MANGANESE NODULE AND SURFACE SEDIMENT COMPOSITIONS:
DOMES SITES A, B, AND C

David Z. Piper and Kam Leong

U.S. Geological Survey
Menlo Park, California

and

William F. Cannon

U.S. Geological Survey
Reston, Virginia

Abstract

Manganese nodules and associated sediment from the equatorial North Pacific have been examined to ascertain relations between nodule abundance, texture, and composition, and sediment composition, lithology and acoustic stratigraphy. Nodules are most abundant in areas where the uppermost acoustically transparent layer of sediment is less than approximately 15 m thick. Abundance drops off sharply in areas where this acoustic unit is thicker than 20 m.

Nodules have average Zn/Mn and Co/Mn ratios which are approximately the same as these ratios for the component of sediment soluble in hydroxylamine hydrochloride-acetic acid. The relations between Cu and Mn and Ni and Mn in the sediment are also approximately the same as in nodules, but only for those nodules which have a smooth surface texture. Granular nodules have relatively more Ni and Cu. Antimony in nodules, similar to Ni, Cu, and Zn, is strongly correlated with Mn, whereas Co, Hf, Th, and U are strongly correlated with Fe.

The insoluble component of sediment has a uniform composition which is similar to the composition of terrigenous shale. This similarity holds for the major oxides as well as for Co, Cr, Zn, Hf, Sb, Th, U, Sc, Cs, Rb, and Ta.

Introduction

The fine fraction of pelagic sediment consists of a mixture of sedimentary components, classified according to their origin as hydrogenous, biogenous, lithogenous, and cosmogenous (Goldberg, 1963). These same components make up ferromanganese nodules, but their relative concentrations are quite different in sediments from their concentrations in nodules. Sediments consist largely of lithogenic and biogenic components, whereas nodules usually contain between 10 and 50% hydrated oxides each of Fe and Mn (hydrogenous component) plus approximately $30\% \pm 20\%$ of aluminosilicates (lithogenous component) and opaline silica (biogenous component) (Riley and Sinhaseni, 1958; Calvert and Price, 1977).

Fig. 1. Location of Deep Ocean Mining Environmental Studies (DOMES) Project area and of DOMES Sites A, B, and C.

Nodules from the equatorial North Pacific, an area that includes the three DOMES sites (Fig. 1), contain relatively high concentrations of Ni and Cu (Horn *et al.*, 1973) within the hydrogenous component, each in the range of 1 to 2%. Other elements are

present in one or more nodule components in concentrations of 10's of ppm up to several ppt. The more abundant elements include Co, Zn, Ba, Mo, Pb, and the light rare earth elements.

As nodules are composed largely of the hydrogenous component, it may be expected that nodule composition is related to this component in the fine fraction of sediment. Attempts to relate the composition of nodules to the composition of various components in sediments, however, have met with limited success (Calvert *et al.*, 1978; Skornyakova, this volume).

In our investigation of the three DOMES sites, we attempted to separate the hydrogenous component in the fine-grain fraction of sediment by a chemical leaching technique (Chester and Hughes, 1967). The aim of this analysis was to ascertain the relations between the composition of this component of sediment with the composition of this component in nodules. Also, the abundance, size, and texture of nodules at each DOMES site were measured to ascertain possible relations with sediment composition, age, lithology, and acoustic stratigraphy.

Techniques

Nodule abundances (A , in kg/m^2) were estimated from photographs of box cores by determining nodule coverage (P) and average maximum nodule diameter (D), and using the following equation: $A = 19.5 DP/100$ (This equation assumes that the vertical nodule axis is 0.57 times D). In the case of 15 box cores, these estimates have been compared to actual nodule weights. With the exception of two box cores, agreement of the two techniques was within 25%. In one core, the surface sediment appeared to be strongly disturbed, which appeared to account for many buried nodules in the upper few centimeters of sediment. In the other core nodule coverage was extremely low, approximately 5%, and the measured weight was three times the value calculated from the photograph.

Bottom photographs also were used to estimate nodule size and abundance. Both estimates are dependent upon an accurate scale. Thus, only those frames that included a compass resting on the bottom give accurate values; these represent only about 200 of 13,000 frames scanned. The values obtained from these photographs and nearby box cores agree to within approximately 25%, but estimates of nodule coverage and abundance are consistently greater from bottom photographs than from box-core photographs.

Nodules selected for bulk analysis were taken from the dominant size class of each box core when possible, after sorting nodules into the following groups based on their maximum dimension: less than 2 cm, 2-4 cm, 4-6 cm, 6-8 cm, and greater than 8 cm. A slice taken through the nodule center, or the entire nodule in the case of small nodules, was used for bulk chemical and mineralogical analysis. Samples were washed free of sediment and sea salt, dried at 110°C , and powdered. Mineralogy was determined by X-ray

diffraction on an aliquot that had been dried at room temperature. Six elements (Ni, Cu, Co, Zn, Fe, and Mn) were determined by atomic absorption spectrophotometry (AA) on the fraction soluble in 6N HCl and dried at 110°C. Nine elements (Fe, Co, Zn, Ba, Hf, Sb, Th, U and Sc) were measured on the bulk nodule sample by neutron activation analysis (NAA). Cobalt and zinc values, measured by both techniques, agreed to within 15%. Iron values measured by AA were 20% higher, on the average, than NAA values. We are unable to account for this difference. Iron values obtained by both techniques for the nodule standard GRLD-126 agree to within 10% of average values obtained by other laboratories (J. Greenslate, 1977, personal communication). We have reported the iron values obtained by AA. These values may be high, but the error is systematic and should not affect our conclusions.

Minor-element composition was measured by NAA of bulk sediment and of the residue of samples leached with hydroxylamine hydrochloride-acetic acid (Chester and Hughes, 1967). Six elements (Fe, Mn, Ni, Cu, Co and Zn) were measured on the acid solutions by AA. Leachable Fe, Co, and Zn, measured by AA, agreed to within 15% at 2σ with NAA measurements of losses of these elements from sediment.

Major-oxide composition of leached and unleached sediment was measured by X-ray fluorescence. Bischoff et al. (this volume) report on the latter. The fraction of sediment soluble in hydroxylamine hydrochloride-acetic acid was determined by weight loss.

Stratigraphy and Lithology

The acoustic stratigraphy for DOMES Sites A, B, and C has been presented by Piper et al. (this volume). Briefly, three acoustic units are recognized at B and C. Unit 1, the uppermost unit, is a transparent layer of highly variable thickness (Fig. 2) with a maximum at Site C of approximately 25 m. Box cores taken in areas where this sediment is at the surface at Site C contain a sparse, poorly preserved assemblage of Quaternary radiolarians and coccolithophorids. At Site B the unit contains a rich assemblage of Quaternary radiolarians mixed with older Tertiary species (Quinterno and Theyer, this volume). Unit 2 has a rather uniform thickness of 25 to 30 m. It consists of a series of acoustically opaque layers that crop out on the seafloor in many areas. Several cores taken at Site C, where the contact between this and the underlying unit appears to be at the surface, contain unmixed early Miocene flora and fauna. Unit 3 is acoustically much more transparent than unit 2. It has a thickness of approximately 35 m at Site C above a poorly defined acoustic basement. This unit is clearly recognized above a strongly reflecting basement at Site B, where its thickness is approximately 55 m.

At Site A the acoustic records are similar to those at Sites

Fig. 2. Comparison of 3.5-kHz profiles from Sites A (upper), B (middle), and C (lower). Acoustic units 1 and 2 are possibly representative of the Clipperton Formation whereas acoustic unit 3 may be representative of the Marquesas Formation (Piper et al. this volume). The distance between horizontal lines equals 36.6 m (20 f) in seawater.

B and C, but units 1 and 2 appear to be significantly thicker than at Sites B and C (Fig. 2). The relief of the top of unit 2 often differs strongly with that of the seafloor, perhaps more so than at Sites B and C. No strong acoustic basement was observed in the records making it impossible to identify acoustic units lower than unit 2.

Box cores from Sites A and B usually exhibited moderate bedding and strongly mottled contacts (Cook *et al.*, 1977). Although moderate bedding was also observed in a few cores from Site C, most Site C box cores exhibited massive bedding.

Sediment Composition

Surface sediment at the three DOMES sites is classified as radiolarian-diatom-bearing pelagic clay to pelagic clay. It averages 85 to 95% lithogenous material, less than 15% biogenic silica, and minor amounts of amorphous metal oxides. Biogenic CaCO_3 was observed in only a few of the samples. Several Site C cores contain an Fe-smectite (Bischoff *et al.* 1979a) of possible hydrothermal origin. The lithogenic material consists of a mixture of clay minerals dominated by smectite and illite (Hein *et al.* this volume) plus a minor amount of phillipsite, and trace amounts of quartz, feldspar, and volcanic debris (Cook *et al.*, 1977; Hein *et al.* this volume).

The bulk sediment was leached with hydroxylamine hydrochloride-acetic acid (HHA). This solution removes amorphous metal oxides, CaCO_3 , and adsorbed ions and attacks weakly any crystalline phases other than CaCO_3 (Chester and Hughes, 1967). There is no significant change in mineralogy from the leaching treatment. The composition of the leachate is listed in Table 1. In two samples in which CaCO_3 was not observed in smear slides, the leached component contained less than 1% of the total Si in the bulk sediment. The major element was Na, with lesser but approximately equal amounts of Mn, Fe, K, Ca, and Mg.

Insoluble Sediment Fraction (ISF)

This fraction of sediment is uniform in composition. At Site C the major oxides exhibit less than 5% variation at 2σ (Table 2) and the minor elements less than 10%. At Sites A and B variations are only slightly greater.

Comparison of the composition of the ISF fraction (Table 2) with that of bulk sediment (Table 3; Bischoff *et al.*, Table 5, this volume) shows that almost all of the SiO_2 , Al_2O_3 , TiO_2 , Ba, Cr, Hf, Sb, and Ta are present in the ISF. Approximately 75 to 95% of the Th, Sc, Cs, and Rb, 25 to 75% of the K_2O , MgO, CaO, and Na_2O , and less than 25% of the P_2O_5 and MnO are present in the ISF. Comparison of the composition of the solution obtained by leaching the sediment with HHA with that of bulk sediment shows that 85 to 95%

Table 1. Composition of the fraction of sediment soluble in hydroxylamine and hydrochloride-acetic acid for two samples from Core 22-28 (Site C). The samples were washed in distilled water and dried at 110°C prior to leaching.

Elemental composition expressed as % of bulk sediment								
	Si	Ca	Mg	Na	K	Fe	Mn	Total [*]
22-28-1	.22	.492	.309	1.25	.655	.371	.651	4.66
22-28-8	.19	.487	.291	1.20	.656	.452	.651	4.60

Oxide composition expressed as % of bulk sediment									
	SiO ₂	CaO	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	MnO	Sum	Total ⁺
22-28-1	.47	.68	.40	1.69	.79	.53	.84	5.02	5.59
22-28-8	.41	.68	.38	1.62	.79	.64	.84	5.02	5.53

*The total represents percent weight loss.

⁺The total represents an adjustment of the weight loss, assuming that all Na, K, Ca, and Mg were present as exchangeable ions and Si, Fe, and Mn were present as oxides. The adjustment, then, is H₂O added corresponding to the amount of Na, K, Mg, and Ca measured in the solution. No adjustment was made to compensate for hydration of Fe₂O₃ and MnO in the sample.

of the Fe₂O₃ and Zn, 25 to 50% of the Cu, and 10 to 30% of the Co, Ni, and Mn are present in the ISF.

The bulk concentrations of the minor elements (Table 3) which occur predominantly in the ISF, exhibit strong interelement correlations (Table 4). The exceptions are Ba and Sc which do not correlate strongly with any elements, and Sb and Zn which correlate with each other and with Co. The relation to Co is somewhat surprising in that most of the Sb and Zn are present in the ISF but only about 15% of the total Co occurs in this fraction.

The average composition of the ISF is similar to that of shale (Turekian and Wedepohl, 1961); the only exceptions are CaO and Ba. The tenfold greater concentration of Ba in pelagic sediment probably is due to the occurrence of barite, a common minor mineral of equatorial sediments. The difference in CaO values may be due to the presence of CaCO₃ in shale. The otherwise close similarity suggests that the ISF has a terrigenous source. The average composition for Site C sediment may represent a close approximation to that of terrigenous material entering the deep ocean by riverine and aeolian transport. This sediment fraction at Sites A and B is diluted 10 to 15% by biogenic silica (Bischoff et al, this volume), which accounts for most of the difference of the major oxide concentrations with those for Site C sediment.

Table 2. The average elemental composition of the insoluble sediment fraction from the three DOMES sites and of shale (Turekian and Wedepohl, 1961). Concentrations are in ppm except where noted otherwise. The values in parentheses represent 2σ for A and C and the range of 4 analyses for B. The minor elements were measured by NAA and the major oxides by XRF.

Element	Site A	Site B	Site C	Shale
Ba (%)	.474 (.05)	.540 (.13)	.583 (.12)	.058
Co	16.1 (.6)	17.8 (.8)	14.9 (1.3)	19
Cr	62.8 (6)	60 (8)	73.8 (3.5)	90
Cs	8.6 (.8)	9.5 (1)	11.2 (.8)	5
Hf	4.2 (.3)	4.4 (.1)	4.7 (.3)	2.8
Rb	90 (8)	102 (8)	129 (12)	140
Sb	2.1 (.2)	2.1 (.6)	2.8 (.6)	1.5
Ta	0.9 (.3)	1.0 (.1)	1.2 (.1)	0.8
Th	13.3 (1)	14.0 (.8)	15.6 (1)	12
U	1.5 (.3)	2.2 (.3)	2.2 (1.1)	3.7
Zn	158 (11)	165 (12)	163 (15)	95
Sc	29.6 (1.1)	28.5 (1.4)	25.3 (.6)	13
SiO ₂	61.80 (.56)	62.08 (.62)	58.41 (.40)	58.43
Al ₂ O ₃	13.66 (.31)	13.64 (.93)	16.36 (.31)	15.15
Fe ₂ O ₃	6.93 (.19)	6.42 (.46)	7.48 (.32)	6.75
MgO	2.36 (.05)	2.27 (.11)	2.55 (.05)	2.49
CaO	0.79 (.03)	0.68 (.08)	0.69 (.01)	3.09
Na ₂ O	1.11 (.06)	1.19 (.04)	1.39 (.07)	1.29
K ₂ O	2.26 (.02)	2.45 (.31)	3.14 (.06)	3.20
TiO ₂	0.78 (.03)	.75 (.05)	0.87 (.01)	0.77
P ₂ O ₅	0.10 (.01)	.09 (.02)	0.09 (.01)	0.16
MnO	.059 (.001)	.054 (.004)	0.060 (.002)	0.11
LOI	9.38	9.12	8.82	
TOTAL	100.23	99.88	101.09	

Table 3. Bulk composition of sediment from DOMES Sites A, B, and C. Sample numbers give station-box core interval, where interval corresponds to 2 cm. For example, 1 = 0 to 2 cm, 2 = 2 to 4 cm, 3 = 4 to 6 cm, etc. Elemental concentrations are given in ppm, except for Fe, which is in percent.

Sample	SITE A											
	Fe	Ba	Co	Cr	Cs	Hf	Rb	Sb	Ta	Th	U	Zn
46-1-1	4.47	3730	79.5	58.5	7.5	3.7	82	2.1	0.79	13.9	1.7	154
46-1-15	4.77	4632	131.5	62.1	7.8	4.1	92	2.3	0.82	14.1	2.2	183
46-1-19	4.96	5977	112.5	65.1	7.2	4.4	84	3.4	0.85	13.7	2.3	210
47-10-1	4.25	3874	74.8	55.4	6.6	3.7	78	2.0	0.77	15.8	1.8	166
47-10-9	4.52	4931	110.7	54.8	7.1	4.1	87	2.0	0.76	15.2	2.0	171
47-10-15	4.90	5717	196.3	49.6	6.5	4.8	84	3.4	0.93	13.6	2.3	231
47-10-20	4.62	5480	181.2	41.4	5.8	4.8	72	5.6	0.56	10.6	2.6	279
50-28-1	3.91	4988	70.3	53.5	6.9	3.3	59	1.6	0.80	10.4	1.6	165
50-28-4	3.65	3978	71.1	48.8	6.5	3.0	79	1.5	0.70	9.9	1.5	141
50-28-10	3.15	3175	19.9	42.0	5.3	3.0	60	1.1	0.57	8.4	1.2	108
SITE B												
51-33-1	4.33	6496	84.0	52.6	7.5	3.8	94	1.9	0.79	12.5	1.9	203
51-33-5	3.70	12773	55.6	26.4	4.3	3.7	75	1.5	0.56	6.8	1.7	227
53-45-1	4.32	4878	75.3	58.8	8.2	3.9	101	1.9	0.95	13.5	2.0	168
54-51-1	4.35	5043	76.9	58.0	8.5	4.5	105	2.4	0.83	12.3	1.8	168
54-51-6	4.56	4607	52.0	61.3	9.1	4.3	131	1.7	0.98	14.0	2.2	176
54-51-13	4.65	5636	81.4	61.5	9.6	4.6	108	2.4	1.00	14.4	2.4	165
54-51-15	4.67	5417	103.5	57.9	9.5	4.6	106	2.0	1.13	14.9	2.3	171

Table 4. Correlation coefficients of elemental concentrations of bulk sediment (Table 3).

	Ba	Co	Cr	Cs	Hf	Rb	Sb	Ta	Th	U	Zn	Sc
Fe	.03	.30	.72	.74	.65	.69	.51	.70	.75	.58	.26	.10
Ba		.00	.40	.24	.14	.06	.06	.14	.39	.10	.47	.32
Co			.03	.1	.28	.1	.75	.10	.14	.24	.71	.26
Cr				.92	.30	.76	.06	.81	.81	.46	.32	.45
Cs					.39	.85	.01	.89	.74	.47	.30	.49
Hf						.46	.53	.55	.51	.77	.14	.49
Rb							.03	.78	.66	.52	.14	.36
Sb								.04	.14	.46	.78	.37
Ta									.75	.56	.20	.26
Th										.52	.10	.10
U											.32	.48
Zn												.62

Variations in the ISF between sites, exclusive of variations in the concentration of biogenic SiO_2 , are seen by normalizing to Al_2O_3 (Table 5). Fe_2O_3 , MgO , CaO , and P_2O_5 increase and K_2O decreases from Site C to B to A. The increase in P_2O_5 may be related to sediment maturity (Bischoff *et al.*, this volume), where maturity is estimated by the relative amount of Tertiary radiolarians mixed with Quaternary species. The mineralogy exhibits a similar trend. Site A sediment has the highest relative concentrations of Tertiary radiolarians (Quinterno and Theyer, this volume), is considered to be the most mature, and has a relatively high smectite concentration (Fig. 3). The trends in major oxide composition are, thus, apparently controlled primarily by this trend in mineralogy of the clays. It is not possible to ascertain the extent to which these trends may be related to sediment diagenesis and to variations in sediment source between the Tertiary and Quaternary.

Soluble Sediment Fraction (SSF)

The soluble sediment fraction consists of amorphous metal oxides (mostly hydrated oxides of Fe and Mn), adsorbed ions (mostly Na^+ , K^+ , Ca^{++} , and Mg^{++}), CaCO_3 , micro-nodules and fragments of larger nodules. The nodules are thought to have contributed to the relatively high metal values of the surface sample from core 2-7 (Table 6). Metal ratios for the SSF of this sample are close

Table 5. Major oxide ratios of the lithogenic component of sediment, i.e., the fraction of sediment insoluble in hydroxylamine hydrochloride-acetic acid.

	<u>Site A</u>	<u>Site B</u>	<u>Site C</u>
$\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$	.517	.471	.457
$\text{MgO}/\text{Al}_2\text{O}_3$	.173	.166	.156
$\text{CaO}/\text{Al}_2\text{O}_3$	.058	.050	.042
$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	.0813	.0872	.0850
$\text{K}_2\text{O}/\text{Al}_2\text{O}_3$	.165	.180	.192
$\text{TiO}_2/\text{Al}_2\text{O}_3$	.057	.055	.053
$\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$	.0073	.0066	.0055
$\text{MnO}/\text{Al}_2\text{O}_3$	.0043	.0040	.0037
$\text{SiO}_2/\text{Al}_2\text{O}_3$	4.52	4.55	3.57

to those for Site C nodules.

Concentrations of Mn, Cu, Ni and Co in the SSF average 0.75%, 200 ppm, 185 ppm, and 75 ppm respectively. The average value for Mn is considerably higher than that reported by Calvert *et al.* (1978) for the Wahine area, approximately 2° west of Site A, but the values for surface sediment at Site A (Table 6) are similar to the range of concentrations measured by them. The three minor metals are strongly correlated with Mn (Table 7). Except for Cu, none of these metals correlates with Fe and, in the case of Cu, the correlation coefficient is only 0.37.

Zinc is similar to Fe in that only about 10% of its total is in the SSF. However, it shows a strong correlation with Mn (Table 7), similar to Cu, Ni, and Co.

Manganese and its related metals (Cu, Ni, Co, and Zn) exhibit a wide range of concentrations in the SSF. Mn varies from 0.05 to 2.41% of the total sediment. The lowest values are associated with carbonate ooze in core 50-28.

The strong correlations between Mn and Cu, Ni, Co and Zn (Table 7) suggest that these metals may be bound largely in a single phase, possibly micronodules. Although micronodules were observed in several cores, no analysis has been made of them and

Fig. 3. Abundance of smectite in DOLES box cores (Hein *et al.*, this volume) versus relative abundance of Pre-Quaternary radiolarians (Quinterno and Theyer, this volume). Individual points represent core intervals for which neither parameter varied by more than 10%, regardless of the length of the interval. The correlation coefficient is 0.79.

Table 6. The concentration and composition of the hydrogenous component of sediment, i.e., the component of sediment soluble in hydroxylamine hydrochloride-acetic acid. Concentrations of Mn, Fe, and Total Soluble are in percent of bulk sediment; Cu, Ni, Co, and Zn are in ppm.

<u>Cruise</u>	<u>Sample</u>	<u>Cu</u>	<u>Ni</u>	<u>Co</u>	<u>Zn</u>	<u>Mn</u>	<u>Fe</u>	<u>Soluble</u>
<u>SITE A</u>								
RP-8-0C-75	46-1-1	185	109	65.5	25.8	0.38	0.35	8.06
"	46-1-15	186	182	130	36.9	0.73	0.31	6.82
"	46-1-19	249	387	108	58.4	1.33	0.34	7.25
"	47-10-1	149	110	59.7	26.9	0.35	0.29	9.38
"	47-10-9	128	93.8	104	23.9	0.27	0.28	5.21
"	47-10-15	337	375	164	45.9	1.33	0.28	6.21
"	47-10-20	383	708	162	90.8	2.41	0.27	10.22
"	48-19-2	206	201	97.4	29.5	0.54	0.34	-
"	48-19-8	152	170	104	30.5	0.54	0.30	-
"	50-28-1	174	167	75.9	26.0	0.40	0.38	17.07
"	50-28-2	178	140	69.0	26.0	0.37	0.31	-
"	50-28-4	171	144	71.4	25.8	0.38	0.33	23.65
"	50-28-10	59.4	14.8	15.8	13.4	0.05	0.22	-
"	50-28-11	51.5	12.4	7.93	11.9	0.05	0.25	37.57
"	50-28-13	61.8	14.8	7.7	10.9	-	0.19	-
<u>SITE B</u>								
"	51-33-1	306	305	85.3	44.6	0.66	0.36	8.37
"	51-33-5	261	274	55.7	57.7	0.57	0.37	11.44
"	51-33-6	289	359	73.7	62.3	0.85	0.33	-
"	53-45-1	164	115	69.9	20.0	0.45	0.38	8.13
"	54-51-1	195	157	75.7	25.9	0.36	0.37	8.35
"	54-51-2	169	84.6	66.7	23.4	0.24	0.31	-
"	54-51-6	107	59.7	37.8	15.9	0.16	0.27	7.51
"	54-51-13	105	27.3	83.5	16.9	0.23	0.27	5.52
"	54-51-15	104	69.7	108	11.9	0.13	0.31	6.44

Table 6. (Cont'd).

<u>Cruise</u>	<u>Sample</u>	<u>Cu</u>	<u>Ni</u>	<u>Co</u>	<u>Zn</u>	<u>Mn</u>	<u>Fe</u>	<u>Soluble</u>
<u>SITE C</u>								
RP-8-0C-76	2-7-1	880	1047	319	102	2.07	0.56	11.43
"	2-7-8	145	141	63.7	25.9	0.44	0.26	7.41
"	2-7-16	157	139	81.4	23.8	0.52	0.31	7.72
"	4-9-1	197	161	83.5	33.8	0.52	0.45	4.64
"	4-9-14	154	134	81.8	20.9	0.52	0.37	5.25
"	7-12-1	194	147	81.8	21.9	0.50	0.38	4.22
"	15-21-1	218	181	83.4	27.7	0.64	0.52	5.70
"	15-21-3	219	179	87.5	29.8	0.63	0.51	4.52
"	15-21-5	186	161	79.3	28.8	0.56	0.36	3.81
"	15-21-7	175	149	69.5	31.8	0.55	0.40	4.73
"	15-21-9	359	383	53.6	85.3	1.98	1.17	14.70
"	15-21-10	345	349	53.8	85.6	2.04	1.31	16.36
"	15-21-12	340	330	38.0	92.9	2.20	1.52	17.08
"	15-21-13	338	308	42.0	88.9	2.22	1.47	16.08
"	18-24-1	185	165	80.0	27.8	0.55	0.38	12.49
"	18-24-2	199	189	90.0	29.8	0.52	0.40	-
"	18-24-7	138	93.7	65.8	30.9	0.41	0.37	19.22
"	18-24-16	169	109	79.6	32.8	0.52	0.38	4.53
"	22-28-1	272	228	95.3	44.7	0.65	0.45	4.66
"	22-28-4	139	102	65.7	27.9	0.38	0.37	3.42
"	22-28-8	246	209	71.5	33.8	0.65	0.37	4.60
"	22-28-15	158	112	69.8	23.9	0.44	0.34	4.31

Table 7. Correlation coefficients of elements in the hydrogenous component of sediment (the sediment fraction soluble in hydroxylamine hydrochloride-acetic acid, Table 6).

	<u>Ni</u>	<u>Co</u>	<u>Zn</u>	<u>Mn</u>	<u>Fe</u>
Cu	.91	.69	.87	.83	.37
Ni		.69	.94	.95	.14
Co			.58	.73	.20
Zn				.88	.14
Mn					.05

no measurement made of their abundance. In smear slides, however, they were infrequently observed, suggesting that their contribution of metals to the SSF component may be minor. Certainly, the phase in which these metals and Fe are bound needs to be identified.

Manganese Nodules

Size, Abundance, and Texture

Box cores from the three DOMES sites contain nodules of two types of populations (Fig. 4), based on surface texture and average maximum nodule diameter (MND). One population consists of K-type nodules, as defined by Meyer (1973). Individual nodules are small, ellipsoidal, have a smooth surface texture, and are commonly intergrown forming polynodules. The population has a well defined modal size that is usually between 1.5 and 3 cm (Fig. 5).

The second population consists of B-type (Fig. 4) and E/S-type nodules. The B-type nodules usually have a granular surface texture on the side in contact with the sediment and a smooth surface in contact with the overlying seawater. The surface is commonly botryoidal. The modal size of the population is greater than 4.5 cm, although it is commonly poorly defined (Fig. 5). These nodules appear to form a series with E/S-type nodules, which are smaller. E/S-type nodules, which have a MND less than approximately 4 cm, often have a granular texture over the entire surface. Nodules with a MND less than 1.5 cm and polynodules seldom occur with B- and E/S-type nodules.

At Site C most of the box cores contained B- and E/S-type nodules, i.e., nodules with a granular surface texture (Table 8). Only four box cores contained smooth K-type nodules (Table 8). Approximately 20% of the box cores at Site B had no nodules and, of

Fig. 4. Photographs of box cores from Sites A, B, and C. Two distinct nodule populations are present. One (A and C) is composed mainly of small nodules, but with considerable variation. It includes 48-20 (Site A) and 18-24 (Site C). The other population (B and D) consists predominantly of large nodules. Representative box cores of this group include 55-55 (Site B) and 22-28 (Site C). Photographs were provided by R. Sorem.

those with nodules, all appear from photographs of box cores to have a population of B- and E/S-type nodules. At Site A, 18 of the 26 box cores had smooth K-type nodules.

At Site C, a 225-km² area (Fig. 6) was surveyed in detail on R/V OCEANOGRAPHER cruise RP-8-OC-76. The area consists of three abyssal hills separated by north-south-trending channels (Fig. 6),

Table 8. Abundance, size and surface texture of nodules in box cores from DOMES Sites A, B, and C. The M.W. Series of samples were collected by the R/V MOANA WAVE.

Station	Box Core	Coverage (%)	Average Diameter (cm)	Concentration (kg/m ²)	Texture *	Station	Box Core	Coverage (%)	Average Diameter (cm)	Concentration (kg/m ²)	Texture *
SITE A											
D. 46	1	10	2.2	1.8	S	D. 48	19	1	4.6	0.4	S
D. 46	4	30	2.7	6.5	S	D. 48	20	30	2.3	5.5	S
D. 46	6	25	1.7	3.4	S	D. 48	22	1	5.7	0.5	G
D. 46	7	50	1.5	6.0	S	D. 48	23	1	-	0.0	
D. 46	8	55	1.6	7.0	S	D. 49	24	1	2.4	0.2	S
D. 46	9	25	2.7	5.4	S	D. 49	25	45	2.5	9.0	S
D. 47	10	0	-	0.0		D. 49	26	40	3.2	10.2	S
D. 47	11	5	5.4	2.2	C	D. 49	27	25	2.8	5.6	C
D. 47	12	20	4.3	6.9	C	D. 50	28	55	2.2	9.7	S
D. 47	13	7	3.3	1.8	G	D. 50	29	55	2.6	11.4	S
D. 47	14	4	4.8	1.5	G	D. 50	30	30	3.1	7.4	S
D. 47	15	4	5.7	1.8	G	D. 50	31	10	3.1	2.5	S
D. 47	16	15	3.4	4.1	G	D. 50	32	30	1.9	4.6	S
D. 47	18	15	3.1	3.7	S	Average:		21	3.0	4.3	S
SITE B											
D. 51	33	2	6.1	1.0	G	D. 55	53	5	1.6	0.6	C
D. 51	34	7	7.1	4.0	G	D. 55	54	10	5.6	4.5	C
D. 51	35	0	-	0.0		D. 55	55	22	7.6	13.4	C
D. 51	36	1	2.0	0.2	G	D. 55	56	35	6.2	17.4	C
D. 52	37	1	2.0	0.2		M.W. 16	27	-	-	0.1	
D. 52	39	5	9.0	3.6	G	M.W. 16	28	-	-	6.4	
D. 52	40	3	4.1	1.0	G	M.W. 16	29	-	-	12.1	
D. 52	41	0	-	0.0		M.W. 16	30	-	-	5.6	
D. 52	42	0	-	0.0		M.W. 16	31	-	-	6.9	
D. 53	43	0	-	0.0		M.W. 16	33	-	-	3.7	
D. 53	44	.5	.7	0.0		M.W. 16	34	-	-	12.7	
D. 53	45	3	8.0	1.9	G	M.W. 16	35	-	-	2.0	
D. 53	46	0	-	0.0		M.W. 16	36	-	-	0.6	
D. 54	47	37	4.8	14.2	G	M.W. 16	37	-	-	1.1	
D. 54	48	5	5.8	2.3	C	M.W. 8	30	-	-	21.2	
D. 54	51	35	5.6	15.7	C	M.W. 8	32	-	-	15.0	
D. 54	52	25	6.9	13.8	C	M.W. 8	33	-	-	5.6	
						Average:	-	10	5.2	5.5	

Table 8. (Cont'd).

SITE C											
D. 3	5	50	2.5	10.0		D. 7	12	45	2.5	9.0	G
D. 6	19	60	5.4	25.9		D. 8	13	35	2.4	6.7	C
D. 9	21	60	1.8	8.6		D. 10	15	20	4.7	7.5	C
D. 20	27	62	1.5	7.4		D. 11	16	30	7.2	17.5	G
D. 24B	29	62	4.3	21.3		D. 12	18	50	2.7	10.8	C
D. 18	32	10	1.7	1.4		D. 13	19	55	2.8	12.3	G
D. 18	33	47	1.3	4.9		D. 14	20	50	5.1	20.4	C
D. 18	35	65	1.5	7.8		D. 15	21	60	2.7	13.0	C
D. 18	37	37	2.6	7.7		D. 16	22	70	2.1	12.8	S
D. 14	38	57	1.4	6.3		D. 17	23	30	2.7	6.5	S
D. 14	39	47	2.4	9.0		D. 18	24	60	2.4	11.5	S
D. 16B	43	62	2.7	13.4		D. 21	27	60	3.4	16.3	C
D. 16B	45	30	2.2	5.3		D. 22	28	45	5.2	18.7	C
D. 16B	48	5	1.9	0.8		M.W. 13A	2	-	-	4.2	
D. 16B	49	35	2.3	6.4		M.W. 13A	3	-	-	3.5	
D. 15B	50	50	2.1	8.4		M.W. 13A	4	-	-	1.9	
D. 27	52	40	1.9	6.1		M.W. 13B	5	-	-	20.0	
D. 11	53	55	1.2	5.3		M.W. 13B	6	-	-	0.1	
D. 57	59	0	-	0.0		M.W. 13B	7	-	-	15.0	
D. 5E	60	60	1.6	7.7		M.W. 13B	8	-	-	11.9	
D. 1	6	20	3.1	5.1	C	M.W. 13B	9	-	-	15.0	
D. 2	7	60	2.9	13.9	C	M.W. 13B	10	-	-	0.6	
D. 3	8	10	2.3	1.8	G	M.W. 13B	11	-	-	30.0	
D. 4	9	45	2.6	9.4	S	M.W. 13B	12	-	-	17.5	
D. 5	10	55	2.5	11.0	C	Average:		43	2.6	9.2	
D. 6	11	40	3.0	9.6	C						

* "S" refers to smooth surface texture, "G" to granular, and "C" to combination of smooth top and granular underside

Fig. 5. Size and mass distribution of nodules in box cores 11-16 and 18-24 from Site C.

with maximum relief of approximately 300 m. The region was divided into five areas on the basis of bathymetry, acoustic stratigraphy (3.5 kHz), and nodule population.

Area 1 is the westernmost abyssal hill (Fig. 6). Acoustic unit 1 (Fig. 2) is apparently present as a thin veneer of sediment less than 10 m thick. E/S-type nodules are present and tend to be small. Seafloor coverage is uniformly high (Fig. 7). The easternmost abyssal hill appears to be similar, but few 3.5-kHz records and box cores were collected from this area.

Area 2 is the channel to the west of the central abyssal hill. Acoustic unit 2 appears to be present throughout much of the area (Piper *et al.*, this volume). The upper transparent layer of sediment, however, is present on several profiles as a sediment wedge, that pinches out toward the center of the channel. Nodule coverage within the channel is variable (Fig. 8); nodule barren areas give way abruptly to areas in which coverage is as great as 70%. This is the only area within the 225-km² region for which box cores and bottom photographs showed that the nodule population consisted of B-type nodules (Fig. 7).

The channel to the east of the central abyssal hill, area 5a, is similar to this western channel, except possibly for size of nodules. Box core 7-12, located in the central part of this channel, recovered small nodules. One box core (57-58) taken just to the north of this area on an earlier cruise and apparently located within this channel, however, contained B-type nodules (Sorem *et al.*, this volume).

Area 3 is the western part of the central abyssal hill (Fig. 6). Acoustic unit 2 and possibly unit 3 are at or very near the

Fig. 6. Bathymetry, box core and camera flight locations for NOAA cruise RP-8-OC-76, Site C. The large numerals designate the five areas that are distinguishable due to nodule population, acoustic stratigraphy and bathymetry (Table 9).

surface. Nodules are small and have granular surface textures. Nodule coverage in box cores was small, but in bottom photographs coverage appears to be equal to that of the other areas.

Area 4 is the eastern half of the central abyssal hill. The transparent layer of sediment was clearly observed in the 3.5-kHz record. Its thickness is quite variable, with a maximum of approximately 20 m. Nodule coverage is high in all box cores and bottom photographs. K-type nodules were recovered in the box cores from this area.

Seafloor coverage of surface nodules throughout Site C is uniformly high (Table 9). The greatest nodule abundance, estimated from bottom photographs and from box cores, is in the western channel, where B-type nodules occur. The average abundance of nodules at Site C is 9.2 kg/m² (Table 8). Abundance measurements for box cores and bottom photographs exhibit a normal

Table 9. Nodule abundance in five areas within Site C, as shown in Fig. 6 and metal reserves (kg/m^2) of Fe, Mn, Cu, Ni, Co, and Zn. Nodule concentrations have been estimated from bottom photographs (column 5) and from nodule weights for box cores (column 7). For 19 box cores, nodule weights were also calculated from photographs (column 8). In calculating the average nodule concentrations for each area (column 9), the average of 200 bottom photographs was given equal weight to that of one box core. The average value listed in column 9 was lowered by 20% to give a nodule concentration on a dry-weight and salt-free basis. Metal concentrations used to estimate resource are listed in Table 10.

Nodule Concentration								
Nodule Area	Camera Flights				Box Cores			
	Flight	Frame	Coverage Ave. (Range)	Conc. kg/m^2	No.	Weight kg/m^2	Photo kg/m^2	Average kg/m^2
1.	3	0-200	50 (10-65)	11	17	-	6	10
	3	200-400	55 (10-65)	13	18	11	12	
	3	400-600	60 (55-65)	16	19	10	-	
2.					7	15	14	14
	1	0-200	25 (0-70)	15	15	7	8	
	1	200-400	70 (60-70)	29	16	19	18	
	3	600-800	55 (10-65)	17	20	20	20	
					27	17	16	
					28	14	19	
3.					6	7	5	8.2
	1	400-600	70 (65-70)	15	8	3	12	
	1	600-800	65 (35-70)	16	9	7	9	
4.					21	13	13	9.1
	2	0-200	55 (45-60)	10	10	11	11	
	4	0-200	60 (55-70)	12	22	14	13	
	4	200-400	60 (5-70)	12	23	-	6	
	4	400-600	60 (55-65)	12	24	11	12	
5.	4	600-800	60 (55-65)	11	13	9	12	8.6
	2	200-400	40 (5-65)	8	11	-	10	
	2	400-600	40 (5-65)	8	12	8	9	
	2	600-800	45 (10-70)	15				

Table 9. (Cont'd).

Metal Resource (kg/m ²)						Area Description
Fe	Mn	Cu	Ni	Co	Zn	
.92	2.29	.082	.110	.024	.0094	Western abyssal hill. Small nodules predominate. Surface sediment possibly Unit 1.
1.03	3.76	.15	.18	.035	.020	Western channel. Large nodules. Surface sediment mostly Unit 2 and Unit 1.
0.71	2.09	.085	.10	.018	.0091	Western part of central abyssal hill. Nodules small to large. Surface sediment mostly Units 2 and 3.
1.10	2.04	.056	.090	.030	.007	Eastern part of central abyssal hill. Small nodules. Surface sediment Unit 1.
0.84	2.26	.079	.10	.025	.010	Eastern portion of area. Nodules variable. Surface sediment Unit 2 in channel and possibly Unit 1 on abyssal hill.

Fig. 7. Bottom photographs of Site C. Photograph A is a view of Area 1 (Fig. 6) taken on camera flight 3. The barren areas are mounds. Photograph B is a view of Area 2 (Fig. 6) frame 226, flight 1. The compass face is 5.7 cm in diameter.

distribution (Fig. 9). The curve based on measurements of bottom photographs, however, is shifted in the direction of greater abundance.

At Site B, average nodule coverage is 5.5 kg/m^2 and the frequency curve exhibits a log-normal distribution with a secondary mode at approximately 13 kg/m^2 (Fig. 9). Similar to Site C, the curve based on bottom photographs is shifted in the direction of greater abundance. Although roughly 40% of the area has few or no nodules, about 30% of the area has a nodule abundance greater than 10 kg/m^2 .

The nodule coverage at Site A is 4.2 kg/m^2 , and the frequency curve based on box cores exhibits a log-normal distribution. The curve based on bottom photographs, however, differs from this curve (Fig. 9).

Mizuno *et al.* (1976) have shown that nodule abundance may be

Fig. 8. Relation between bathymetry, seafloor coverage of nodules, average nodule long axis, and nodule abundance for camera flight 1 (Fig. 6). Basically, two nodule populations are observed. One has an average long axis of approximately 3.5 cm, camera frames 0 through 280. The other population has an average long axis of 1.3 cm, camera frames 350 through 800.

Fig. 9. Nodule abundance at Sites A, B, and C versus frequency of occurrence, as estimated from box cores (block diagram and solid curve) and from bottom photographs (dots and broken curve). The two curves represent floating-point averages of three points.

related to the distribution of the uppermost acoustically transparent sediment layer. They reported that in the Central Pacific Basin nodules were most frequently observed where this layer of sediment was less than 20 m thick. Nodular pavement was occasionally observed where the transparent layer was absent. Our data tend to support their observation. Nodules are most abundant at Site C where acoustic unit 1, the transparent layer, is very thin or absent (Piper *et al.* this volume). Nodules are least abundant at Site A where this acoustic unit is thickest.

The data for individual stations at Site B suggest that this relationship may hold for an area as small as individual sites. At Stations 52 and 53 acoustic unit 1 has its greatest distribution and thickness, averaging about 30 m (Piper *et al.* this volume). Nodules averaged about 1.5 per box core for 10 box cores (Sorem *et al.* this volume). At Stations 54 and 55, unit 1 is absent over much of the seafloor and, where present, it usually is less than 15 m thick. Nodules averaged approximately 22 per box core and the smallest number observed in any box core was 5.

Nodule texture and size are highly variable over distances of only a few hundred meters. At Site C there is a possible relation between nodule size and bathymetry, (Fig. 8). Large B-type nodules apparently are restricted to the channels between abyssal hills (Figs. 4,7,8). The K-type nodules appeared to be restricted to area four (Fig. 6), the area where the uppermost transparent layer of sediment, acoustic unit 1, is observed as having a continuous areal distribution. No such relations, however, appear to hold for Sites A and B.

Mineralogy

The minerals todorokite and δ -MnO₂ are present in all nodules, as deduced from X-ray diffraction peaks at 9.6, 2.44, and 1.44 Å. The convention used for their identification is that suggested by Burns and Burns (1977). In most samples, a peak at 7 Å was also observed, suggesting the presence of birnessite. In those samples that exhibited a rather intense 7 Å reflection, however, other reflections corresponding to the weaker reflections of phillipsite were always present.

Chemical Composition

Hydrated oxides of Mn and Fe constitute the major fraction of the hydrogenous component in nodules. The lack of major element analyses, particularly for Al and Si, precludes, however, our ascertaining quantitatively the concentrations of biogenic and lithogenic material. Comparison of the composition of the ISF (Table 2), dominantly lithogenic material, with that of nodules (Table 10) shows that within nodules essentially all of the Co, Zn, Sb, Ni, and Cu and most of the Th, Hf, and U are associated with Mn and Fe oxides. Calvert and Price (1977) arrived at this same conclusion for nodules for which they had major element analyses. Interelement correlations of the minor elements with Mn and Fe (Table 11)

Table 10. Bulk compositions of nodules from DOMES Sites A, B, and C. Concentrations are in ppm except where noted otherwise. The averages for each site enclosed in parentheses include analyses reported by Mouget *et al.* (1976).

Station- Box Core	Lat. (North)	Long. (West)	Depth (Meters)	Fe (%)	Mn (%)	Cu (%)	Ni (%)
46-3	9°19.0'	150°52.5'	4900	11.6	19.3	0.49	0.77
46-3	9°19.0'	150°52.5'	4900	9.7	25.6	0.71	1.12
46-7	9°19.6'	150°50.7'	5116	6.7	22.3	0.77	1.24
46-7	9°19.6'	150°50.7'	5116	6.3	12.1	0.40	0.61
47-12	9°03.5'	151°11.1'	5005	4.1	26.8	1.39	1.59
47-12	9°03.5'	151°11.1'	5005	5.9	25.6	1.35	1.37
47-13	9°02.3'	151°11.2'	5039	5.4	24.3	1.34	1.38
47-13	9°02.3'	151°11.2'	5039	4.0	26.2	1.57	1.54
48-21	8°17.6'	151°13.2'	5097	5.6	22.0	1.17	1.17
49-25	8°28.5'	150°44.5'	5005	7.0	25.2	0.99	1.29
49-27	8°30.2'	150°47.8'	5039	5.8	26.7	1.26	1.46
50-28	8°41.7'	150°18.7'	5009	10.7	22.8	0.56	0.95
50-29	8°43.8'	150°18.7'	5033	11.6	24.1	0.58	0.95
50-29	8°43.8'	150°18.7'	5033	11.9	22.2	0.59	0.65
50-30	8°41.1'	150°15.1'	4928	10.9	23.4	0.59	0.98
50-30	8°41.1'	150°15.1'	4928	11.3	22.0	0.57	0.98
50-32	8°43.1'	150°14.1'	4948	10.4	24.7	0.64	1.05
Average (Site A)				8.17 (9.2)	23.3 (20.7)	0.85 (0.79)	1.12 (1.00)
51-34	11°42.4'	139°10.8'	4925	2.9	26.8	1.27	1.23
54-47	12°10.4'	137°44.1'	4930	4.3	26.4	1.26	1.51
54-49	12°12.0'	137°44.7'	4942	3.0	26.9	1.31	1.52
54-50	12°08.5'	137°46.0'	4978	5.6	25.6	1.21	1.41
Average (Site B)				4.0 (5.5)	26.4 (28.1)	1.26 (1.20)	1.42 (1.54)
1-6	15°13.9'	125°58.4'	4380	8.7	28.9	1.18	1.36
2-7	15°14.5'	126°02.6'	4359	8.3	27.5	1.08	1.26
3-8	15°15.4'	126°59.3'	4363	8.5	28.8	1.27	1.29
4-9	15°14.6'	126°01.6'	4490	9.1	16.2	0.53	0.82
5-10	15°13.0'	125°55.9'	4465	9.5	26.7	0.99	1.03
6-11	15°10.9'	125°53.6'	4442	8.6	26.8	1.05	1.38
7-12	15°12.3'	125°52.1'	4601	10.1	25.5	0.86	1.12
8-13	15°12.4'	125°57.2'	4367	11.3	25.9	0.81	1.14
9-14	15°11.3'	126°01.5'	4444				
10-15	15°11.4'	126°02.2'	4516	8.9	27.2	1.05	1.21
11-16	15°11.7'	126°03.9'	4524	7.4	27.3	1.24	1.30
12-18	15°11.6'	126°05.9'	4459	9.1	24.3	0.89	1.21
13-19	15°08.2'	126°06.4'	4481	9.4	21.5	0.74	0.95
14-20	15°08.2'	126°03.7'	4586	7.7	25.4	1.05	1.31
15-21	15°08.4'	126°02.7'	4501	8.6	24.7	0.95	1.26
16-22	15°07.9'	125°59.4'	4442	10.6	21.8	0.61	1.04
17-23	15°08.3'	125°57.3'	4376	14.2	21.4	0.63	0.88
18-24	15°06.3'	125°57.4'	4426	11.7	24.1	0.61	1.05
19-25	15°08.4'	126°00.9'	4465	9.3	26.8	1.17	1.31
21-27	15°05.9'	126°02.1'	4522	6.9	26.0	1.15	1.33
22-28	15°06.4'	126°02.8'	4641	6.8	26.9	1.06	1.34
15-50	15°45.6'	126°00.5'	4552	5.6	26.5	1.08	1.19
16-49	15°46.7'	126°11.2'	4552				
57-57	15°17.8'	125°55.3'	4520	7.41	25.3	.93	1.35
58-60	15°17.8'	125°28.4'	4375	7.92	24.5	0.87	1.20
58-61	15°20.6'	125°26.8'	4414	5.83	28.0	1.25	1.33
Average (Site C)				8.8 (8.5)	25.4 (27.0)	0.97 (0.99)	1.20 (1.48)

Table 10. (Cont'd).

Co	Zn	Ba	Hf	Sb	Th	U	Sc
2680	630	1455	10.7	23.3	25.2	5.8	16.87
3360	900	-	-	-	-	-	-
2140	920	1240	7.9	27.4	22.9	4.0	13.95
1360	620	1582	-	14.5	22.5	3.1	14.88
1710	1200	1777	4.6	27.4	9.0	1.1	11.54
1660	1700	2478	4.2	34.3	9.2	3.8	11.56
1440	1200	1617	6.0	21.9	10.1	2.8	18.14
1730	1200	1769	3.7	27.4	9.3	3.6	10.47
1490	920	2151	4.9	35.6	10.0	5.2	10.92
2300	980	2010	6.9	28.3	17.7	5.0	10.26
1950	1200	2729	6.3	30.1	12.2	4.4	12.37
3140	760	1919	12.2	34.2	31.8	8.6	12.77
3580	830	1587	11.1	33.4	31.7	8.6	13.12
3620	700	1745	11.3	27.8	34.3	6.2	12.57
3310	780	1823	11.2	31.9	25.6	7.2	12.66
3170	740	1452	10.7	31.2	29.4	7.8	12.33
3570	820	2396	14.2	32.9	30.1	6.9	12.42
2480 (2400)	950 -	-	-	-	-	-	-
1450	1100	1756	2.7	43.9	9.4	1.2	7.40
2970	1100	1771	3.6	35.8	18.5	3.6	8.63
1780	1500	1755	3.9	36.2	13.6	3.1	8.88
2040	1300	1642	4.4	43.4	16.0	3.4	9.53
2060 (2900)	1250 -	-	-	-	-	-	-
2550	1600	1894	2.8	42.6	13.2	3.0	9.08
2160	1500	2593	4.2	40.7	17.0	3.1	10.26
2050	1700	2144	2.7	47.4	12.4	4.3	9.33
2050	690	1878	5.2	18.2	19.3	3.2	13.95
2720	1400	1269	4.0	34.8	18.8	4.5	9.32
2960	1200	2421	4.9	37.1	16.7	4.1	9.87
3060	1100	1886	5.3	41.4	24.2	5.3	9.27
2960	1300	1885	5.9	36.1	23.8	6.2	9.67
2502	652	1963	7.3	22.0	29.4	5.2	12.24
2370	1400	2258	2.6	45.5	11.6	1.0	8.96
2730	1400	2345	3.4	43.5	15.8	2.8	9.08
2640	1000	2115	5.6	34.1	19.0	3.7	11.97
2250	940	2118	6.3	32.6	24.2	5.6	14.75
3090	950	2947	3.7	33.4	13.9	4.3	9.91
2140	1200	2800	4.5	34.5	17.0	3.9	11.18
3420	770	1686	8.4	31.0	35.1	5.3	11.16
4310	640	-	-	-	-	-	-
2190	920	1904	8.9	32.8	38.4	6.6	11.02
2320	1500	-	-	-	-	-	-
2430	1600	1626	4.6	24.7	21.0	3.4	15.34
2380	1500	2676	4.1	36.0	13.8	4.1	10.08
2380	1100	1576	3.9	35.4	17.3	5.1	7.79
2460	1300	1279	3.6	40.7	20.0	6.3	7.32
2640 (2700)	-	-	-	-	-	-	-

Table 11. Correlation coefficients of metal concentrations in DOMES nodules.

	Mn	Cu	Ni	Co	Zn	Ba	Hf	Sb	Th	U	Sc
Fe	-.30	-.77	-.69	-.76	-.44	.00	.65	.00	.78	.71	.24
Mn		.72	.76	.00	.76	.30	-.57	.73	-.42	-.24	-.63
Cu			.89	-.56	.77	.24	-.78	.39	-.85	-.65	-.44
Ni				.41	.72	.33	-.66	.39	-.70	-.57	-.42
Co					-.40	.00	.10	.14	.67	.56	.24
Zn						.24	-.73	.58	.64	-.50	-.45
Ba							-.20	.24	-.30	-.17	-.10
Hf								-.44	.79	.60	.55
Sb									-.26	-.14	-.76
Th										.75	.30
U											.20

also support this conclusion.

Barium may be present as barite, as this mineral has been identified in nodules (Dugolinsky, 1976). Calvert and Price (1977) observed a strong correlation between Ba and Mn and suggested that much of the Ba may be in the oxide phase. However, DOMES nodules show a weak correlation (Table 11). Scandium may be restricted to the lithogenous component of nodules, in which it is approximately threefold more concentrated than in nodules.

The composition of nodules from all three DOMES sites are quite similar. The relation between Ni plus Cu and the Mn/Mn + Fe ratio (Fig. 10) suggests only very subtle differences between the three sites. This relation for Site A nodules has a correlation coefficient of 0.95. Nodules from Site C fall along the curve, but on the high Ni + Cu side. Site B nodules plot on the low Ni + Cu side, but only four nodules from Site B were analyzed. The relation between Zn and Mn/Mn + Fe (Fig. 10), however, clearly distinguishes Site A and Site C nodules: Site C nodules have a relatively higher Zn concentration and show a poor correlation of 0.59. Nodules from the Wahine area (Calvert *et al.*, 1978) tend to fall on the low minor-element side of the curves of Site A nodules (Fig. 10).

Calvert and Price (1977) have used plots of Ni versus Mn and Cu versus Mn to show that nodules from the pelagic environment of the Pacific Ocean belong to one of two populations. One population contains δ -MnO₂ and the other todorokite plus δ -MnO₂.

Fig. 10. Relations between Zn and Ni plus Cu and Mn/Mn + Fe for nodules from Sites A, B, and C. The curves are a linear regression by method of least squares using only the data for Site A nodules. The equation for the Zn curve is $y = .24x - .087$, $\sigma = 0.95$; the equation for the Ni plus Cu curve is $y = 7.88x - 3.85$, $\sigma = 0.97$. The Wahine samples are from $8^{\circ}20'N$, $153^{\circ}W$ (Calvert *et al.* 1978).

Fig. 11. Relation between Mn and Cu, Ni, Zn, and Co for nodules from Sites A, B, and C (Table 10). The shaded areas include all K-type nodules. The unshaded areas include all B- and E/S-type nodules. The broken lines are curves of best fit, for the two populations, determined by method of least squares. The solid lines are the extrapolated curves of elemental relations within the SSF.

Although both populations exhibit strong interelement correlations, the slopes of the curves for the δ -MnO₂ population are significantly less and their curves extrapolate to the origin and approximately through the field for the composition of bulk sediment.

The DOMES nodules at first might not appear to fall into these two groups, principally because they all contain todorokite. Plots of Ni versus Mn and Cu versus Mn (Fig. 11), however, show that nodules with relatively low Ni and Cu fall along curves that parallel the curves for δ -MnO₂ nodules. The remaining nodules scatter about a curve that parallels the curves for todorokite-bearing nodules.

Although all DOMES nodules contain todorokite, they can be divided into two populations on the basis of surface textures. The smooth, K-type nodules from DOMES cores have a composition similar to the δ -MnO₂ nodules analyzed by Calvert and Price (1977). The second population consists of B- and E/S-type nodules and they have relatively high Ni and Cu values, similar to nodules analyzed by Calvert and Price which contain todorokite. The compositions of these two populations have very limited overlap (Fig. 11).

The curves of Ni versus Mn and Cu versus Mn for the SSF, when extrapolated into the compositional field of nodules, define exceedingly well the composition of smooth nodules. The sediment curves, however, are displaced slightly in the direction of low Ni and Cu values (Fig. 11).

Several investigators have suggested that K-type nodules grow by incorporation of metals from seawater, whereas B- and E/S-type nodules derive an additional metal component from interstitial water during sediment diagenesis. For example, Marchig and Gundlach (1978) observed a decrease in micronodule abundance with depth, in box cores, accompanied by a slight decrease in their Ni and Cu concentrations relative to Mn. Thus, one possible explanation for the relation between the composition of the SSF and macronodules analyzed in this study is that both the K-type nodules and the SSF derive metals from seawater. During sediment diagenesis, Ni and Cu go into solution more so than Mn. These metals are then incorporated into B- and E/S-type nodules.

This interpretation suggests that the SSF may represent the residue resulting from sediment diagenesis. The distribution of Sb between nodules and sediment tends to support this interpretation. Its concentration in nodules (Table 10) is approximately 30 times its concentration in bulk sediment (Table 3), similar to the partitioning of Mn. Unlike Mn, however, essentially all Sb present in sediments is in the ISF.

The relation between Zn and Mn (Fig. 11) in nodules is similar to that between Cu and Mn (Fig. 11). The curve defining their distribution in the SSF, however, passes through the compositional fields for both types of nodules, rather than paralleling the curve that defines the composition of K-type nodules.

Within the SSF the concentration of Co correlates strongly with Mn (Table 7) but it correlates with Fe in nodules (Table 11).

When the nodule values are plotted against Mn, however, the two populations based on textural differences exhibit separate ranges of composition, where the K-type nodules are relatively enriched in Co. The curve which defines their relation in the SSF lies between the two nodule fields (Fig. 11).

Mineral Resource

The composition and abundance of nodules at Site C are known well enough to estimate the variations in resource for a small area. Throughout the area shown in Fig. 6, abundance is quite high (Table 9). The somewhat greater nodule abundance in area 2 accounts for the greater metal resource of this area over that of areas 1, 3, and 5. The low Ni, Cu, and Zn resources of area 4, however, reflect the low grade of K-type nodules of this area, rather than low nodule abundance.

Fig. 12. Relation between Ni plus Cu and nodule abundance for DOMES Sites A, B, and C.

No relationship between nodule grade and abundance was observed for area C (Fig. 12). For the box cores from Site A, however, a possible negative correlation is suggested, as observed by Menard and Frazer (1978) for nodules from throughout the Pacific. However, few data are available for Site A and even fewer for Site B.

Conclusions

1. The major- and minor-element compositions of the lithogenous component of sediment at DOMES Sites A, B, and C are extremely uniform. The main difference is slight dilution of this component at Sites A and B with biogenic silica. The composition of this sedimentary component is nearly identical to that of terrigenous shale. Several elements have been measured (Cr, Cs, Hf, Rb, Sb, Ta, and Sc) for which few analyses have been published previously.

2. The fraction of sediment soluble in hydroxylamine hydrochloride-acetic acid, the hydrogenous component of sediment, consists mostly of adsorbed ions of Na^+ , K^+ , Ca^{++} , and Mg^{++} , amorphous oxyhydrates of Fe and Mn, and minor amounts of Co, Cu, Ni, and Zn. The last four metals correlate strongly with Mn.

3. Nodules can be divided into two populations by surface texture, size, and frequency of polynodules. K-type nodules (smooth surface texture, maximum dimension usually less than 3 cm, polynodules abundant) have low Ni, Cu, and Zn and high Co concentrations relative to B- and E/S-type nodules (granular surface texture, maximum diameter usually greater than 5 cm for B-type nodules but less for E/S-type nodules, polynodules rare).

4. The relations between Ni and Mn and between Cu and Mn in K-type nodules is similar to their relation in the hydrogenous component of sediment, but with the nodules slightly enriched in Ni and Cu relative to Mn. B- and E/S-type nodules are strongly enriched in Ni and Cu. One possible interpretation for the marked enrichment of Ni and Cu in B-type and E/S-type nodules is that the composition of K-type nodules resembles the initial composition of the hydrogenous component of sediment. During sediment diagenesis this component within the fine-grained fraction of sediment loses Ni and Cu relative Mn, and B- and E/S-type nodules take up Ni and Cu. The distributions of Co and Zn between nodules and the hydrogenous component of the sediment, however, can not be accounted for by this explanation.

5. The abundance of nodules at the DOMES sites appears to be related to the thickness of the uppermost acoustically transparent layer. Nodules are abundant (greater than approximately 5 kg/m^2) where this layer of sediment is less than approximately 15 m thick and significantly less abundant where it is thicker than 20 m.

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References

- Bischoff, J.L., Piper, D.Z., and Quinterno, P., (1979a) Nature and origin of metalliferous sediment in DOMES Site C, Pacific manganese nodule province, In Sur la Genese des Nodules de Manganese (editor, C. Lalou) (in press).
- Bischoff, J.L., Heath, G.R., and Leinen, M., (1979b) Geochemistry of deep-sea sediments from the Pacific manganese nodule province: DOMES Sites A, B, and C: (this volume).
- Burns, R.G. and Burns, V.M., (1977) Mineralogy. In Marine Manganese Deposits, (editor, G.P. Glasby), Elsevier Ocean. Ser. 185-248.
- Calvert, S.E. and Price, N.B. (1977) Geochemical variation in ferromanganese nodules and associated sediments from the Pacific Ocean, Mar. Chem. 5, 43-74.
- Calvert, S.E., Price, N.B., Heath, G.R., and Moore, T.C., Jr. (1978) Relationship between ferromanganese nodule compositions and sedimentation in a small survey area of the equatorial Pacific, J. Mar. Res. 35, 161-183.
- Chester, R. and Hughes, M.J. (1967) A chemical technique for the separation of ferromanganese minerals, carbonate minerals, and adsorbed trace elements from pelagic sediment, Chem. Geol. 2, 249-262.
- Cook, H.E., Piper, D.Z. and Gardner, J.V., (1977) Geologic and oceanographic framework of DOMES Sites A, B, and C: Central Equatorial Pacific, In Deep Ocean Environmental Study: Geology and Geochemistry of DOMES Sites A, B, and C, Equatorial North Pacific, (compiler, D. Piper), U.S. Geol. Survey Open-file Rept. 77-778, 15-81.
- Dugolinsky, B.K. (1976) Chemistry and morphology of deep-sea manganese nodules and the significance of associated encrusting protozoans, PhD dissertation, Dept. Ocean., Univ. Hawaii, 228 p.
- Goldberg, E.D., (1963) Mineralogy and chemistry of marine sedimentation, In Submarine Geology (F.P. Shepard), New York, Harper and Row, 436-466.
- Hein, J.R., Ross, C.R., Alexander, E. and Yeh, H-W (1979) Mineralogy and diagenesis of surface sediment from DOMES Areas A, B, and C: (this volume).
- Horn, D.R., Delach, M.N. and Horn, B.M., (1973) Metal content of

- ferromanganese deposits of the oceans, IDOE Tech. Report No. 3, NSF, Washington, D.C., 55p.
- Marchig, V., and Gundlach, H., (1978) Diagenetic changes in the radiolarian oozes of the Central Pacific and their influence on the growth of manganese nodules, (in press).
- Menard, H.W., and Frazer, J.Z., (1978) Manganese nodules on the sea floor: inverse correlation between grade and abundance, Science 199, 969-971.
- Meyer, K., (1973) Surface sediment and manganese nodule facies, encountered by R/V VALDIVIA cruises 1972/1973: In The Origin and Distribution of Manganese Nodules in the Pacific and Prospects for Exploration, (editor, M. Morgenstein), Hawaii Inst. Geophys., Honolulu, 125-135.
- Mizuno, A., Chuijo, J. and Yamakade, N., (1976) Prospecting of manganese deposits of the eastern central Pacific Basin, 3rd Intern. Devel. Conf., Tokyo 5, 322-335.
- Monget, J.M., Murray, J.W. and Mascle, J., (1976) A world-wide compilation of published, multicomponent/analysis of ferromanganese concretions: NSF-IDOE Tech. Report 12, 127 pp.
- Piper, D.Z., Cook, H.E., and Gardner, J.V., (1979) Lithic stratigraphy and acoustic stratigraphy of the equatorial North Pacific, DOMES Sites A, B, and C (this volume).
- Quinterno, P., and Theyer, F., (1979) Biostratigraphy of the equatorial North Pacific DOMES Sites A, B, and C (this volume).
- Riley, J.P. and Sinhaseni, P., (1958) Chemical composition of three manganese nodules from the Pacific Ocean, J. Mar. Res. 17, 466-482.
- Skornyakova, N.S., (1979) Zonal regularities in occurrence, morphology and chemistry of the Pacific Ocean manganese nodules (this volume).
- Sorem, R.K., Reinhart, W.R., Fewkes, R.H., and McFarland, (1979) Occurrence and character of manganese nodules in DOMES Sites A, B, and C east equatorial Pacific Ocean (this volume).
- Turekian, K.K., and Wedepohl, K.H., (1961) Distribution of the elements in some major units of the earth's crust: Geol. Soc. Amer. Bull. 72, 175-192.