

XIII. MINOR CHEMICAL COMPOSITION OF DEEP-SEA SEDIMENTS FROM THE GH80-5 AREA IN THE CENTRAL PACIFIC BASIN

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Introduction

The moisture content and the minor elements, such as Mn, Fe, Co, Ni, Cu, Zn and Pb, were determined for 109 sediment samples from the GH80-5 area, in order to elucidate the origin of manganese nodules. The total 109 sediment samples consist of 22 surface sediment samples and 87 core segment samples, whose maximum depth below the bottom surface attains to about 8 m in the longest core. From the results, general distribution of metal contents and the correlations among each element are described for surficial and core segment samples.

Sample preparation and analytical method

The methods of sample preparation and analysis were the same as those in our preceding work (MITA *et al.*, 1982). The outline of them are as follows.

The sediment samples which contain sea water were dried in air enough. After grinding, the sample was weighed out into platinum dish and then mixed with nitric acid, hydrofluoric acid and perchloric acid. The dish was heated to dryness. The salts were dissolved with hydrochloric acid and the acidity of HCl was adjusted to 0.3 N. Then the contents of Mn, Fe, Co, Ni, Cu, Zn and Pb in the samples were determined by atomic absorption spectrophotometry. The moisture contents at 110°C were determined for another aliquot.

Results and discussions

The dry basis contents of Mn, Fe, Co, Ni, Cu, Zn and Pb in the 109 samples are shown in Table XIII-1. The averages, minimums, maximums and standard deviations for each element in all samples and in three sample groups based on the sediment facies, i.e. siliceous fossil rich clay (SRC), pelagic clay (PC) and zeolitic clay (ZC), are shown in Table XIII-2.

On previous cruise, GH80-1, it has been noted that the sediment in the Penrhyn Basin is extraordinary rich in metal elements, such as those mentioned above. Maximum contents are 2.22% for Mn, 8.81% for Fe and 1134 ppm for Cu, for examples (MITA *et al.*, 1982). On this cruise, however, maximum contents of them are 1.74% (Mn), 5.9% (Fe) and 903 ppm (Cu).

Table XIII-1 Minor chemical composition of bottom sediments in the GH80-5 area (in dry basis)

Analysis No.	Sample No.	Sediment Type	Mn %	Fe %	Co ppm	Ni ppm	Cu ppm	Zn ppm	Pb ppm
1	P194 (1)77- 82	SRC	0.56	4.91	105	120	429	539	62
2	P194 (2)25- 30	PC	0.72	5.16	120	184	465	643	47
3	P194 (2)75- 80	PC	0.74	5.38	128	181	517	506	53
4	P194 (3)25- 30	PC	0.87	5.43	130	287	611	323	50
5	P194 (3)75- 80	PC	0.95	4.66	152	399	846	387	52
6	P194 (4)25- 30	ZC	0.80	4.19	151	325	797	231	45
7	P194 (4)75- 80	ZC	0.87	4.17	134	260	878	317	62
8	P194 (5)25- 30	ZC	0.91	4.57	148	267	903	235	53
9	P194 (5)75- 80	ZC	1.08	5.16	166	306	838	423	59
10	P194 (6)25- 30	ZC	1.14	4.08	119	249	703	263	55
11	P194 (6)75- 80	ZC	1.11	3.88	122	251	709	272	51
12	P194 (7)25- 30	ZC	1.18	4.10	128	277	286	252	46
13	P194 (7)75- 80	ZC	1.38	4.94	186	399	724	249	53
14	P194 (8)25- 30	ZC	0.47	1.83	42	55	299	87	18
15	P194 (8)83- 88	SO	0.95	3.71	99	223	650	217	38
16	P195 (2)18- 23	SRC	1.07	3.83	112	225	610	179	39
17	P195 (2)65- 70	ZC	1.07	4.54	121	246	493	197	48
18	P195 (3)15- 20	ZC	0.91	4.18	109	176	459	198	58
19	P195 (3)65- 70	ZC	1.02	4.08	111	188	506	192	41
20	P195 (4)15- 20	ZC	1.02	4.05	115	185	511	181	37
21	P195 (4)65- 70	ZC	0.99	4.35	111	207	505	182	50
22	P195 (5)15- 20	ZC	1.02	4.21	122	265	536	222	38
23	P195 (5)65- 70	ZC	1.04	4.40	122	268	574	201	37
24	P195 (6)15- 20	ZC	1.01	4.43	113	216	526	218	43
25	P195 (6)65- 70	ZC	1.01	4.50	105	213	507	186	36
26	P195 (7)15- 20	ZC	0.98	4.57	102	220	442	192	37
27	P195 (7)65- 70	ZC	1.02	4.44	108	219	461	196	45
28	P195 (8)15- 20	ZC	0.96	4.24	111	196	463	186	38
29	P195 (8)65- 70	ZC	0.99	4.36	118	195	500	189	31
30	P198 (1)93- 98	SRC	0.56	4.69	99	136	383	140	38
31	P198 (2)38- 43	PC	0.64	4.86	107	161	414	194	37
32	P198 (2)88- 93	PC	0.66	4.95	108	155	402	193	36
33	P198 (3)38- 43	PC	0.69	5.12	114	162	482	147	47
34	P198 (3)88- 93	PC	0.67	5.01	106	162	439	140	52
35	P198 (4)38- 43	PC	0.66	4.89	103	157	420	136	41
36	P198 (4)88- 93	PC	0.63	4.97	101	165	414	159	89
37	P198 (5)38- 43	PC	0.74	5.01	114	173	482	149	86
38	P198 (5)88- 93	PC	0.70	5.12	117	150	494	212	55
39	P198 (6)38- 43	PC	0.71	5.02	115	165	514	143	41
40	P198 (6)88- 93	PC	0.79	5.23	125	193	585	166	52
41	P198 (7)38- 43	PC	0.82	5.04	133	238	576	242	55
42	P198 (7)88- 93	PC	0.83	4.98	137	238	630	225	44
43	P198 (8)38- 43	PC	0.83	4.89	126	222	595	161	37
44	P198 (8)88- 93	PC	0.88	4.93	138	281	695	157	49

Table XIII-1 (continued)

Analysis No.	Sample No.	Sediment Type	Mn %	Fe %	Co ppm	Ni ppm	Cu ppm	Zn ppm	Pb ppm
45	P204 (2) 3- 8	SRC	0.80	5.24	130	184	428	139	51
46	P204 (2) 40- 45	PC	0.90	5.32	133	241	460	171	57
47	P204 (2) 90- 95	PC	0.95	5.50	141	264	498	177	54
48	P204 (3) 40- 45	PC	1.04	5.33	153	310	554	187	44
49	P204 (3) 90- 95	PC	1.15	5.12	152	383	607	174	52
50	P204 (4) 40- 45	PC	0.45	5.16	128	126	604	178	59
51	P204 (4) 90- 95	PC	1.36	5.42	176	371	674	249	63
52	P204 (5) 40- 45	ZC	1.14	4.50	183	390	597	385	47
53	P204 (5) 90- 95	ZC	1.01	4.61	165	353	816	464	56
54	P204 (6) 40- 45	ZC	1.17	5.28	165	352	468	606	43
55	P204 (6) 90- 95	ZC	1.13	4.50	153	345	613	266	44
56	P204 (7) 40- 45	ZC	1.19	4.35	141	385	749	260	39
57	P204 (8) 40- 45	SO	0.06	0.29	6	16	60	22	2
58	P204 (8) 90- 95	SO	0.05	0.21	3	13	44	40	8
59	P206 (2) 65- 70	SRC	0.61	4.78	119	125	397	376	48
60	P206 (3) 15- 20	PC	0.74	5.16	130	145	414	226	42
61	P206 (3) 65- 70	PC	0.78	5.29	138	157	442	236	56
62	P206 (4) 15- 20	PC	0.70	5.02	120	153	423	127	54
63	P206 (4) 65- 70	PC	0.69	5.00	115	148	408	332	78
64	P206 (5) 15- 20	PC	0.88	5.13	131	209	468	136	44
65	P206 (5) 65- 70	PC	0.70	5.28	132	169	507	215	50
66	P206 (6) 15- 20	PC	0.82	5.41	134	201	504	199	44
67	P206 (6) 65- 70	PC	0.90	5.55	148	211	538	238	51
68	P206 (7) 15- 20	PC	0.99	5.34	164	299	563	221	50
69	P206 (7) 65- 70	PC	0.88	5.15	139	204	518	145	49
70	P206 (8) 15- 20	PC	0.95	5.01	154	254	633	190	54
71	P206 (8) 65- 70	PC	0.92	5.02	153	224	546	261	46
72	P207 (1) 95-100	SRC	0.37	4.44	99	78	305	382	54
73	P207 (2) 45- 50	SRC	0.74	5.26	126	178	411	129	36
74	P207 (2) 95-100	PC	0.88	5.69	149	203	473	175	40
75	P207 (3) 45- 50	PC	1.00	5.55	142	311	515	174	52
76	P207 (3) 95-100	PC	0.87	5.61	152	228	516	178	50
77	P207 (4) 45- 50	PC	0.90	5.95	171	240	550	234	48
78	P207 (4) 95-100	PC	0.50	5.53	137	168	576	166	56
79	P207 (5) 45- 50	PC	0.49	5.52	227	215	736	209	51
80	P207 (5) 95-100	ZC	1.74	5.22	125	715	640	255	47
81	P207 (6) 45- 50	ZC	1.12	4.65	142	513	526	228	39
82	P207 (6) 95-100	ZC	1.01	4.53	124	442	524	205	37
83	P207 (7) 45- 50	ZC	1.06	4.21	135	366	647	304	40
84	P207 (7) 95-100	ZC	0.79	4.03	82	281	558	243	30
85	P207 (8) 45- 50	ZC	0.29	1.54	27	83	233	90	30
86	P207 (8) 95-100	CO	0.11	0.58	18	39	87	150	36
87	P194 cc	CH	0.53	4.83	88	151	604	145	36
88	B33	PC	0.58	4.71	96	160	534	156	30

Table XIII-1 (continued)

Analysis No.	Sample No.	Sediment Type	Mn %	Fe %	Co ppm	Ni ppm	Cu ppm	Zn ppm	Pb ppm
89	B34	SRC	0.51	4.65	86	125	489	139	28
90	B35	PC	0.53	4.60	102	114	396	129	36
91	B36	SRC	0.52	4.69	80	118	395	136	35
92	B37	SC	0.38	4.37	72	82	427	121	26
93	B38	SRC	0.58	4.72	91	150	484	158	42
94	B39	SRC	0.50	4.49	88	115	388	123	44
95	B40	SRC	0.68	4.69	105	197	513	140	40
96	B41	SRC	0.55	4.32	91	119	394	123	34
97	B42	SRC	0.46	4.15	84	185	365	144	33
98	B43	SRC	0.79	4.58	110	226	489	151	37
99	B44	SRC	0.54	4.39	88	115	407	134	30
100	B45	SRC	0.68	4.44	106	190	439	145	27
101	B47	SRC	0.53	4.37	86	121	390	138	35
102	B48	SRC	0.60	4.38	100	159	414	127	37
103	B49	SRC	0.78	4.22	107	234	476	148	33
104	B50	SRC	0.86	4.38	112	260	519	142	39
105	B51	SRC	0.90	4.28	107	268	544	141	34
106	B52	SRC	0.58	4.34	92	139	418	125	34
107	B53	SRC	0.50	4.14	86	112	365	158	29
108	B54	SRC	0.76	4.51	113	217	485	196	37
109	B55	SRC	0.74	4.26	106	221	465	139	38

Table XIII-2 Averages, minimums, maximums, and standard deviations. Unit of concentrations is % for Mn and Fe, or ppm for the other elements

<u>(a) All samples (n=109)</u>								<u>(b) Siliceous fossil rich clay facies (n=26)</u>							
	Mn	Fe	Co	Ni	Cu	Zn	Pb		Mn	Fe	Co	Ni	Cu	Zn	Pb
AVE.	0.80	4.59	118	216	509	209	44	AVE.	0.65	4.51	101	163	439	177	38
MIN.	0.05	0.21	3	13	44	22	2	MIN.	0.37	3.83	80	105	365	125	27
MAX.	1.74	5.95	227	715	903	643	89	MAX.	1.07	5.26	130	268	544	539	62
S.D.	0.27	0.95	34	102	145	102	12	S.D.	0.16	0.31	13	53	65	97	8

<u>(c) Pelagic clay facies (n=44)</u>								<u>(d) Zeolitic clay facies (n=33)</u>							
	Mn	Fe	Co	Ni	Cu	Zn	Pb		Mn	Fe	Co	Ni	Cu	Zn	Pb
AVE.	0.80	5.18	134	213	528	213	51	AVE.	1.02	4.26	124	285	575	248	43
MIN.	0.45	4.60	96	145	408	136	37	MIN.	0.29	3.88	82	185	461	186	31
MAX.	1.36	5.95	227	383	736	643	63	MAX.	1.74	5.28	186	715	816	606	56
S.D.	0.17	0.28	24	67	95	97	11	S.D.	0.23	0.73	33	122	161	99	9

Horizontal and vertical distribution of the elements

Any systematic change cannot be recognized in horizontal distribution of the elements for the surface sediments which all belong to siliceous fossil rich clay. Vertical distribution of the elements in six sediment cores are shown in Fig. XIII-1. It is rather uniform in the cores obtained from the detailed survey area 1 (Figs. XIII-1 (a)~(c)) than those from the detailed survey area 2 (Figs. XIII-1(d)~(f)).

Manganese contents in the uppermost portion of each core are usually lower than those in the second depth. Increasing tendency of manganese to the deeper part is common in pelagic clay facies. In zeolitic clay facies, however, both decreasing and increasing tendencies are observed depending on the core. Abrupt decreasing of

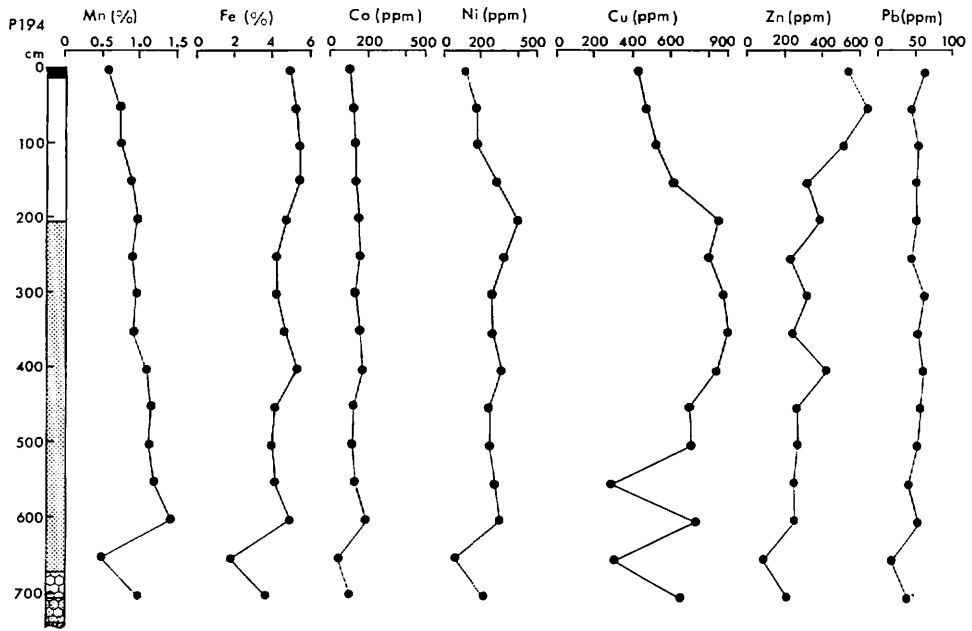


Fig. XIII-1 (a)

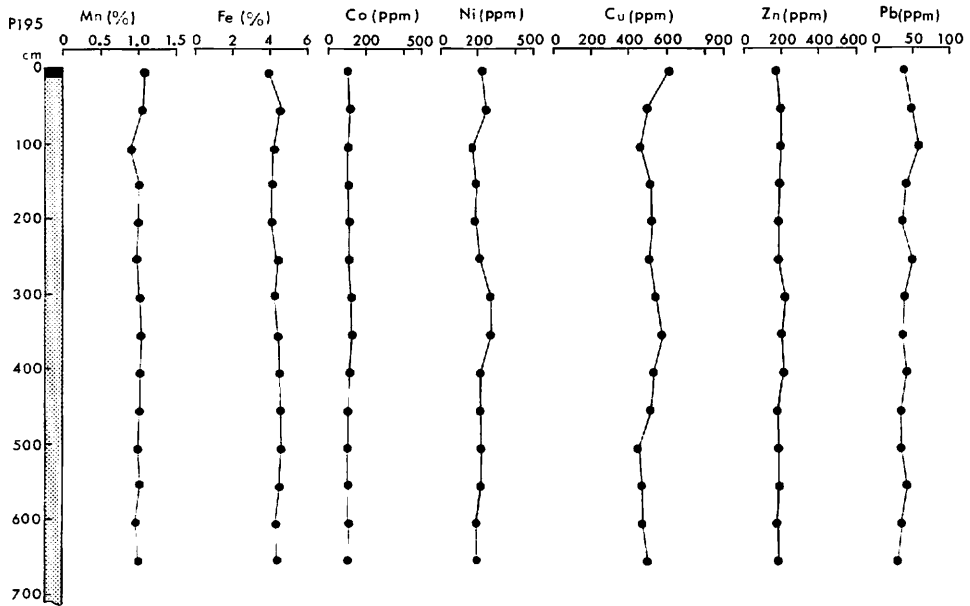


Fig. XIII-1 (b)

Fig. XIII-1 Vertical distribution of minor chemical composition in some selected cores. Sediment types (shown in the figure(e) in the columns, are 1: siliceous fossil rich clay, 2: siliceous clay, 3: siliceous ooze, 4: pelagic clay, 5: zeolitic clay, 6: calcareous ooze and 7: chert.

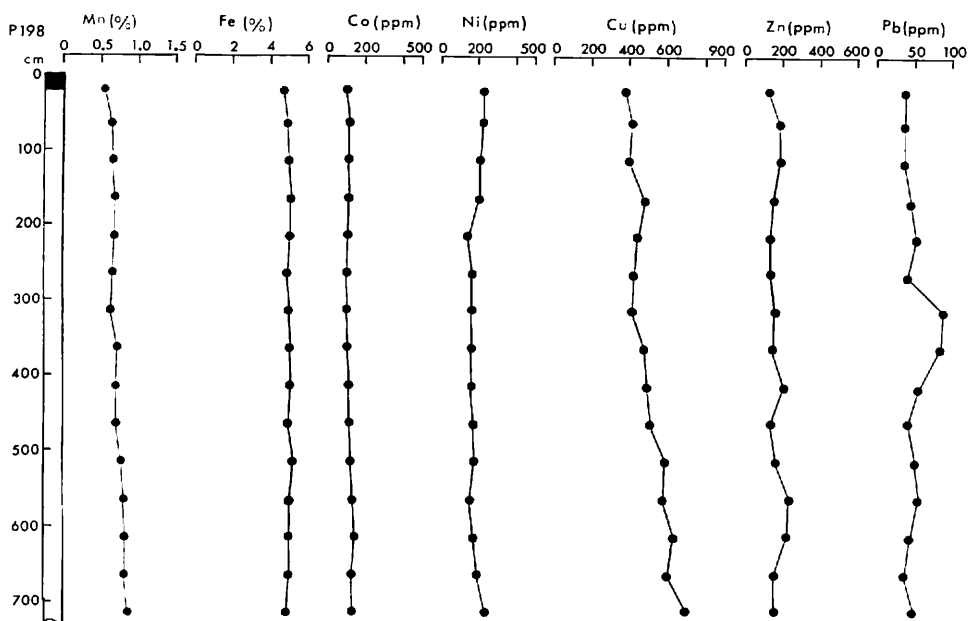


Fig. XIII-1 (c)

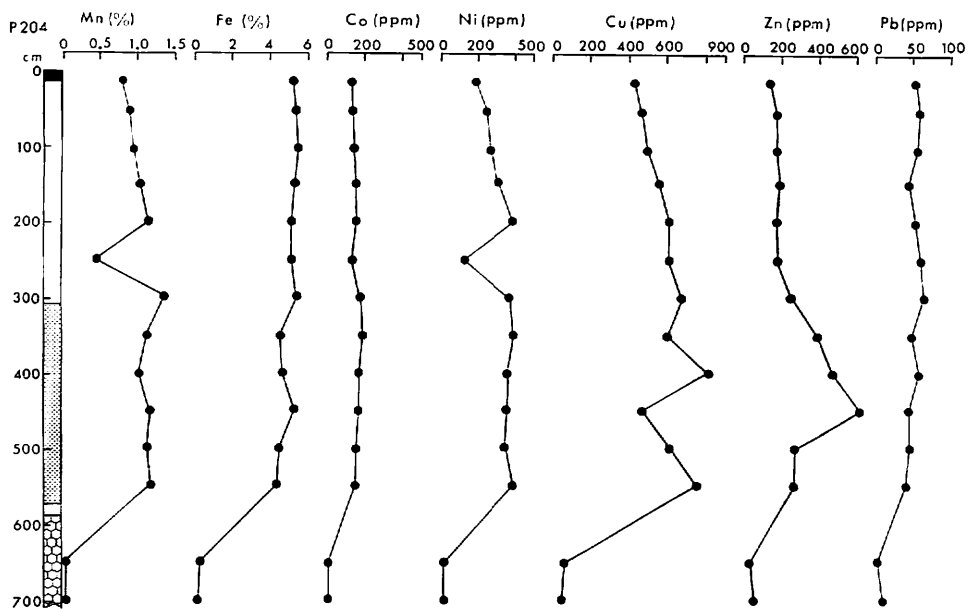


Fig. XIII-1 (d)

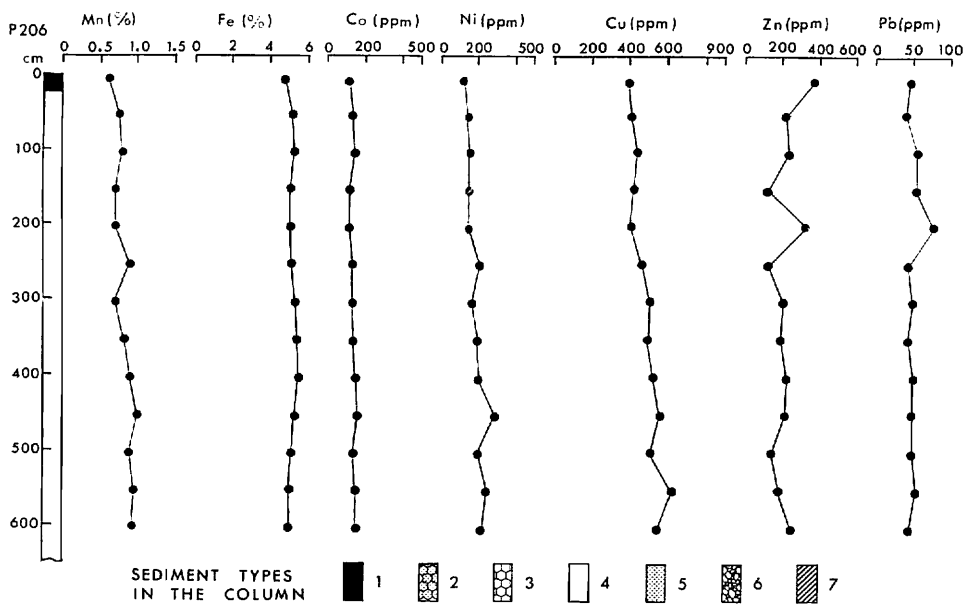


Fig. XIII-1 (e)

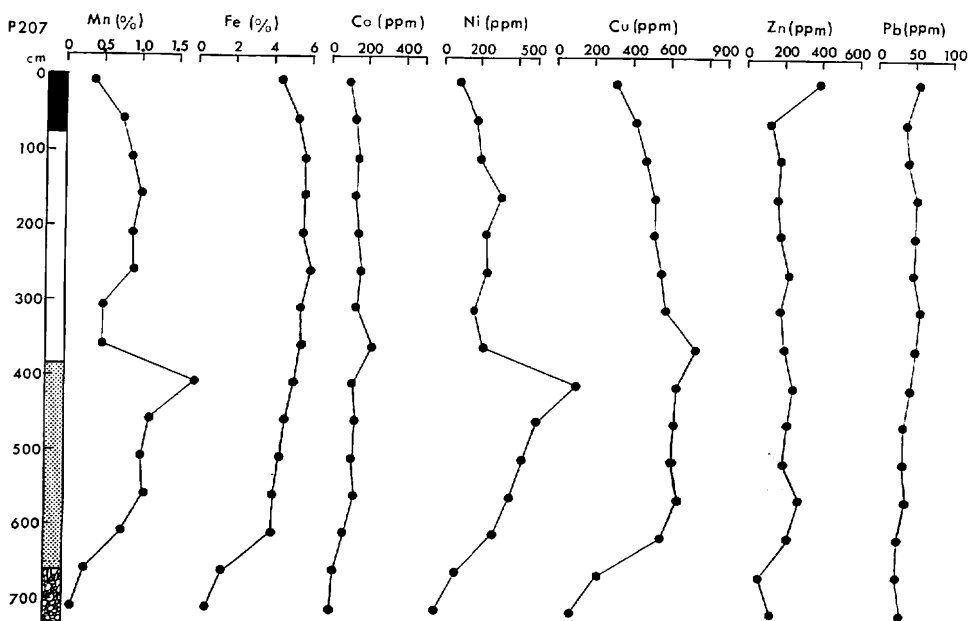


Fig. XIII-1 (f)

manganese content is observed in the cores (1) P194, lowermost part of zeolitic clay, around the portion of 650 cm deep, (2) P204, lower part of pelagic clay, around 250 cm deep, (3) P204, near the bottom of the core (siliceous ooze), around 650 cm and 700 cm deep, (4) P207, bottom part of pelagic clay, around 300 cm and 350 cm deep, (5) P207, bottom part of the core (calcareous ooze), around 650 and 700 cm deep.

Among these portions, (2) and (4) are obviously decolorized (NISHIMURA, in this cruise report) suggesting a reducing process in sedimentary or diagenetic environment of those. Nickel has the commonest behavior with that of manganese in those cases, whereas copper behaves dependently or even on the contraries though it is well known that there is an intimate correlation between nickel and copper in the Pacific manganese nodules.

On the other hand, the portions (3) and (5) shows siliceous ooze facies and calcareous ooze facies respectively (NISHIMURA, this cruise report). Outstandingly low contents of those elements in siliceous or calcareous ooze are reported in KATO *et al.* (1979) and MITA *et al.* (1982). In the cases in this cruise, almost all elements

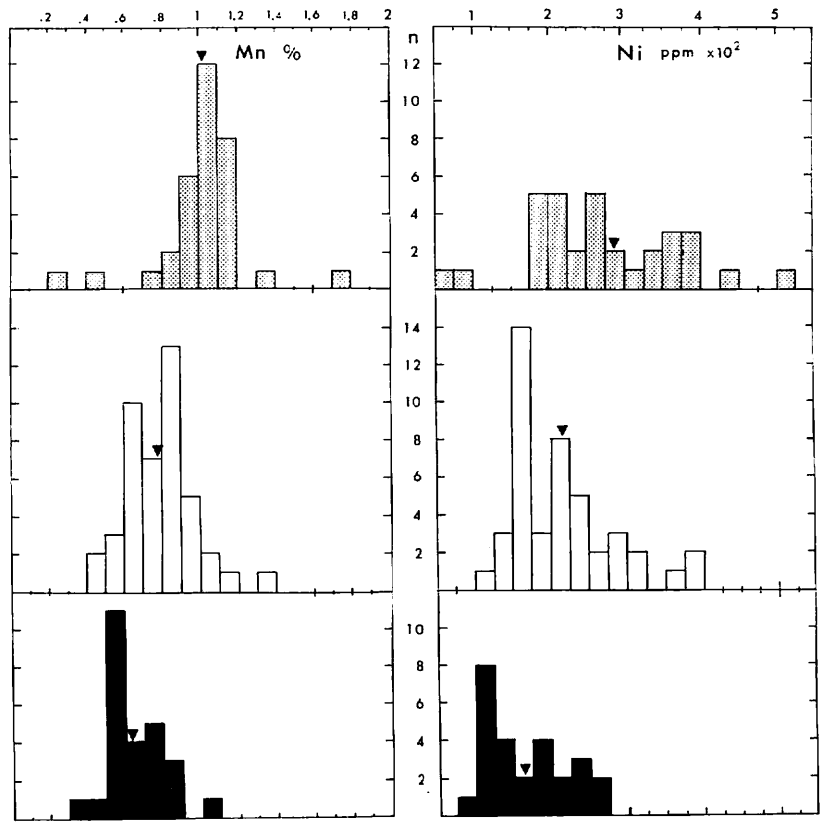


Fig. XIII-2 (a)

Fig. XIII-2 Histograms of the concentration of minor chemical composition for all samples and each major sediment facies.

analyzed have same tendencies, suggesting very low concentrations of them in siliceous or calcareous organic remains.

There is one portion showing abrupt increasing of manganese in P207 (uppermost part of zeolitic clay, around 400 cm deep), being concordant with that of nickel both accompanied by upward increasing tendency of these two elements in zeolitic clay layer. According to NISHIMURA (this cruise report), a manganese crust occurs near the top of this zeolitic clay layer. Hence the abrupt increasing of manganese mentioned above is thought to be of diagenetic origin.

Somewhat irregular behavior of copper is observed, in P194 (around 550 cm), P195 (around the top), P204 (around 400 cm and 450 cm) or P207 (around 350 cm). Inconsistency of that compared with the other elements supports the hypothesis by Arrhenius (1963) that the source of the copper in the equatorial high productivity zone is most likely planctonic organisms.

Sediment facies and concentrations of the elements

Fig. XIII-2 shows histograms of the elements for each major sediment facies, i.e. siliceous fossil rich clay (bottom), pelegic clay (middle) and zeolitic clay (top). The elements in the figure (a) or (b) have a common tendency, namely average concentration of those is highest in zeolitic clay facies and is lowest in siliceous fossil

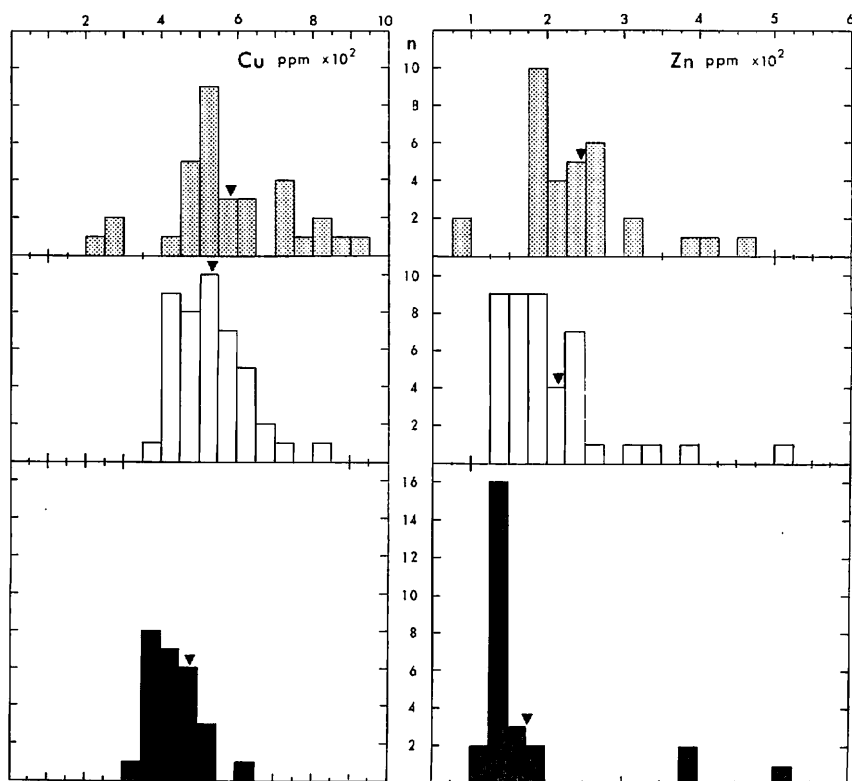


Fig. XIII-2 (b)

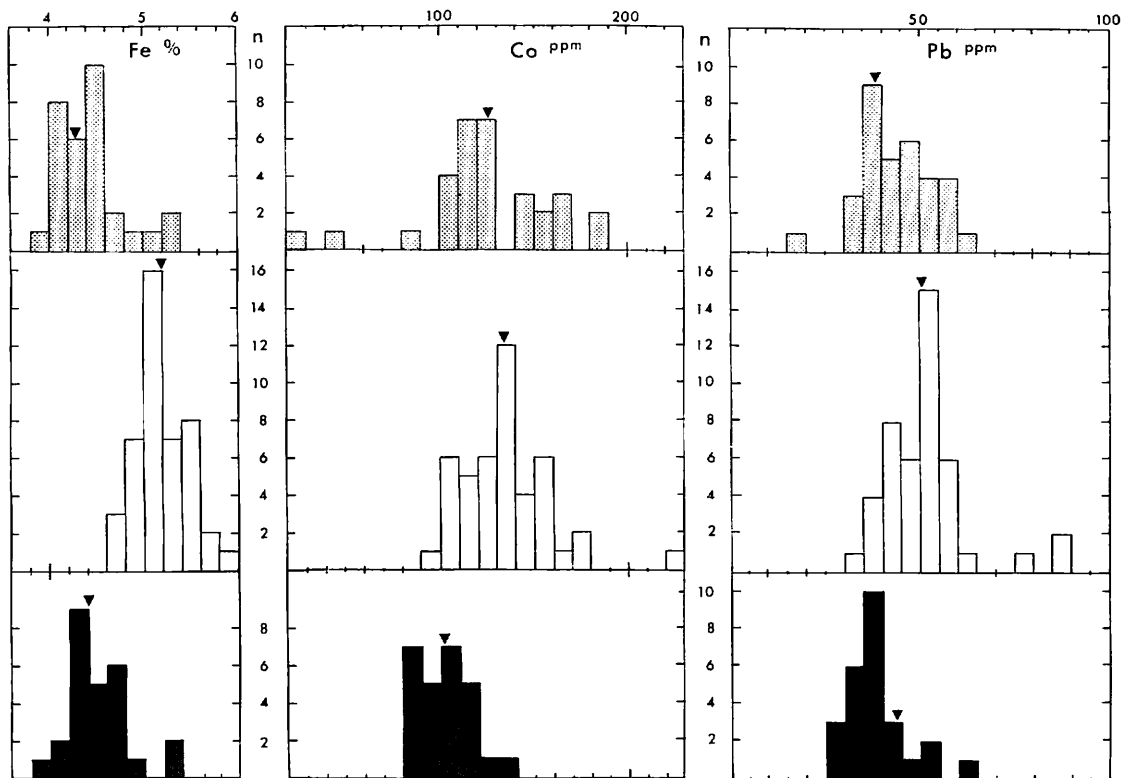


Fig. XIII-2 (c)

rich clay facies. On the other hand, Fe, Co, and Pb, in the figure (c), of which the highest averages appear for pelagic clay facies, and the lowest averages appear for zeolitic clay facies except Co.

Absolutely or relatively low averages of the elements, in siliceous fossil rich clay facies also suggest rather insignificant contribution of the siliceous fossils to concentrate those elements. MARCHING (1979) reported, in this connection, "radiolarian fraction" (coarser than $63\ \mu\text{m}$, nonmagnetic part) contains Fe, Mn, Cu, Ni and Co of which concentrations are far less than those in the fraction finer than $63\ \mu\text{m}$. On the other hand, higher concentrations of Mn, Ni, Cu and Zn in zeolitic clay facies than in pelagic clay facies may owe to a selective condensation of these elements during the genesis of manganese micronodules or selective adsorbance of them on zeolite minerals. Further study is necessary to solve this problem.

Lower concentrations of Fe, Co and Pb in zeolitic clay facies than in siliceous fossil rich clay facies and/or pelagic clay facies may owe largely to reduction of them in zeolite minerals. According to STONECIPHER (1978), phillipsites in north Pacific deep-sea sediments contain FeO (total iron as inclusion impurities, namely not included in cell contents) up to 0.98%, and clinoptilolites also in north Pacific deep-sea sediments does FeO up to 0.80%. Besides, in the relation to genesis of phillipsite, HONNOREZ (1978) reported an enrichment of Fe in an altered residual

glass at the initial stage of palagonitization. Among the other two elements, especially Pb probably has similar behavior with Fe in that stage. KASTNER and STONECIPHER (1978) point out that the most common precursor for phillipsite seems to be palagonite, and that possible precursors for clinoptilolite include rhyolitic to andesitic glass, basaltic glass + silica (mainly biogenic), smectite + phillipsite + biogenic silica, and perhaps smectite + biogenic silica and biogenic silica + Al and K. Hence, the behavior of these elements during the genesis of clinoptilolite, which is major zeolite mineral in the zeolitic clay facies according to NISHIMURA (this cruise report), should not be simple unless exact precursor is specified.

Correlation among the elements

Coefficients of correlation among the elements in all samples and in the three sediment facies are shown in Table XIII-3. Estimation of the correlation among the elements, being carried out at 5% of level of significance, is as follows. For all samples (n=109), any correlation cannot be observed if the coefficient (r) is less than 0.20. Critical value of the coefficient is 0.37 for siliceous fossil rich clay facies (n=26), 0.29 for pelagic clay facies (n=44) or 0.33 for zeolitic clay facies (n=33) as well.

Outstandingly high coefficients (>0.75) are observed between Mn and Ni, and Fe and Co for all samples. Besides all the coefficients for all samples are more than the critical value, namely 0.20. In the case of siliceous fossil rich clay facies, There are strong correlation among Mn, Ni, and Cu. However coefficients between Cu and Mn or Ni decrease down to less than 0.7.

It is characteristic that the coefficients between Zn and the others less than the critical value, namely 0.29 as well as those between Pb and the others for pelagic clay facies.

There are strong correlations between Mn and Fe, Mn and Ni, and Fe and Co for the zeolitic clay facies. Among those the coefficients between Mn and Fe, and Fe and Co are, however, less than the critical value (0.37) for siliceous fossil rich clay facies. Besides, higher coefficients are observed among the elements for zeolitic

Table XIII-3 Coefficients of correlations among the elements.

<u>(a) All samples (n=109)</u>								<u>(b) Siliceous fossil rich clay facies (n=26)</u>							
Mn								Mn							
0.44	Fe							0.12	Fe						
0.67	0.76	Co						0.69	0.42	Co					
0.86	0.36	0.64	Ni					0.91	0.13	0.61	Ni				
0.63	0.50	0.73	0.65	Cu				0.84	0.20	0.37	0.81	Cu			
0.35	0.30	0.46	0.36	0.38	Zn			0.21	0.22	0.20	0.29	0.20	Zn		
0.34	0.57	0.56	0.26	0.43	0.41	Pb		0.06	0.44	0.37	0.16	0.15	0.77	Pb	
<u>(c) Pelagic clay facies (n=44)</u>								<u>(d) Zeolitic clay facies (n=33)</u>							
Mn								Mn							
0.30	Fe							0.81	Fe						
0.45	0.59	Co						0.66	0.79	Co					
0.84	0.21	0.58	Ni					0.76	0.63	0.60	Ni				
0.35	0.08	0.64	0.69	Cu				0.34	0.49	0.66	0.41	Cu			
0.08	0.09	0.11	0.15	0.16	Zn			0.40	0.57	0.71	0.43	0.46	Zn		
0.04	0.10	0.02	0.03	0.01	0.07	Pb		0.42	0.52	0.62	0.27	0.64	0.49	Pb	

clay facies compared to other two sedimentary facies. It may suggest these elements have a relatively common behavior during the genesis of zeolite minerals.

References

- ARRHENIUS, G. (1963) Pelagic sediments. In Hill, M. N. (ed.), *The sea* vol. 3, p. 655–727, Interscience Publishers, New York.
- HONNOREZ, J. (1978) Generation of phillipsites by palagonitization of basaltic glass in sea water and the origin of K-rich deep-sea sediments. In Sand, L. B. and Mumpton, F. A. (eds.), *Natural Zeolites*, p. 199–220, Pergamon Press.
- KATO, K., MORITANI, T. and NAKAO, S. (1979) Chemical composition of surface sediments from the GH77-1 area. *Geol. Surv. Japan Cruise Rept.*, no. 12, p. 155–157.
- MARCHIG, V. (1979) Verhalten von Radiolarienschalen aus dem Zentralpazifik bei der Diagenese. *Geologischen Rundschau*, vol. 68, p. 1037–1054.
- MITA, N., NAKAO, S. and KATO, K. (1982) Minor chemical composition of bottom sediments from the Central Pacific Wake-Tahiti Transect. *Geol. Surv. Japan Cruise Rept.*, no. 18, p. 313–338.
- STONECIPHER, S. A. (1978) Chemistry of deep-sea phillipsite, clinoptilolite, and host sediments. In Sand, L. B. and Mumpton, F. A. (eds.), *Natural Zeolites*, p. 221–234, Pergamon Press.