101-103	185.82	59	52	16	13	19	47	47	5	1
A	55-1, 101-103	188.32	60	59	11	12	18	61	30	7	2
A	56-1, 101-103	190.32	61	67	12	7	14	58	33	7	2
A	57-1, 121-123	192.52	62	77	6	7	10	54	38	6	2
	46-1, 137-139	193.48	63	74	10	5	11	82	3	11	4
A	58-1, 101-103	194.32	64	62	14	8	16	57	35	6	2
A	60-1, 101-103	198.32	65	80	6	4	10	64	27	7	2
A	61-1, 101-103	200.32	66	70	9	7	14	54	39	6	1
	48-1, 52-54	201.43	67	72	10	6	12	53	41	5	1
	62-1, 38-40	201.79	68	64	14	8	14	62	29	7	2
A	63-1, 121-123	204.52	69	74	8	6	12	75	14	8	3
	49-1, 22-24	205.53	70	76	8	7	9	82	5	10	3
A	65-1, 121-123	208.52	71	67	8	8	17	56	35	7	2
A	66-1, 101-103	210.32	72	80	6	5	9	59	33	6	2
C	28-1, 102-104	211.23	73	77	8	5	10	73	18	6	3
A	67-1, 51-53	211.82	74	79	7	5	9	72	18	7	3
A	68-1, 101-103	213.82	75	79	8	6	7	85	4	8	3
C	29-1, 81-83	214.02	76	59	12	12	17	79	7	10	4
C	30-1, 121-123	216.42	77	77	10	5	8	67	25	6	2
C	31-1, 121-123	217.92	78	83	7	4	6	60	33	5	2
C	32-1, 71-72	219.91	79	77	8	5	8	69	29	5	2
C	33-1, 81-83	222.52	80	71	9	9	11	73	16	7	4
C	34-1, 81-83	224.52	81	76	6	7	11	71	18	7	4
C	35-1, 47-48	226.17	82	82	5	5	8	78	11	7	4
C	36-1, 31-33	227.02	83	79	8	4	9	71	20	6	3
C	37-1, 6-8	227.77	84	77	7	5	11	58	35	5	2

tite contents decrease uphole whereas illite, chlorite, and kaolinite increase.

Site 503

Site 503 from the north flank of the Galapagos spreading center was divided into three units (A–C).

Unit A from 0–8.45 meters sub-bottom is oxidized siliceous-bearing marl or ooze from the Quaternary, containing iron oxides which cause the light yellowish brown, dark grayish brown, or pale brown colors. $CaCO_3$ is abundant (see Table 2, Fig. 2), whereas quartz, feldspar, apatite, and barite occur only in rare or trace amounts. Clay minerals (smectite dominates) are abundant in Unit A.

Unit B (8.45 to 226.2 m sub-bottom; Quaternary, Pliocene to late Miocene) is a reduced sediment, which—according to shipboard analysis—contains small amounts of pyrite and often rhodochrosite nodules. Colors are different shades of green and gray. Principal lithologies include siliceous-bearing calcareous oozes, marls, and siliceous nannofossil-oozes. Calcite is common to abundant, and our XRD yielded minor dolomite contents in many Quaternary and Pliocene samples. Dolomite becomes scarcer downwards (that is, in early Pliocene and late Miocene samples); barite, quartz, and feldspar are present in minor amounts throughout Unit B. Barite occurs in the $<2\ \mu m$ fraction and is of tabular or columnar habitus.

Zones of pyrite enrichment, which occur especially in burrows, have been described by the shipboard crew, but no sulfide minerals were detected by XRD. Smectite is the dominant (or, in Miocene samples, the only) clay mineral. A few Pliocene samples contain illite, whereas

Table 2. X-ray mineralogy of sediments from Site 503.

				Clay Mineralogy			Bulk Mineralogy					
Hole	Sample (interval in cm)	Depth (m)	No.	Smectite	Illite	Kaolinite + Chlorite	Clay Minerals + Amorphous	Carbonates	Quartz	Feldspar	Barite	Other
A	1-1, 70–72	0.71	1	67	—	33	27	71	1	1	Tr.	—
A	1-2, 70–72	3.01	2	50	14	36	58	36	2	2	2	—
B	2-2, 70–72	5.01	3	85	—	7.5/7.5	47	48	1	2	2	—
B	3-2, 70–72	9.41	4	89	—	11	31	65	1	1	1	—
A	4-2, 120–122	13.31	5	93	—	7	45	49	1	1	1	Dolomite 2
B	4-2, 70–72	13.81	6	96	—	4	43	54	1	1	1	—
A	5-2, 70–72	17.21	7	96	—	4	48	48	1	1	1	—
B	5-2, 70–72	18.21	8	98	—	2	37	63	Tr.	Tr.	Tr.	—
B	6-2, 70–72	22.61	9	95	—	5	65	29	1	1	1	Dolomite 2
A	7-2, 70–72	26.01	10	96	—	4	49	46	1	2	1	—
B	7-2, 70–72	27.01	11	96	—	4	62	16	1	3	3	Dolomite 2 Gypsum 2
B	8-2, 70–72	31.42	12	98	—	2	57	36	1	2	1	Dolomite 2
A	9-2, 72–74	34.89	13	92	—	8	85	6	2	3	2	Gypsum 2
A	10-2, 72–74	89.21	14	97	—	3	70	25	1	1	1	Dolomite 1
B	10-2, 73–75	40.24	15	96	—	4	40	52	Tr.	1	1	Dolomite 5
A	11-2, 70–72	43.61	16	97	—	3	28	24	1	1	1	—
B	11-2, 70–72	44.61	17	97	—	3	39	57	1	1	1	—
A	12-2, 72–74	48.03	18	95	—	5	61	33	1	1	1	Dolomite 1
B	12-2, 70–72	49.01	19	95	—	5	59	33	1	1	2	Dolomite 2
A	13-2, 70–72	52.41	19a	95	—	5	55	39	1	1	1	Dolomite 2
A	13-2, 70–72	53.41	20	93	—	7	72	22	1	1	2	—
A	14-2, 70–72	56.81	21	95	—	5	48	48	Tr.	1	1	Dolomite 2
B	14-2, 70–72	57.80	22	96	—	4	54	40	1	Tr.	2	Dolomite 2
A	15-2, 70–72	61.21	23	97	—	3	56	40	1	1	1	Gypsum Tr.
B	15-2, 70–72	62.21	24	94	—	6	57	37	2	1	2	—
A	16-2, 70–72	65.61	25	98	—	2	60	37	1	1	1	—
B	16-2, 70–72	66.61	26	95	—	5	71	21	2	2	3	Gypsum Tr.
B	17-2, 70–72	79.01	27	95	—	5	67	25	3	2	2	—
B	18-2, 70–72	75.41	28	91	2	3.5/2.5	78	13	3	2	3	Gypsum 0.5
A	19-2, 70–72	78.81	29	95	—	5	64	28	2	2	3	—
B	19-2, 70–72	79.81	30	93	3	3/1	61	29	2	1	2	—
A	20-2, 70–72	83.21	31	85	9	6	61	32	2	2	2	—
B	20-2, 70–72	84.21	32	90	—	10	78	~10	2	2	3	Gypsum 3 Dolomite 2
A	21-2, 70–72	87.61	33	89	4	3.5/3.5	45	51	1	1	1	—
B	21-2, 70–72	88.61	34	92	3	5	42	55	1	Tr.	1	—
B	22-2, 70–72	93.01	35	91	5	4	66	25	2	3	3	Gypsum Tr.
A	21-2, 120–122	88.11	36	98	—	2	28	64	Tr.	Tr.	Tr.	Dolomite 2
A	24-2, 132–134	101.43	37	89	5	6	66	~30	1	1	1	—
B	24-2, 70–72	101.81	38	97	—	3	62	31	2	1	3	—
B	25-2, 70–72	106.21	39	98	—	2	43	53	1	1	1	—
B	26-2, 70–72	110.61	40	91	5	4	50	43	2	1	2	Gypsum 1
A	29-2, 70–72	122.81	41	97	—	3	34	65	Tr.	Tr.	Tr.	—
A	30-2, 72–74	127.23	42	97	—	3	31	69	Tr.	Tr.	Tr.	—
A	31-2, 70–72	131.61	43	98	—	2	54	44	Tr.	Tr.	1	—
A	34-2, 70–72	144.81	44	99	—	1	31	68	—	—	Tr.	Dolomite 1
A	36-2, 70–72	153.63	45	100	—	—	34	63	—	—	Tr.	Dolomite 3
A	41-2, 70–72	175.61	46	100	—	—	62	32	1	1	2	—
A	42-2, 30–32	179.32	47	100	—	—	57	41	Tr.	1	1	—
A	43-2, 70–72	184.41	48	100	—	—	55	44	—	1	Tr.	—
A	44-2, 70–72	188.81	49	100	—	—	56	44	Tr.	Tr.	Tr.	—
A	48-2, 73–75	206.44	50	100	—	—	31	69	Tr.	Tr.	Tr.	—
A	50-2, 70–72	215.21	51	100	—	—	41	59	Tr.	—	Tr.	—
A	51-2, 70–72	219.61	52	100	—	—	45	55	Tr.	—	Tr.	—
A	52-2, 70–72	224.01	53	100	—	—	51	49	—	—	—	—
A	54-2, 70–72	232.81	54	100	—	—	71	27	Tr.	Tr.	1	—

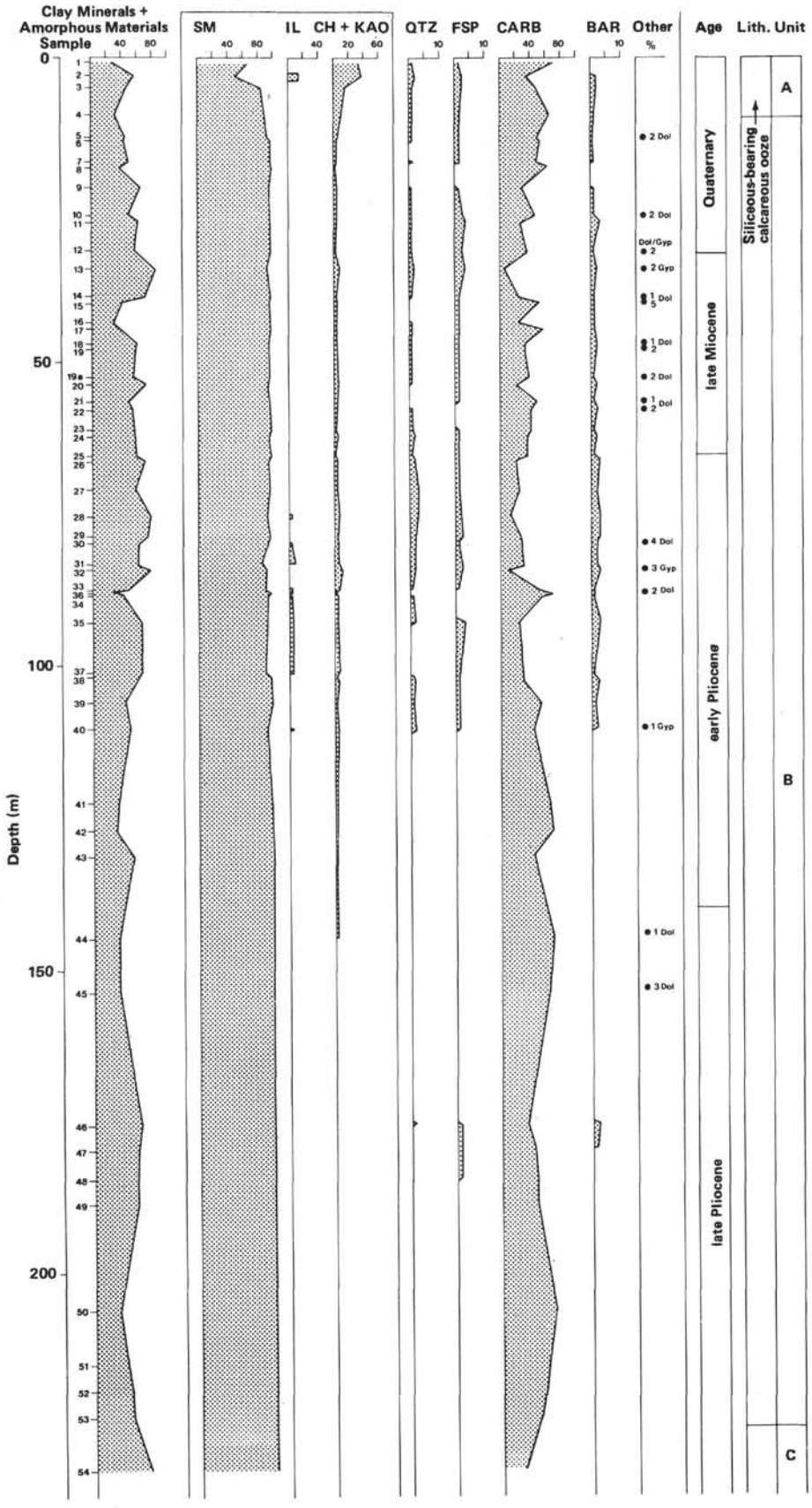

Figure 2. X-ray mineralogy of sediments from Site 503. (See Fig. 1 caption for identification of abbreviations.)

most have some chlorite and/or kaolinite. Barite seems to be positively correlated to quartz and negatively correlated to carbonate content. We do not yet know whether this suggests a common (detrital?) origin for both quartz and barite.

Only one sample (no. 54) of Unit IC has been X-rayed (Sample 503A-54-2, 70–72 cm). It is from a siliceous-bearing marl/calcareous-bearing siliceous clay suite. Its clay content is relatively high (71%)—characteristic for Unit C. Another major component of this sample is $CaCO_3$. Only traces of detritals are present (as in the lowermost samples of Unit B).

Minor amounts of apatite are probably present throughout the whole sedimentary column of Site 503.

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