36. GEOCHEMICAL HISTORY OF POST-JURASSIC SEDIMENTATION IN THE CENTRAL NORTHWESTERN PACIFIC, NORTHERN HESS RISE, DEEP SEA DRILLING PROJECT SITE 464[1]

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ABSTRACT

Results describe the chemical composition of post-Jurassic sediments penetrated by Deep Sea Drilling Project Hole 464 (northern Hess Rise), peculiar features in the distribution of chemical components through the section, and modes of their occurrence determined by factor analysis and from the data on mineralogy, lithology, and accumulation rates of sediments and chemical components.

Three main stages in the geochemical history of sedimentation in the region are outlined: I. Late Mesozoic stage (Early Albian–Cenomanian). Ia. Early phase (Late Aptian–Early Albian). This early phase is characterized by accumulation of dark-red and brown, calcareous silica-clay oozes, considerably enriched by volcanogenic (mostly hyalopelite basalt volcaniclastic) material. High accumulation rates of sediments (22.5 mm $10^{-3}yr^{-1}$) and chemical components are noted. Ib. Late phase (late Albian–Cenomanian). Accumulation of relatively light-colored, calcareous, essentially silicic sediments took place at that time. The amount of volcaniclastic material, iron, and other heavy metals in these sediments is much less than in the early Albian deposits. Relatively high accumulation rates of sediments (17.9 mm $10^{-3}yr^{-1}$) and of some of the components (SiO_2, Al_2O_3, etc.) were recorded. The obtained data are in good correlation with the model which implies that in the Albian the northern part of Hess Rise was in the equatorial zone, with high biological productivity, while the Pacific Plate moved northward. II. Late Cretaceous (Early Turonian?–Middle Miocene). During that time, relatively local accumulation of fine volcaniclastic material (ash) took place; this material was transformed into clay (montmorillonite–hydromica) enriched by ferric hydroxide, and to a lesser degree by Mn-hydroxide and associated heavy metals. III. Late Cenozoic stage (upper Miocene–Pleistocene) was the time of accumulation of clay–silica, mostly radiolarian oozes, in chemical composition and accumulation rates similar to the typical clay–silica sediments of the modern open ocean at depths below the level of carbonate compensation. The outlined stages, phases of geochemical history of sedimentation in the region, represent the evolution of sediment accumulation in the basin.

INTRODUCTION

Hess Rise is one of the largest submarine aseismic structures of the northwestern Pacific. The Shatsky and Magellan Rises, the Ontong–Java and Manihiki submarine plateaus, and the Mid-Pacific Mountains also belong to this kind of structure. The data now available allow us to surmise that during the greater part of post-Jurassic time these structures were normally above the carbonate-compensation depth (CCD). Therefore, they may contain a relatively complete section of sediments.

The objective of this work is to outline the major features of the geochemical history of sedimentation in that region, as recorded in the chemical and mineral composition of sediments, on the basis of study of the chemistry of major components, heavy metals, trace elements, and data on mineralogy and lithology.

This article is one of the series of works on the geochemical history of sedimentation in the northwestern Pacific bored on DSDP Leg 62 by D/V *Glomar Challenger* (see Varentsov et al., this volume).

MATERIALS AND METHODS

The work is based on observational data on chemical and mineral composition, and lithologic features of deposits penetrated by Hole 464, as analyzed at the Geological Institute, U.S.S.R. Academy of Sciences. Data on lithologic-mineralogical studies are presented in other parts of this volume. The technique of research is given in greater detail in the paper on geochemical history of sedimentation for Hole 463 (Varentsov et al., this volume).

Determination of chemical components of sediments was made at the Geological Institute: the main components by the method of bulk chemical analysis, and heavy metals by optical emission spectroscopy, with application of international reference standards (Zolotarev and Choporov, 1978).

The chemical analyses were recalculated on a terrigenous-free, silica-free, carbonate-free basis to exclude the diluting effect of biogenic and clastic components, and to adjust the sediment to a certain geochemically comparable basis (Varentsov and Blazhchishin, 1976).

Analytical data were processed by a computer (EC-1022) at the Laboratory of Mathematical Methods of Research, Geological Institute (D. A. Kazimirov, P. K. Riabushkin), using the program of factor analysis (R-, Q-mode; Davis, 1973; Harman, 1967).

It should be noted that the section of Hole 464 is represented by a comparatively limited number of core samples, especially the Mesozoic deposits (early Cenomanian–Albian), mostly composed of carbonate silicic rocks.

The shortage of core samples and their inadequate paleontological and biostratigraphical characteristics, and the few chemical analyses make the obtained conclusions only tentative and speculative for the northern part of Hess Rise. Interpretation of this material can be made only within the context of geological, lithologic, and geochemical, information on that region.

The stratigraphic subdivision of the "brown clay" unit was made, therefore, according to the results of study of ichthyolith remains (Doyle and Riedel, this volume). Moreover, the stratigraphic capacity of the lower part of the unit (Cores 9 and 10) dated by these authors on the whole as Late Cretaceous, is conditionally interpreted in the paper as Turonian–Maastrichtian, from correlation with adjacent regions (Holes 171 and 310). It was inferred that the "brown clay" unit is composed of genetically similar deposits which accumulated without notable hiatuses.

[1] *Initial Reports of the Deep Sea Drilling Project*, Volume 62.

PARAGENETIC ASSEMBLAGES OF COMPONENTS

The study of paragenetic assemblages of components was carried out using the analytical data processed by factor analysis. Two types of determinations were investigated: (1) actual data of chemical analyses, represented in weight percent to air-dry weight, (2) recalculation to a terrigenous-free, silica-free, carbonate-free basis. In the first case, the determined groups of chemical components, clusters, are definitely related to existing mineral phases. In the second case, provided in particular that the carbonate- and silica-dilution effect is eliminated, clearly outlined features of a number of authigenic mineral phases become more evident: hydroxides, hydrothermal exhalates, products of post-sedimentary transformations, etc.

Data of Chemical Analysis (Tables 1-3; Fig. 1)

Assemblage IA (+): SiO_2(0.98)-C_{org}(0.21)-Ca(0.12). This assemblage is represented by biogenic silica of the opal-CT type, with which C_{org} associates rather weakly. The assemblage is most conspicuous in the Cenomanian opal-clay sediment (Sample 11-1, 28-29 cm) with essentially altered hyalopelite material, relics of diatoms, patches of chalcedony, quartz. Early Pliocene tuffogenic sediments (Sample 3-1, 60-64 cm; Fig. 1) are similar in composition; the content of relics of diatoms in them is up to 40%, of spicules of siliceous sponges up to 20%, of radiolarians up to 10%.

Assemblage IB (−): Al_2O_3(−0.29)-Mg(−0.97)-N_2O (−0.52)-K_2O(−0.36)-Fe(0.86)-Mn(−0.70)-P (−0.17)-Cr(−0.34)-Ni(−0.49)-V(−0.74)-Cu(−0.34)-Co(−0.25)-Pb(−0.56)-Mo(−0.48). This assemblage is represented by essentially altered hyalopelite basaltic volcaniclastic material, composed of tephra remains, Fe- and Mn-hydroxides, montmorillonite-illite components. This group can be considered as an example of multistage formation of an assemblage: (1) oxidation of basaltic hyalopelite volcaniclastics, development of crusts and patches of Fe- and Mn-hydroxides (Samples 9-1, 30-32 cm; 5-5, 70-72 cm, etc.) after volcanogenic particles promoting concentration of heavy metals; (2) transformation of volcaniclastic material into mixed-layer, fine-grained phases, i.e., montmorillonite-mica (Fig. 2) was followed by scavenging of Mg and K from solutions and from the bottom water.

Distinct localization of this group of components in the section should be noted (Fig. 1). Its most obvious manifestation is observed in sediments marking the beginning of a burst of explosive basalt volcanism, mainly at the base of volcanogenic "brown clay" unit of the Late Cretaceous-middle Miocene (Doyle and Riedel, this volume); these clays are deposited on red-brown silicates, to a lesser extent limestones of the Cenomanian. To a relatively lesser extent, this assemblage is developed in the lower layers of essentially volcanogenic siliceous clays of the middle Miocene, and at the base of argillaceous radiolarian oozes and argillaceous siliceous oozes of the late Pliocene-Pleistocene.

Assemblage IIA: SiO_2(0.13)-Al_2O_3(0.38)-Na_2O (0.78)-P(0.73)-Cr(0.32)-V(0.33)-Cu(0.72)-Mo(0.37). Comparison of the combination of components in this group with observational data on mineral composition gives grounds to assume that this assemblage is represented by aluminosilicate phases of the zeolite type, with closely associated phosphorus, copper, and a number of heavy metals. The group is confined to volcanogenic siliceous hyalopelite sediments in the top layers of the early Cenomanian, and to the volcanogenic "brown clay" unit of the Late Cretaceous-middle Miocene.

Assemblage IIB (−): CaO(−0.86)-CO_2(0.87)-C_{org} (−0.62)-Ge(−0.62). This assemblage is represented by biogenic calcium carbonate, with which C_{org} is closely bound. Being one of the group, Ge is obviously associated with C_{org} and forms metallo-organic compounds. The assemblage occurs in deposits of the early Pliocene-Pleistocene, with carbonate nannofossil micrite remains (up to 20%).

Assemblage IIIA (+): Al_2O_3(0.80)-MgO(0.16)-K_2O (0.65)-Fe(0.35)-Mn(0.67)-P(0.53)-Cr(0.80)-Ni(0.82)-V(0.49)-Cu(0.30)-Co(0.93)-Pb(0.57)-Ga(0.90)-Ge (0.47)-Mo(0.72). Results of mineralogical studies and the composition of this assemblage provide evidence to believe that it is represented by fine hyalopelite basaltic material, essentially altered to illite components. This transformation may have been accompanied by the appearance of Fe- and Mn-hydroxide patches, encrustations, and aluminophosphate and iron phosphate compounds in close association with heavy metals such as Cr, Ni, Co, Ga, and Mo.

Assemblage IIIB (−): CO_2(−0.46)-SiO_2(−0.09)-C(−0.01)-CaO(?). The nature of phases in this assemblage is not quite clear from the study of its compo-

Table 1. Chemical composition of Mesozoic-Cenozoic deposits, central northwestern Pacific, northern Hess Rise, Site 464.

Sample (interval in cm)	Components (wt.%)														(wt.% × 10^{-4})								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	CO_2	C	P_2O_5	Fe	Mn	P	Cr	Ni	V	Cu	Co	Pb	Ga	Ge	Mo
464-2-1, 115-119	40.53	4.67	6.74	16.30	3.22	0.17	4.00	2.05	11.30	—	0.11	4.71	0.13	0.05	18	48	43	115	13	16	5	<1	1.6
3-1, 60-64	51.51	3.96	5.25	8.30	2.62	0.21	4.53	2.01	5.10	0.15	0.07	3.67	0.16	0.03	20	112	49	108	20	16	7	1.3	2.8
4-1, 130-134	43.73	4.48	5.88	11.81	3.12	0.07	4.21	2.40	7.75	0.01	0.13	4.11	0.05	0.06	22	65	72	62	18	19	7	1.2	1.5
5-5, 70-72	44.85	12.53	10.15	3.74	3.81	2.27	3.46	3.29	—	—	1.48	7.10	1.76	0.65	58	500	140	202	87	67	9	1	80
6-2, 95-97	46.53	12.77	13.68	3.01	3.12	0.84	2.51	3.72	—	—	0.72	9.57	0.65	0.31	58	178	170	190	44	36	11	1.1	30
6-3, 94-96	46.75	14.65	7.98	3.97	2.94	1.77	3.18	3.29	—	—	1.40	5.58	1.37	0.61	62	500	130	160	84	59	9	1.4	100
7-3, 120-122	46.36	12.98	11.33	1.40	3.62	0.28	3.46	4.58	—	—	0.24	7.92	0.22	0.10	60	98	135	135	24	11	8	1	3.9
8-2, 13-15	46.99	12.93	12.28	1.63	2.87	0.40	2.89	6.10	—	—	0.38	8.59	0.31	0.17	70	75	142	130	32	14	8	<1	89
9-1, 30-32	26.59	7.96	28.77	2.63	5.48	2.69	2.99	2.44	—	—	0.99	20.12	2.08	0.43	40	215	400	245	27	64	5	<1	80
11-1, 28-29	82.68	3.68	2.14	0.82	1.76	0.01	1.05	0.96	—	—	0.55	1.50	0.01	0.24	14	15	28	152	10	10	5	<1	1.5

Table 2. Results of factor analysis (R-mode) for chemical components (wt.%), Cenozoic and Mesozoic sediments of central northwestern Pacific, northern Hess Rise, Site 464.

No.	Component	Factor Loading (after rotation) I	II	III
1	SiO_2	0.98	0.13	−0.09
2	Al_2O_3	−0.29	0.38	0.80
3	CaO		−0.86	
4	MgO	−0.97	0.03	0.16
5	Na_2O	−0.52	0.78	
6	K_2O	−0.36		0.65
7	CO_2	0.01	−0.87	−0.46
8	C	0.21	−0.62	−0.01
9	Fe	−0.86		0.35
10	Mn	−0.70		0.67
11	P	−0.17	0.73	0.53
12	Cr	−0.34	0.32	0.80
13	Ni	−0.49	−0.06	0.82
14	V	−0.74	0.33	0.49
15	Cu	−0.34	0.72	0.30
16	Co	−0.25		0.93
17	Pb	−0.56		0.57
18	Ga	0.12		0.90
19	Ge		−0.62	0.47
20	Mo	−0.48	0.37	0.72
Input in dispersion (%)		51.13	19.96	11.77
Total dispersion (%)		−51.13	71.09	82.87

Table 3. Stratigraphic distribution of factor scores (R-mode) for chemical components (wt.%) in Cenozoic and Mesozoic sediments of central northwestern Pacific, northern Hess Rise, Site 464.

No.	Sample (interval in cm)	Age	Factor Score (after rotation) I	II	III
1	2-1, 115–119	U. Plio.	−0.60	−0.82	−1.46
2	3-1, 60–64	L. Plio.	0.63	−1.86	−0.02
3	4-1, 130–134	L. Plio.	0.06	−1.38	−0.56
4	5-5, 70–72	Mio.	−0.42	0.43	1.03
5	6-2, 95–96	U. Eoc. L. Mio.	0.09	0.43	0.95
6	6-3, 94–96	U. Eoc. L. Mio.	0.39	−0.16	1.75
7	7-3, 120–122	Paleoc.	−0.08	0.38	0.05
8	8-2, 13–15	Paleoc.	0.14	0.51	0.36
9	9-1, 30–32	U. Cret.	−2.21	0.94	−0.71
10	11-1, 28–29	Cenom.	2.00	1.52	−1.39

nents, but correlation of the intervals of its most definitely manifested development with the actual mineral composition of sediments, as observed in thin sections under microscrope and revealed by X-ray diffractograms, implies that it is represented by calcium carbonate, which occurs as nannofossil micritic remains. In this aspect, the group is similar to assemblage IIB (−) discussed above. As indicated, the latter is represented mostly by calcium carbonate in the form of foraminifer and nannofossil micritic components.

Data on Chemical Analysis Recalculated (Tables 4–6; Fig. 3)

Assemblage IA (+): Fe(0.84)–Mn(0.72)–P(0.31)–Cr(0.64)–Ni(0.39)–V(0.79)–Co(0.15)–Ga(0.29)–Mo(0.79). This assemblage is represented mostly by oxyhydroxide compounds of iron and manganese, and associated heavy metals. The ferrous phosphate phases are apparently of special importance. The group is distinctly confined to the volcanogenic "brown clay" unit (Unit II) of the Late Cretaceous–middle Miocene. Elimination of the diluting effect of silicate components allows the revelation of the geochemical significance of Fe- and Mn-hydroxides in basaltic volcaniclastics, and as separate patches (see assemblages IIA (+), IIIA (+); Fig. 1; Tables 1–3). The combination of components of this assemblage testifies, therefore, that the geochemical role of collectors, concentrating heavy metals, belongs mostly to Fe- and Mn-hydroxides.

Assemblage IB (−): CaO(−0.12)–MgO(−0.85)–Na_2O(−0.83)–Cu(−0.36). The combination of components in this group, peculiar features of its occurrence in the section (Fig. 3), and the data on mineral composition allow us to state that the group is represented by a smectite phase. This phase is not connected with volcaniclastics, which are a rather essential component of the intervals in the section of the lower Pliocene/Pleistocene and lower Cenomanian (Fig. 3).

Assemblage IIA (+): CaO(0.35)–Mg(0.17)–K_2O(0.59)–P(0.65)–Cr(0.72)–V(0.39)–Cu(0.67)–Co(0.43)–Ga(0.90)–Ge(0.58)–Mo(0.15). This assemblage is represented by illite phases, which occur separately and as mixed-layer components of the montmorillonite–mica type, developed in fine volcaniclastic, mostly hyalopelite material of basaltic composition. Phosphorus (alumophosphate compounds) and heavy metals, predominantly Cr, Ga, Cu, Ge, etc., are closely associated with the illite minerals proper. The group is confined to sediments in the top part of the lower Cenomanian and to the volcaniclastic "brown clay" (Unit II), probably Late Cretaceous–middle Miocene (Fig. 2).

Assemblage IIB (−): Na_2O(−0.39)–Fe(−0.12)–Mn(−0.27). This assemblage is represented by hydroxides of manganese and to a lesser extent iron, and by associated sodium. The assemblage contains no heavy metals, and it is located at the base of the volcaniclastic "brown clay" and siliceous, essentially volcanogenic sediments (Units IA, IB; early Pliocene–Pleistocene); these facts allow to state that this group is represented by late-diagenetic, epigenetic patches of Mn-hydroxides, with a slight iron admixture, which formed as the result of volcaniclastic alteration. Similar patches are distinctly observed, in fairly limited amounts, in thin section under the microscope (not more than 5%).

Assemblage IIIA (+): Na_2O(0.12)–K_2O(0.24)–Fe(0.31). This assemblage is represented by hydroxides of iron and K- and Na-bound alkalis. The genetic nature of this group and its occurrence in the section are similar to those of assemblage IIB (−), described above. In this

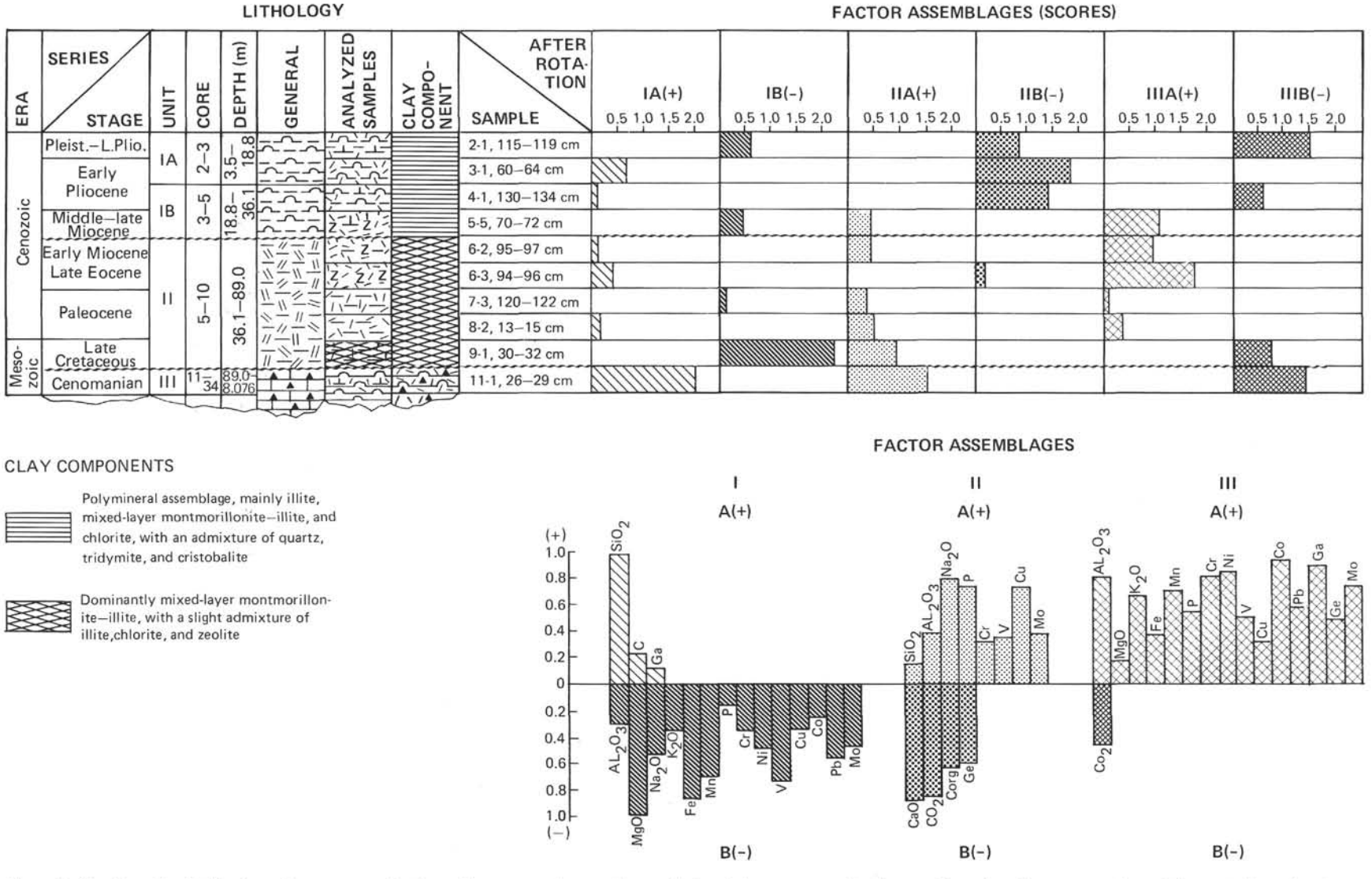

Figure 1. Stratigraphic distribution of factor scores for the main paragenetic assemblages of chemical components in the post-Jurassic sedimentary section of the central northwestern Pacific, northern Hess Rise, DSDP Site 464 (chemical analyses recalculated to air-dry weight). Lithologic symbols are those used in the DSDP *Initial Reports*.

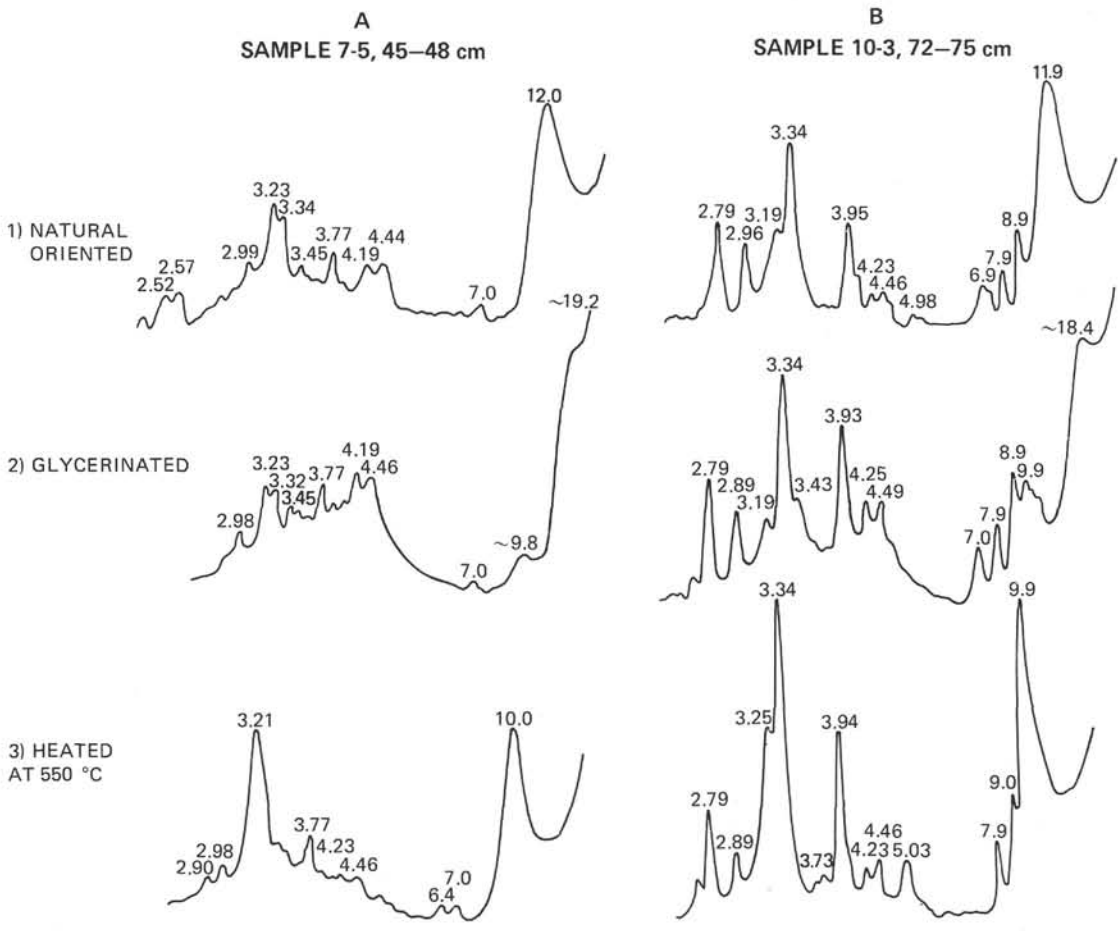

Figure 2. X-ray diffractograms of natural samples of volcanogenic "brown clays" (radiation: CuKα), Site 464. 1. Natural, oriented sample. 2. Oriented after saturation with glycerine. 3. After heating to 550°C. Sample 7-5, 45–48 cm is represented by disordered, rather finely dispersed mixed-layer montmorillonite–mica, with variable contents of expanding and non-expanding layers; trace quantities of hydromica are present; admixture: basic plagioclase of labradorite–bytownite type, zeolite of phillipsite type, quartz. Sample 10-3, 72–75 cm is composed of rather finely dispersed, mixed-layer, disordered montmorillonite–mica; admixture: hydromica, zeolite of clinoptilolite type, quartz.

Table 4. Chemical composition of Mesozoic–Cenozoic sediments, central northwestern Pacific, northern Hess Rise, Site 464.

Sample (interval in cm)	Component (wt.%, recalc.)															
	CaO	MgO	Na_2O	K_2O	Fe	Mn	P	Cr	Ni	V	Cu	Co	Pb	Ga	Ge	Mo
464-2-1, 115–119	8.149	20.694	29.080	10.750	30.085	0.875	0.246	—	0.019	0.009	0.078	0.006	0.008	—	0.0004	0.001
3-1, 60–64	8.894	17.740	35.479	11.903	24.465	1.198	0.122	—	0.076	0.019	0.079	0.013	0.010	0.001	0.001	0.002
4-1, 130–134	8.705	20.169	30.877	13.690	25.831	0.270	0.331	—	0.033	0.033	0.038	0.010	0.011	—	0.0005	0.001
5-5, 70–72	15.633	15.925	14.462	13.752	29.677	7.357	2.717	0.024	0.209	0.059	0.084	0.036	0.028	0.004	0.0004	0.033
6-2, 95–97	13.108	13.587	10.931	16.200	41.676	2.831	1.350	0.025	0.078	0.074	0.083	0.019	0.016	0.005	0.005	0.013
6-3, 94–96	18.859	13.966	15.107	15.629	26.508	6.508	2.898	0.029	0.238	0.062	0.076	0.040	0.028	0.005	0.001	0.048
7-3, 120–122	6.558	16.957	16.208	21.454	37.100	1.031	0.468	0.028	0.046	0.063	0.063	0.011	0.004	0.004	0.0005	0.002
8-2, 13–15	7.207	12.690	12.779	26.972	37.982	1.371	0.752	0.031	0.033	0.063	0.057	0.014	0.006	0.004	0.0004	0.039
9-1, 30–32	7.250	15.106	8.242	6.726	55.461	5.734	1.185	0.011	0.059	0.110	0.068	0.007	0.018	0.001	0.0003	0.022
11-1, 28–29	12.886	27.657	16.500	15.086	23.571	0.157	3.771	0.022	0.024	0.044	0.239	0.016	0.016	0.008	0.002	0.002

case, however, the leading part belongs to Fe-hydroxides (instead of Mn-hydroxides).

Assemblage IIIB (−): CaO(−0.91)-Mn(−0.56)-P(−0.54)-Cr(−0.19)-Ni(−0.84)-Co(−0.79)-Pb(−0.92)-Ga(−0.24)-Mo(−0.50). This assemblage is composed of basaltic volcaniclastics, essentially enriched in calcium oxide and in alteration products, i.e., Mn-hydroxides, phosphate compounds, and associated heavy metals (mostly Ni, Co, Pb). The assemblage is observed predominantly at the top of the volcaniclastic unit (II) of "brown clay" (Late Cretaceous–middle Miocene), in the basal sediments of Unit IB (middle Miocene), represented by siliceous, essentially volcanogenic clays.

Table 5. Results of factor analysis (R-mode) for chemical components (recalculated wt.%) of Cenozoic–Mesozoic sediments, central northwestern Pacific, northern Hess Rise, Site 464.

		Factor Loading (after rotation)		
No.	Component	I	II	III
1	CaO	−0.12	0.35	−0.91
2	MgO	−0.85	0.17	
3	Na_2O	−0.83	−0.39	0.12
4	K_2O		0.59	0.24
5	Fe	0.84	−0.12	0.31
6	Mn	0.72	−0.27	−0.56
7	P	0.31	0.65	−0.54
8	Cr	0.64	0.72	−0.19
9	Ni	0.39		−0.84
10	V	0.79	0.39	
11	Cu	−0.36	0.67	
12	Co	0.15	0.43	−0.79
13	Pb	0.08	0.06	−0.92
14	Ga	0.29	0.90	−0.24
15	Ge		0.58	
16	Mo	0.79	0.15	−0.50
Input in dispersion (%)		43.77	21.57	14.61
Total dispersion (%)		43.77	65.34	79.95

Table 6. Stratigraphic distribution of factor scores (R-mode) for chemical components (recalculated wt.%) in Cenozoic–Mesozoic sediments, central northwestern Pacific, northern Hess Rise, Site 464.

			Factor Scores (after rotation)		
No.	Sample (interval in cm)	Age	I	II	III
1	2-1, 115–119	U. Plio.	−1.11	−1.10	0.67
2	3-1, 60–64	L. Plio.	−1.08	−0.98	−0.20
3	4-1, 130–134	L. Plio.	−0.93	−0.98	0.41
4	5-5, 70–72	Mio.	0.40	−0.08	−1.58
5	6-2, 95–97	U. Eoc.-L. Mio.	0.63	0.80	−0.31
6	6-3, 94–96	U. Eoc.-L. Mio.	0.33	0.13	−1.83
7	7-3, 120–122	Paleoc.	0.51	0.55	−1.39
8	8-2, 13–15	Paleoc.	1.19	0.55	1.20
9	9-1, 30–32	L. Cret.	1.51	−1.03	0.20
10	11-1, 28–29	Cenom.	−1.45	2.13	0.05

Among the altered volcaniclastic components of the volcanogenic unit (II) of brown clay, two groups can be distinguished: (1) the main, dominating group, IA (+), represented by hydroxides of iron and to a lesser extent manganese, by ferrous phosphates and associated heavy metals; it occurs mainly in the lower half of the unit (Late Cretaceous–Paleocene; Fig. 3); (2) a relatively subordinate group, IIIB (−), which contains Mn-hydroxides, phosphates, and associated heavy metals, and appears in the upper half of the unit (late Eocene/late–middle Miocene; Fig. 3). The separation obvious throughout the section between groups of components associated with Fe- and Mn-hydroxides suggests varying contributions from volcanic exhalates and hydrothermal solutions, along with the dominating volcaniclastic material at the initial and final phases of sedimentary accumulation in this unit. Iron compounds were prevalent in initial phases; manganese compounds dominated at final stages.

AVERAGE CONTENTS AND ACCUMULATION RATES OF COMPONENTS (Table 7; Figs. 4–6)

Distribution of Average Contents

The basic elements of calculation of average contents were discussed in our paper on site 463 (Varentsov et al., this volume). It should be noted that in order to reveal general geochemical tendencies in the history of sedimentation the average contents were calculated for definite lithologic types of the main geochronological subdivisions.

Analysis of distribution of average contents of components (Table 7; Figs. 4, 5) in the studied section allows to distinguish three major geochemical stages of sedimentation: (1) late Mesozoic (late Aptian–Cenomanian); (2) Late Cretaceous (Turonian?)/middle Miocene (time of accumulation of the volcanogenic "brown clay" unit); (3) late Cenozoic (late Miocene–Pleistocene).

Late Mesozoic (late Aptian–Early Cenomanian)

Lithologic and geochemical data on the sediments constituting this interval of the section are rather fragmentary and tentative. According to the shipboard files (see Site 464 report, this volume), the sediments form a unit of red-brown cherts (III). However, considering the extreme core shortage, waste of debris of chalk, marl, lithified clays, and speed of drilling, the authors of the site report (Thiede, Vallier, et al., this volume) believe that chalk and marl dominate in the composition of the unit, whereas chert makes not more than 10%. Therefore, the data on average contents and accumulation rates given below can be analyzed only provided an allowance is made for the noted restrictions.

On the whole, the late Mesozoic is characterized by accumulation of maximally high contents of silica and phosphorus in this section of Mesozoic and Cenozoic deposits (Table 7; Fig. 4).

Recalculation of data (Fig. 5) distinctly reveals excessive amounts of K_2O and MgO, which might indirectly indicate the presence of illite–smectite components formed after volcaniclastic material.

Late Cretaceous (Turonian?)/Middle Miocene(?) (accumulation period of the "brown clay" volcanogenic unit)

In this volume, the age interval of this stage is determined by ichthyoliths (Doyle and Riedel, this volume).

Volcanogenic nature of these deposits and their impregnation by Fe- and Mn-hydroxides are distinctly recorded in concentrations of iron, manganese, phosphorus, and associated heavy metals, which are unusually high for normal sediments (Tables 1, 7; Fig. 4). The occurrences of these components are described above. The data on recalculation (Table 4; Fig. 5) also give evidence of high contents of Fe, Mn, and heavy metals, as compared to sediments in the other intervals of the section.

The following features should be emphasized: (1) the lower, basal horizons of the unit (Turonian–Maastrichtian?) are distinguished by maximal contents of Fe (20.12%) and Mn (2.08%), at relatively low values of aluminosilicate components (SiO_2, 26.59%; Al_2O_3,

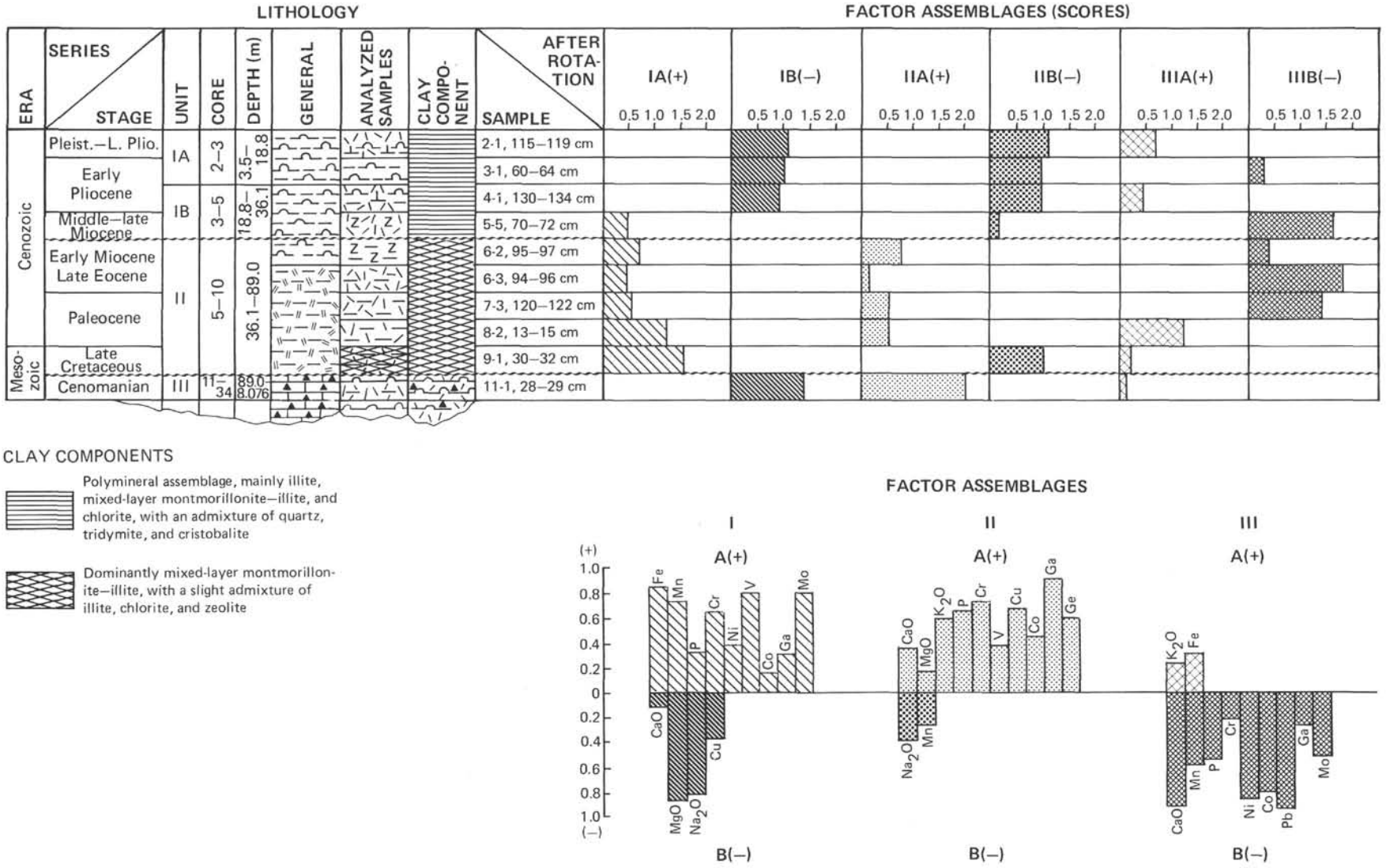

Figure 3. Stratigraphic distribution of factor scores for the main paragenetic assemblages of chemical components in the post Jurassic section of sediments in the central northwestern Pacific, northern Hess Rise, DSDP Site 464 (chemical analyses recalculated). Symbols as in Figure 1.

Table 7. Average contents and mean linear accumulation rates of chemical components for major geochronological subdivisions of the section of post-Jurassic sediments, central northwestern Pacific, northern Hess Rise, Site 464.

Unit	Lithology	Cores	Sub-bottom Depth (m)	Thickness (m)	Stratigraphy	Core	Sub-bottom Depth (m)	Thickness (m)	Density (g/cm^3)	Water Content (%)
IA	Clayey radiolarian oozes, clayey silicic oozes	2-3	3.5-18.8	15.3	L. Pleist.	To 1,CC	0-3.5	3.5	1.20	80.0(?)
					U. Plio.	1,CC to 2-5	3.5-11.0	7.5	1.20	71.0
					L. Plio.	2-5 to 3-0	11.0-18.8	7.8	1.20	72.4
IB	Siliceous clays	3-5	18.8-36.1	17.3	U.-M. Mioc.	3-0 to 4,CC	18.8-32.0	13.2	1.20	72.4
						5-1 to 5-3	32.0-36.5	4.5	1.20	72.4
II	Brown volcanogenic clays	5-11	36.1-89.0	52.9	M. Mioc.	5-4 to 5,CC	36.5-41.5	5.0	1.34	57.6
					L. Mioc.-U. Eoc.	6-0 to 6-4	41.5-46.0	4.5	1.34	57.6
					L. Eoc.-Paleoc.	6-4 to 6,CC	46.0-51.00	5.0	1.34	57.6
					U. Cret.	7-1 to 8,CC	51.0-70.0	19.00	1.34	57.6
					U. Maastr.(?)-Turonian(?)	9-1 to 11-1	70.0-89.0	19.00	1.34	57.6
III	Red-brown silica, chalk, limestone	11-34	89.0-307.6	218.6	Cenom.-M. Alb.	11-1 to 26,CC	8 9.0-241.0	152.0	2.03	5.0
					L. Alb.	27-1 to 34,CC	241.0-308.5	67.5	2.03	5.0(?)

7.96%). In higher horizons (Paleocene-middle Miocene) the content of iron drops by about 2 to 3 times, whereas concentrations of SiO_2 and Al_2O_3 increase, respectively, by a close value. It is peculiar that a sudden increase in the contents of Mn (1.49%) and P (0.65%) occurs in the top part of volcanogenic brown clays (middle Miocene) (Table 7).

Late Cenozoic (late Miocene-Pleistocene)

The limited number of core samples and consequently few chemical analyses allow us to operate with only tentative average contents of components of this stage (Tables 1-7, Figs. 4, 5). On the whole, siliceous oozes, with a notable admixture of basaltic volcaniclastics (in separate intervals, acid volcaniclastics), are characterized by slightly variable values of average contents of $CaCO_3$, SiO_2, Al_2O_3, Fe, Mn, P, and heavy metals, which are shown recalculated to air-dry weight.

Distribution of Average Accumulation Rates of Components

The technique of calculation of average accumulation rates of sediments and components and the length of geochronological intervals are given in the paper on geochemical history of sedimentation at Site 463 (Varenstov et al., this volume).

It should be emphasized that the limitations of this section (few core samples and inadequate stratigraphic justification of some of the intervals) allow only tentative handling of accumulation-rate values in the general context of data on sedimentation of the region.

Average Accumulation Rates (Table 7; Fig. 6)

Analysis of average sedimentation rates provides grounds to outline three major stages in the section; they coincide with the stages established by analysis of average distribution of components.

Late Mesozoic (late Aptian-Cenomanian)

This stage is peculiar for the maximal sediment accumulation rates (mm $10^{-3} \cdot yr.^{-1}$) in the post-Jurassic history of this region: late Aptian-early Albian, 22.5; middle Albian-Cenomanian, 17.9 (Table 7; Fig. 6). Comparison of these values with those obtained for the equatorial zone of high biological productivity shows that accumulation rates of sediments in the early Albian-early Cenomanian were two to three times less at Site 464 (see data on Site 463; Varentsov et al., this volume; Arrhenius, 1963, 1967; Bogdanov and Chekhovskikh, 1979; Bezrukov and Romankevich, 1970; Lisitzin, 1974, 1978). If we assume that during the Albian the northern part of Hess Rise was in the zone of high biological productivity, the Pacific Plate generally moving northward, then such low sedimentation-rate values can be attributed to sediment accumulation essentially below the lysocline level, and in some intervals below the CCD.

Relatively high accumulation rates of SiO_2, Al_2O_3, and Fe, with relatively moderate Mn values, are the result of high sedimentation rates at this stage and a fairly specific composition of accumulating sediments (essentially siliceous rocks) (see Table 7; Fig. 6).

Late Cretaceous (Turonian-Maastrichtian?)/ Middle Miocene (time of accumulation of volcanogenic "brown clay" unit)

As shown by the study of ichthyoliths (Doyle and Riedel, this volume), the age of volcanogenic "brown clay" corresponds to the Late Cretaceous (Turonian?) to middle Miocene. Accumulation rates, calculated for separate intervals of that period, stay within limits characteristic of pelagic sedimentation (Table 7; Fig. 6). The change of accumulation rates of the major com-

Table 7. (Continued).

Age (m.y.)	Sedimentation Rates (mean linear) (mm • 10^{-3}yr^{-1})	(mg•cm^{-2}• 10^{-3}yr^{-1})	Average content (wt.%) and Accumulation Rates of Components (mg•cm^{-2}•10^{-3}•yr^{-1})											
			SiO_2		Al_2O_3		$CaCO_3$		Fe		Mn		P	
			(%)	Acc. Rate	(%)	Acc. Rate	(%)	Acc. Rate	(%)	Acc. Rate	(%)	Acc. Rate	(%)	Acc. Rate
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1.0	7.5	367.5	40.53	148.9	4.67	17.16	25.70	94.44	4.71	17.30	0.13	0.50	0.05	0.18
2.0	10.5	499.8	—	—	—	—	—	—	—	—	—	—	—	—
			47.62	238.0	4.22	21.1	14.61	73.02	3.89	19.44	0.10	0.50	0.04	0.20
10.0	0.45	21.42	—	—	—	—	—	—	—	—	—	—	—	—
4.5	1.11	84.80	44.85	38.03	12.53	10.62	—	0.0	7.10	6.02	1 76	1.49	0.65	0.55
25.0	0.18	13.75	46.14	6.34	13.71	1.89	—	0.0	7.58	1.04	1.01	0.14	0.46	0.06
4.5	1.11	84.80	—	—	—	—	—	0.0	—	—	—	—	—	—
11.5	1.65	126.06	46.68	58.84	12.96	16.34	—	0.0	8.26	10.41	0.27	0.34	0.14	0.18
27.0	0.70	53.48	26.59	14.22	7.96	4.26	—	0.0	20.12	10.76	2.08	1.11	0.43	0.23
8.5	17.88	3540.24	82.68	2927.07	3.68	130.28	—	0.0	1.50	53.10	0.01	0.35	0.24	8.50
3.0	22.50	4455.0	—	—	—	—	—	—	—	—	—	—	—	—

ponents in these fine volcaniclastic sediments is rather significant. The highest accumulation rates of Fe (mg•cm^{-2}•10^{-3}•yr^{-1}) are observed in the early (Late Cretaceous and Paleocene: 10.76) and final (middle Miocene: 6.02) accumulation intervals of the unit. This tendency for Mn is expressed with greater contrast (Late Cretaceous, 1.11; middle Miocene, 1.49). In the intermediate intervals, Mn and Fe accumulation rates are much lower, apparently because of the diluting effect of aluminosilicate volcaniclastic components.

If only Mn and Fe accumulation rates proper are taken into account, then they will not exceed the rates recorded for pelagic areas of the open ocean: Fe, 2.4 to 9.0; Mn, 0.4 to 4.0 mg•cm^{-2}•10^{-3}•yr^{-1}) (Arrhenius, 1967; Boström, 1973; MacArthur and Elderfeld, 1977), whereas they are approximately an order of magnitude higher for the metalliferous sediments of the East Pacific Rise: Mn, 24 to 35; Fe, 63 to 110 (Boström, 1973; Bender et al., 1971).

However, considering the Mn and Fe contents, the forms of their occurrence, and the nature of geochemical associations, mentioned above, it is reasonable to admit that hydrothermal and exhalation products could have had a certain role in the initial and final phases of accumulation of these sediments.

Late Cenozoic (late Miocene–Pleistocene)

The fragmentary character of the available data was noted above. The accumulation rates of clayey siliceous oozes, established for the early and late Pliocene, are 10.5 to 7.5 mm 10^{-3}•yr^{-1}. The sediments were deposited below the CCD, with appreciable amounts of basaltic ash, and to a lesser extent acid volcaniclastic explosive material arriving from the surrounding islands.

Accumulation rates of the major components, in particular Mn, do not exceed values typical of pelagic areas of the open ocean (Table 7; Fig. 6). Somewhat higher values were recorded for Fe (mg•cm^{-2}•10^{-3}•yr^{-1}): early Pliocene, 19.4; late Pliocene, 17.3; they are apparently connected with a notable admixture of altered, deeply oxidized volcaniclastics.

GEOCHEMICAL HISTORY OF SEDIMENTATION

Three major stages are distinguished in the geochemical history of sedimentation in the region, in accordance with analysis of the available data on geochemistry, mineralogy, and lithology of Mesozoic and Cenozoic sediments penetrated by Hole 464. These stages correspond to subdivisions established earlier, during the study of average-contents distribution of components and their accumulation rates.

Late Mesozoic (late Aptian–Cenomanian)

As repeatedly noted above, the sediments accumulated during this stage are inadequately covered by core material, and consequently by paleontological and analytical mineralogical determinations. As described by shipboard files (see site report, this volume), Cores 20 to 32 represent dark-red and brown, calcareous-siliceous oozes (limestones, chalk, chert intercalations), which alternate with appreciable amounts of clayey marl sediments (Albian). The amount of clayey components grows towards the base of the section, reaching 70 to 90% (Cores 29–32, upper Aptian–lower Albian). Typical samples for this part of the section (e.g., 27-1, 63–65 cm) are represented by ashy (30%) and essentially siliceous and radiolarian (20%) limestones. The groundmass is composed of nannofossil micrite (30%) and foraminifer remains (10%), impregnated with scattered Fe-hydroxides (10%).

Above core 20 (to core 11), calcareous, notably siliceous, light-colored sediments dominate (Upper Albian–Cenomanian). The amount of volcanogenic admixture and Fe-hydroxides in these sediments is essentially less than in the underlying Albian deposits.

As noted above, accumulation rates of Albian deposits are peculiar in their maximal values for the Mesozoic and Cenozoic of this region (mm•10^{-3}•yr^{-1}): late Aptian–early Albian, 22.5; middle Albian–Cenomanian, 17.9 (Table 7; Fig. 6).

The limited number of recovered core samples, and consequently of chemical determinations, induces spe-

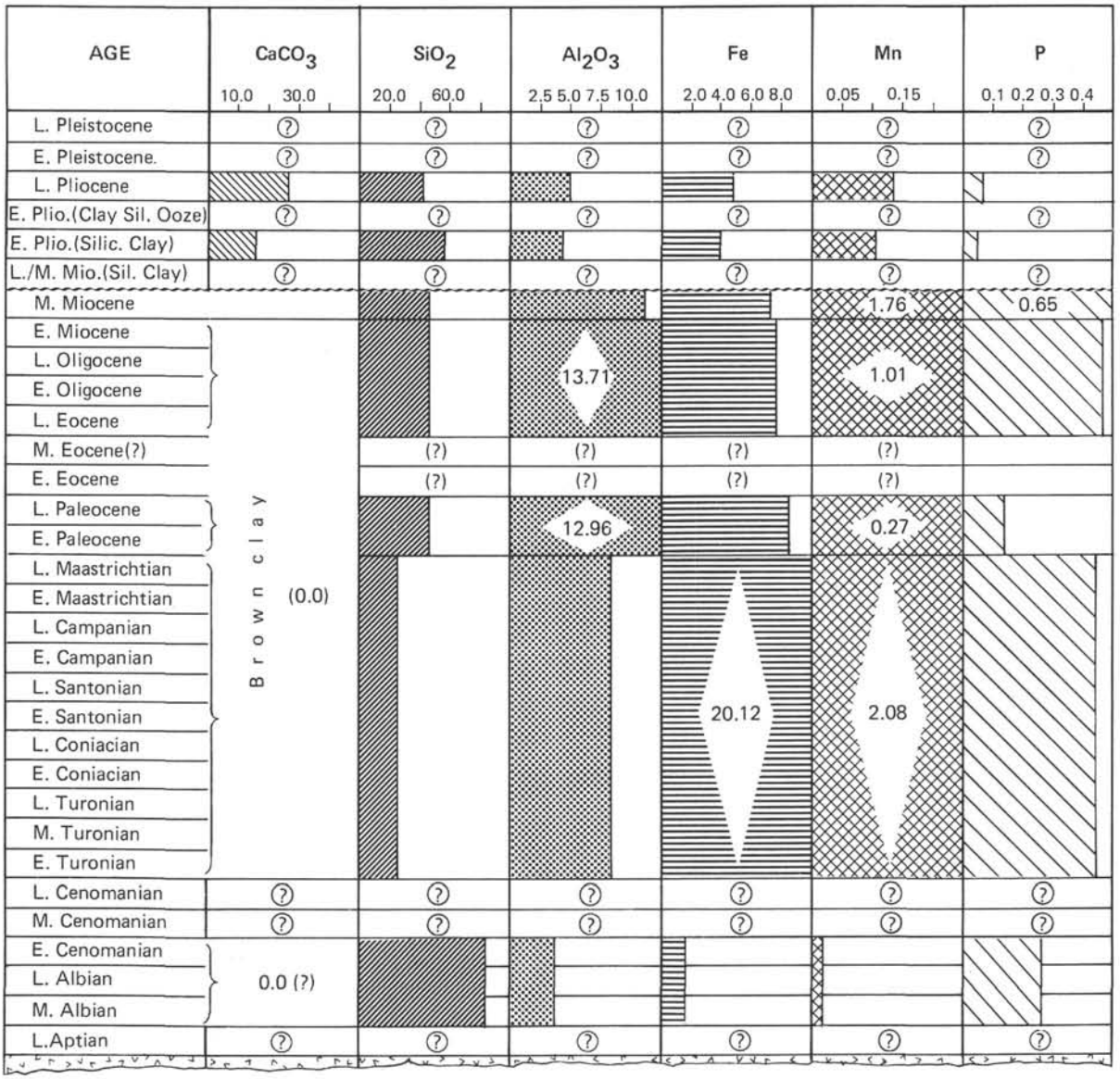

Figure 4. Distribution of average contents (wt. %, air-dry) of SiO_2, Al_2O_3, Fe, Mn, P, and the normative molecule $CaCO_3$ in post-Jurassic sediments of the central northwestern Pacific, northern Hess Rise, DSDP Site 464.

cial handling of actual values of accumulation rates of components (Table 7, Fig. 6). Nevertheless, assuming on the basis of mineralogy and lithology of these sediments a reasonable variation range of the chemical composition of late Aptian–early Albian and middle Albian–Cenomanian deposits, it is possible to note relatively high accumulation rates of SiO_2, Al_2O_3, and other components. These data can be interpreted as evidence that the northern part of Hess Rise during the Albian was in the equatorial zone of high biological productivity, with the general northward movement of the Pacific Plate. Somewhat reduced values of these rates, as compared to the known values of that zone, and large amounts of siliceous material, imply that sediment accumulation took place considerably below the lysocline, and sometimes below the CCD.

Early phases of this stage are extremely interesting. Limited amounts of material allow to assume only that during the late Aptian–Early Albian a significant role in the total sedimentation balance belonged to accumulation of volcaniclastic material, i.e., products of explosive volcanism from the surrounding islands, whereas at the very base of the section the same role belonged to metal-bearing sediments (Site 464 report, this volume).

Late Cretaceous (Turonian–Maastrichtian?)/ Middle Miocene (accumulation time of volcaniclastic "brown clay" unit)

As emphasized earlier, the data on ichthyoliths (Doyle and Riedel, this volume) allows us to believe that the volcanogenic "brown clay" unit (53-m thick) covers the period from Late Cretaceous (Turonian?) to middle (Late?) Miocene. The bottom part (Cores 8–10; Late Cretaceous–Paleocene) contains particles of brown basalt glass of sand–silt size (up to 20–40%), hyalopelite material essentially altered to clayey matter, patches of

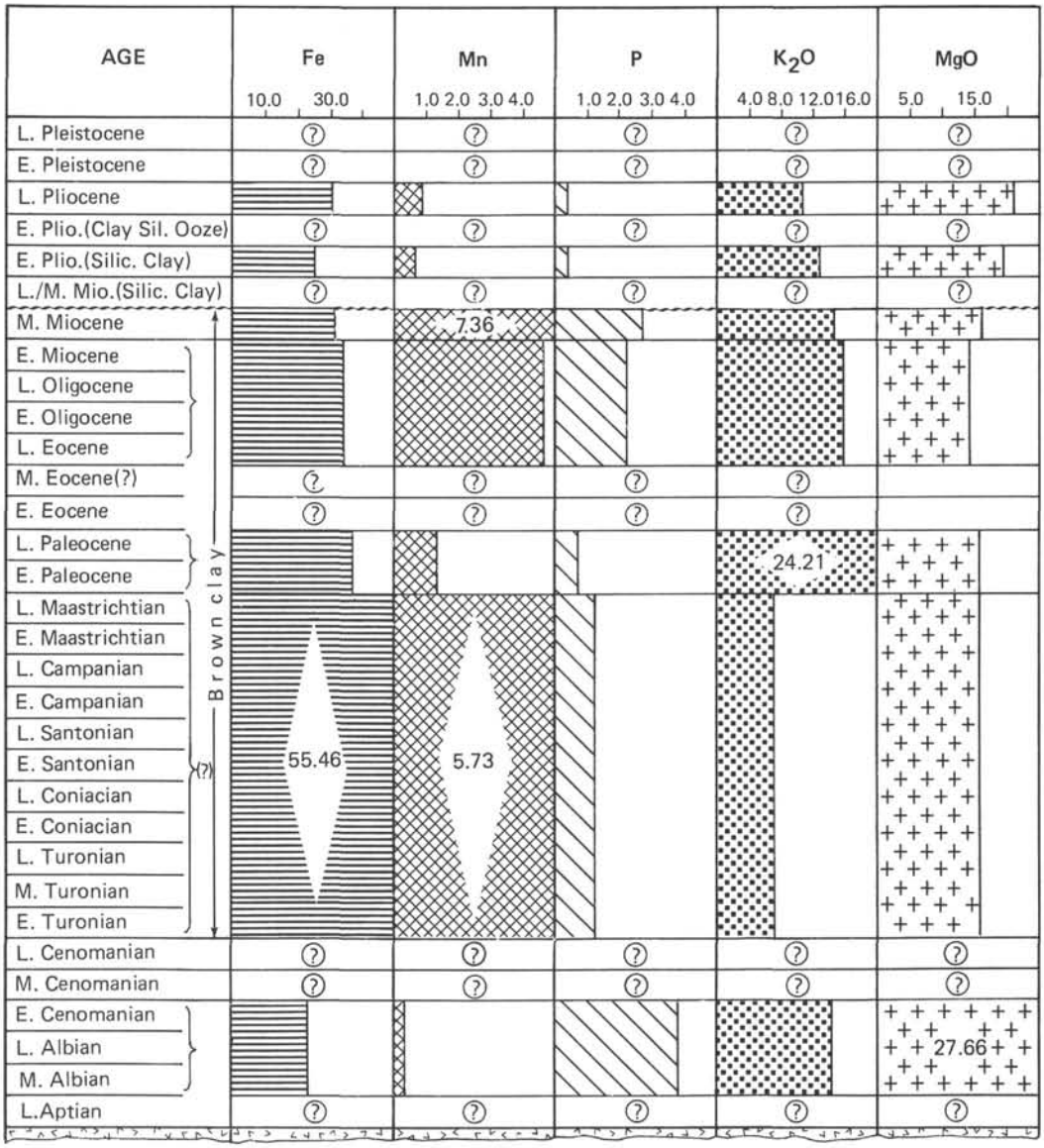

Figure 5. Distribution of average content (wt. %, recalc.) of Fe, Mn, P, K_2O, and MgO in the section of post-Jurassic sediments of the central northwestern Pacific, northern Hess Rise, DSDP Site 464.

hematite (up to 20%), zeolite (up to 10–20%), basic plagioclases (labradorite–bytownite; up to 5–10%). The basal part (Turonian–Maastrichtian?) of the unit sample 9-4, 106–109 cm) contains gravel debris of recrystallized silicified limestones. It is important to note that the groundmass (up to 70–90%) of these sediments is composed of hyalopelite and silty basaltic material essentially transformed into clayey matter. Analysis of X-ray diffractograms of these sediments (Fig. 2) shows that the main components are represented by a combination of disordered, finely dispersed mixed-layer phases, i.e., montmorillonite–mica, with a variable content of expanding (montmorillonite) and non-expanding (mica) layers; quartz, heulandite, and plagioclases of labradorite–bytownite type are present as admixtures. In the upper half (middle Miocene–Paleocene) of the unit (Sample 5-7,CC), the general mineral composition of sediments, on the whole, remains the same. It should be noted, however, that in separate intervals occur appreciable amounts of colorless glass of acid to intermediate composition (up to 10–20%; for example in the Paleocene, Sample 7-6, 43–46 cm), patches of nannofossil micrite, opal–quartz material, and relative reduction in the amount of Fe-hydroxides (by as much as 10%). According to X-ray diffractograms, the type of zeolite is changed; phillipsite dominates.

Mineral compositions have good correlation with geochemical results, in particular with the distribution of paragenetic groups of chemical components, analyzed above (Figs. 1, 2).

These data allow us to believe that the "brown clay" unit is a deep-water (below CCD) accumulation of relatively fine-grained hyalopelite volcaniclastic materials of basaltic composition, which are products of explosive

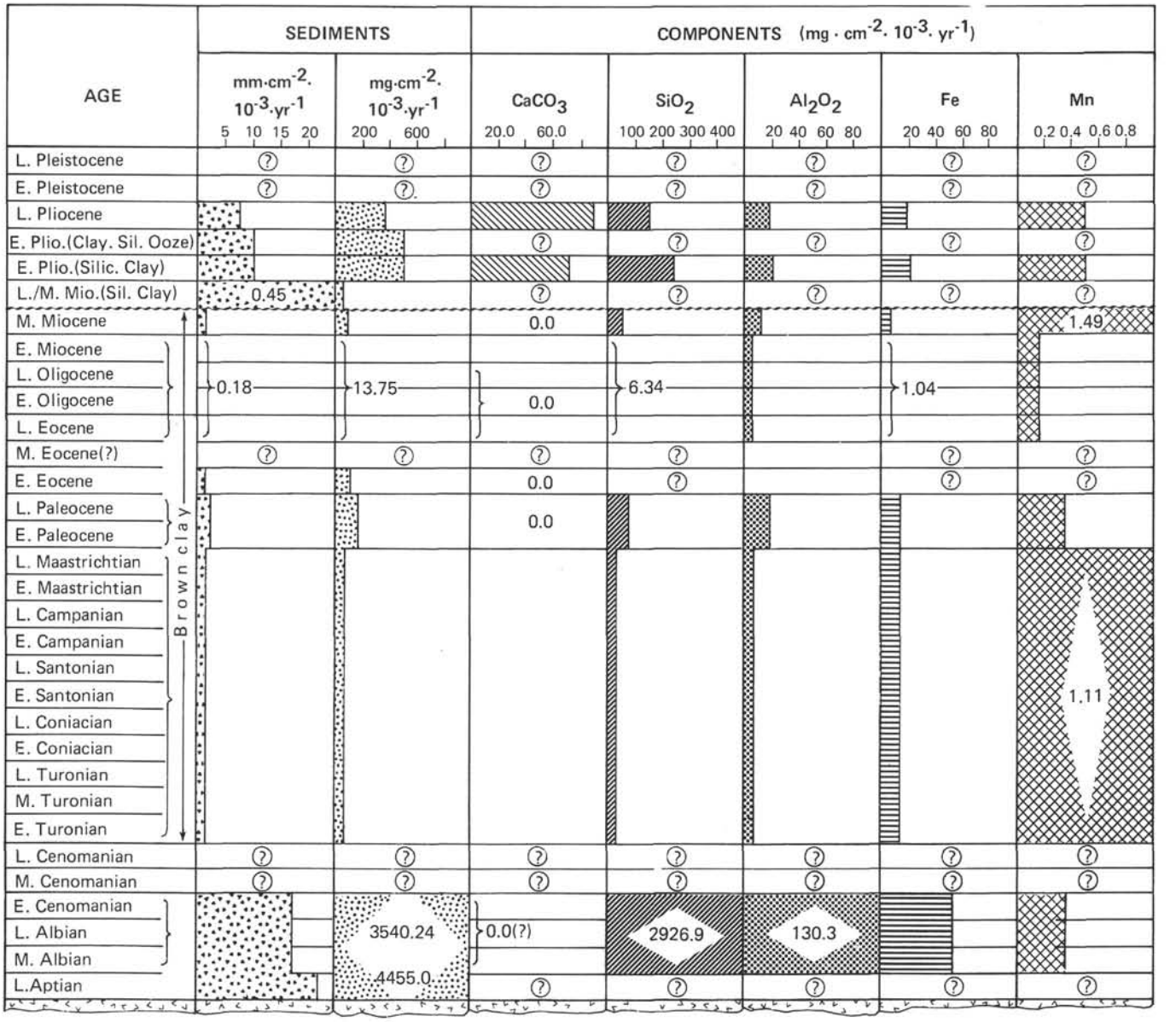

Figure 6. Distribution of average sedimentation rates ($mm \cdot cm^{-2} \cdot 10^{-3} \cdot yr^{-1}$; $mg \cdot cm^{-2} \cdot 10^{-3} yr \cdot^{-1}$) and accumulation of components ($mg \cdot cm^{-2} \cdot 10^{-3} \cdot yr^{-1}$), i.e., $CaCO_3$, SiO_2, Al_2O_3, Fe, and Mn, in the section of post-Jurassic sediments of the central northwestern Pacific, northern Hess Rise, DSDP Site 464.

eruptions of fairly closely located island volcanoes. If Late Cretaceous to middle or late Miocene is assumed as the age of this unit, then accumulation rates of sediments do not exceed values (0.3–6 mm. $10^{-3} yr^{-1}$; (Bezrukov and Romankevich, 1970; Arrhenius, 1963, 1967) typical of deep-water red clays (Table 7; Fig. 6). Comparison of their mineral composition with geochemical features gives evidence that these two types of sediments are largely different. The content of Fe in deep-water red clays of the Pacific is 3.28 to 9.88% (average 5.64%); the content of Mn is 0.16 to 3.00% (average 0.76%) (cf. Bezrukov, and Romankevich, 1970). Concentration of these components is much higher in the studied brown volcanogenic clays (Tables 1, 7; Figs. 4–7).

Somewhat higher accumulation rates of Fe and Mn in the initial and final accumulation phases of that unit and the composition of paragenetic heavy-metal assemblages associated with them (Figs. 1, 2, 6; Table 7) provide grounds to admit the contribution of a certain share of these components in the form of hydrothermal and exhalation products. It should be emphasized that an appreciable admixture of biogenic components of normal oceanic sedimentation is observed only in the upper half of the "brown clay" unit.

Therefore, despite the scantiness of available data, the volcanogenic nature of the deep-sea "brown clay" unit appears to be definite. Apparently, these formations are associated with the activization of some of the structural blocks in the northern part of Hess Rise.

Late Cenozoic (late Miocene–Pleistocene)

During this period, pelagic clayey–siliceous sediments accumulated, forming Sub-units IA (clayey radiolarian oozes, clayey siliceous oozes) and IB (siliceous clays). These sediments (Unit IB) are deposited on volcanogenic "brown clay" (Site 464 report, this volume).

The major biogenic components of both sub-units contain in variable proportions remains of radiolarians, diatoms, sponge spicules, and to a lesser extent nannofossil micrite. The groundmass is represented by fine hyalopelite material altered to clay matter. A characteristic admixture is represented by sand–silt particles of brown basalt (up to 5–15%), to a lesser extent by colorless acid glass. A slight admixture of micronodules of Fe- and Mn-hydroxides is also noted.

The following tendency is observed in this interval: on the one hand, a relative reduction of volcaniclastic components upward in the section, and, on the other hand, an increase in the content of siliceous (and to a lesser extent carbonate) biogenic remains.

According to X-ray structural analysis, the greater part of the clay (Cores 2–5) is represented by two major components present in approximately equal proportions: (1) illite and a mixed-layer phase of mica–montmorillonite with a few (< 10%) expanding layers; (2) Mg,Fe-chlorite. There is a fairly small amount of rather finely dispersed, poorly crystallized, disordered, mixed-layer montmorillonite–mica. Quartz and feldspars are observed in low abundance.

The chemical composition and accumulation rates of sediments at this stage (Tables 1–7; Figs. 1–6) change within a relatively limited range and are almost identical with typically pelagic clay–silica sediments of the open ocean.

Accumulation of sediments took place in an environment similar to the recent one; in the northern oligotrophic zone of the Pacific at depths below the modern CCD. The presence of an insignificant quartz and feldspars admixture in sediments can serve as a criterion for evaluating the contribution of eolian, terrigenous components. The origin of clay components is more obscure. They are represented mostly by illite and Mg,Fe-chlorite minerals, which might be regarded as ultimate links in the chain of deep transformation of hyalopelite fine volcaniclastic material in the marine environment.

CONCLUSIONS

Three major stages are identified in the geochemical history of post-Jurassic sedimentation in the northern part of Hess Rise.

Late-Mesozoic (late Aptian–early Albian–Cenomanian)

The initial phases (late Albian) are peculiar in their accumulation of dark-red and brown, calcareous–siliceous-clayey sediments, essentially enriched by volcanogenic (mainly hyalopelite basaltic volcaniclastic) material. In later phases (middle Albian–early Cenomanian), accumulation of notably siliceous sediments dominated in light-colored sediments. The amount of iron and volcaniclastics in these sediments was much lower than that in the early to middle Albian sediments.

Maximal sedimentation-rate values were established for this stage in the Mesozoic and Cenozoic of the region ($mm \cdot 10^{-3} \cdot yr^{-1}$), i.e., late Aptian–early Albian, 22.5; middle Albian–Cenomanian, 17.9. Rather high accumulation rates of SiO_2, Al_2O_3, and other components were recorded accordingly.

The obtained results are in agreement with the assumptions of the model according to which the northern part of Hess Rise was in the equatorial zone of high biological productivity during the Albian, with the general northward movement of the Pacific Plate. Accumulation of sediments occurred considerably below the lysocline of that epoch.

Late Cretaceous (Turonian?)/Middle Miocene (accumulation time of volcanogenic "brown clay" unit)

These sediments are represented by sand–silt particles of brown basalt glass, groundmass (up to 70–90%) of hyalopelite material altered to clay, patches of hydroxides of Fe (to a lesser extent of Mn), zeolites, and basic plagioclases. The lower part of the unit is relatively enriched in iron; an appreciable admixture of colorless acid glass is observed in the upper part. The clay is represented by a combination of finely dispersed, disordered, mixed-layer phases of montmorillonite–mica, with variable content of expanding and non-expanding layers.

The major paragenetic groups of heavy metals have definite association with Fe- and Mn-hydroxides, alteration products of fine, mostly basaltic volcaniclastics. Accumulation rates of these sediments do not exceed values obtained for deep-water red clays (0.3–6.0 $mm \cdot 10^{-3} yr^{-1}$), but relatively high concentrations of Fe in the initial phases and of Mn in initial and final stages of accumulation of these sediments, and the composition of heavy-metal assemblages associated with them, indicate a definite role of exhalation and hydrothermal products in the contribution of these components.

It is believed that "brown clays" are sediments connected with the activization of certain structural blocks in the northern part of Hess Rise, accompanied by local volcanism during a long period (81 m.y.).

Late Cenozoic (late Miocene–Pleistocene)

Pelagic clayey–siliceous, mostly radiolarian oozes accumulated during this stage. The clay groundmass is composed of hyalopelite material altered to clay (mainly illite and Mg,Fe-chlorite). An admixture of brown basalt, and to a lesser extent of colorless acid glass, is typical.

Chemical composition and accumulation rates of these sediments vary within a relatively limited range and are similar to typical clayey–siliceous oozes of the open ocean.

Accumulation of sediments took place in the environment close to that of the Recent, i.e., in the northern oligotrophic zone of the Pacific, at depths below the modern CCD.

Thus, in the geochemical history of post-Jurassic sedimentation of the northern part of Hess Ress, the most essential phases of development can be outlined, with different degrees of clarity, which reflect the general evolution of the basin.

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