Distribution, Morphology, and Geochemistry of Manganese Nodules from the *Valdivia* 13/2 Area, Equatorial North Pacific¹

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ABSTRACT: Manganese nodules were collected during cruise 13/2 of R.V. Valdivia in 1976 in a small area of the equatorial north Pacific characterized by abyssal hill topography. The sediments are dominantly siliceous oozes in which extensive dissolution of siliceous material has taken place. Three principal nodule morphologies were recovered: polynucleate nodules, mononucleate nodules, and manganese crusts. Polynucleate nodules occur throughout the entire depth range studied whereas mononucleate nodules are found principally below 5000 m: manganese crusts are restricted to the abyssal hill environments. Nodule density remains on average roughly constant (>7 kg/m²) with water depth (although varying considerably, 0-27 kg/m², throughout the area), but the form in which the nodules occur changes with water depth. Nodule composition was investigated as a function of water depth, nodule size, and nodule morphology and shown to be related principally to nodule morphology. Mononucleate nodules have higher contents of Mn, Ni, Cu, and Zn and lower contents of Fe and Co than polynucleate nodules. The lithogenous fraction in the nodules is similar in both morphologies, although it varies considerably with nodule size. Both morphologies contain todorokite and δ -MnO₂ as the principal manganese oxide phases, but todorokite is relatively more abundant in the mononucleate nodules.

The data are best interpreted in terms of the diagenetic supply of the transition elements Mn, Ni, Cu, and Zn to the nodules resulting from the in situ dissolution of siliceous tests in the sediment column. This process is more pronounced in the abyssal regions than on the flanks of the abyssal hills and leads to the enrichment of these elements in the larger mononucleate nodules embedded at the sediment —water interface there. This enhanced supply of transition elements also leads to the stabilization of todorokite in these nodules. Polynucleate nodules appear to be preferentially formed under conditions of higher sedimentation rate on the flanks of abyssal hills in an environment where abundant seeds are available. Mononucleate nodules are formed in abyssal environments characterized by lower sedimentation rate where enhanced rates of supply of biogenically derived elements can take place.

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The data emphasize the variations in nodule character on a localized scale in the equatorial north Pacific nodule belt which are related to abyssal topography. Determination of the precise nature of such variations will be of importance in the development of nodule mine sites in the region.

To date, few studies have dealt in detail with the variation in the density, morphology, composition, and mineralogy of manganese nodules over localized areas of the sea floor (Bezrukov 1973, Bischoff and Piper 1979, Calvert et al. 1978, Cronan and Tooms 1967, Friedrich and Plüger 1974, Glasby, Tooms, and Howarth 1974, Halbach and Özkara 1979, Hubred 1970, Roonwal and Friedrich 1980). As a result, the precise factors controlling these variations are not particularly well understood.

In this paper, we report on the influence of submarine topography on nodule density, morphology, composition, and mineralogy from a limited area in the equatorial north Pacific in order to study these problems in more detail. The area chosen for study is approximately 35 km \times 35 km, centered at 9°25′ N and 146°00′ W, and is situated between the Clarion and Clipperton fracture zones. It was sampled between 9 February and 10 March 1976 as part of cruise 13/2 of R.V. Valdivia (von Stackelberg 1976). The study area is characterized by abyssal hill topography in the depth range 5400-4740 m and consists of three small sea peaks named by Andrews and Friedrich (1979) North Peak, East Peak, and West Peak, each with a relief of 400-500 m. It constitutes part of the siliceous ooze nodule province where much of the exploration activity for "economic-grade" manganese nodules has taken place. The area was chosen as a follow-up to a previous survey of the area during cruise VA-08 of R.V. Valdivia (cf. Friedrich, Plüger, and Kunzendorf 1976 for references). Preliminary accounts of this work have been presented by Friedrich et al. (1976) and Andrews and Friedrich (1979). In particular, the occurrence of three principal nodule morphologies in the area (Fe-rich polynodules, Fe-poor mononodules, and crusts) was noted. The distribution of these morphologies was thought to be related to topography (cf. Andrews and Friedrich

1979:35, table 1). Kiggen (1979) has described the petrography of some selected nodules from this area and Friedrich and Schmitz-Wiechowski (1980) the characteristics of a large manganese crust. Von Stackelberg (1979) has also described in detail the sediment stratigraphy of the area and its relation to nodule formation, and von Stackelberg (1982) discusses the relation of nodule formation to the occurrence of sediment hiatuses. Kunzendorf and Friedrich (1977) have reported on the uranium distribution in the nodules.

The study area is very similar in topographic setting, location, and sediment type to that of the Wahine area described in detail by Calvert et al. (1978) and references therein. It will therefore be particularly useful to compare the results from the two study areas. It was also chosen to be very similar in character to the area studied during the Valdivia 13/1 cruise to the west (Craig 1979a, Halbach and Özkara 1979, 1980, Heye 1979, Marchig and Gundlach 1979a, b, Marchig, Gundlach, and Schnier 1979). A schematic map showing the locations of these three areas is given in Figure 1, and the topographic setting of the Valdivia 13/2 area is shown in Figure 2. Other small areas in the equatorial north Pacific in which the manganese nodule distribution has been studied include DOMES sites A, B, and C (Piper, Leong, and Cannon 1979, Sorem et al. 1979b) and area C of the ICIME Project (Friedrich et al. 1979). Although the Valdivia 13/2 area is characterized by the occurrence of three sea peaks, for convenience, in many cases, the data are discussed as a function of water depth; this serves as a measure of the elevation of the station above the abyssal sea floor (and therefore to some extent of the environment of deposition of the nodule). A discussion of the influence of water depth on nodule composition has been given by Frazer and Fisk (1981).

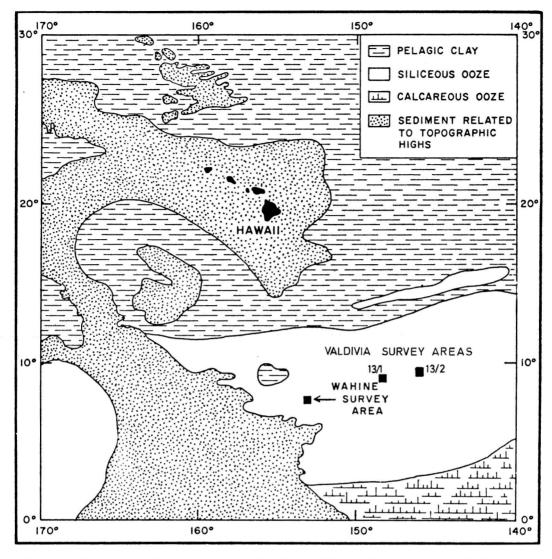


FIGURE 1. Schematic map showing the location of the *Valdivia* 13/2 area. The locations of the *Valdivia* 13/1 and *Wahine* areas are given for comparison. Map modified from Calvert et al. (1978).

NODULE MORPHOLOGY AND DENSITY

Table 1 summarizes the size distribution of nodules by number and weight and the surface density of the nodules as a function of water depth. In all, 5219 nodules weighing 91.9 kg were recovered during the *Valdivia* 13/2 cruise by free-fall grab and box core. From Table 1, it is seen that there is a change in size structure of the nodules with water

depth with larger nodules (> 60 mm) being more abundant with increasing water depth; the percentage of nodules greater than 60 mm (by weight) more than triples on average below a depth of 5000 m compared to that above 5000 m, from 12 percent above 5000 m to 44 percent below 5000 m. This increase in size does not appear to be sustained below 5300 m. In spite of this, nodules greater than 60 mm make up only a minority (by number)

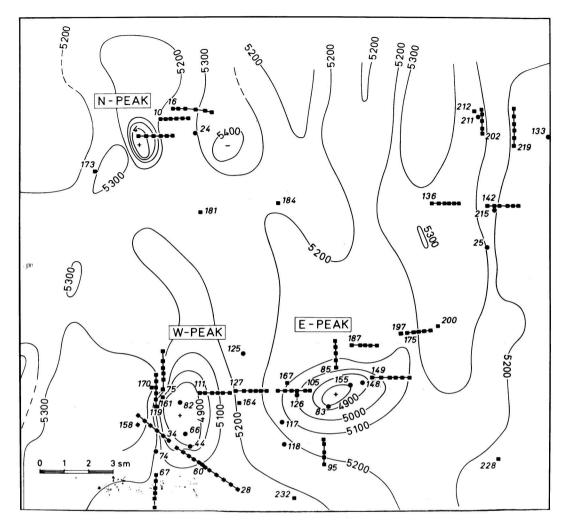


FIGURE 2. Schematic map showing the bathymetry and the sample locations of the *Valdivia* 13/2 area. Depths in meters. The squares represent free-fall grabs and the circles box cores. For convenience, only the first station number in a sequence is given. Map taken from Andrews and Friedrich (1979).

of nodules below 5000 m (4.4 percent). Nodules less then 40 mm make up the majority (by number) of the nodules (> 79 percent) at all water depths. Nodules are therefore smaller on average than those at area C of the ICIME Project. By contrast, nodule density remains on average roughly constant with water depth, although showing wide variations in density between stations within a given water depth. Overall, the nodule density in the area varies in the range 0–27 kg/m², in agreement with the observation of Craig

(1979a) of such localized variations in nodule density in the equatorial north Pacific. The magnitude of such variations in nodule density is of particular importance in assessing an area as a potential mine site. As a matter of sampling technique, it should be noted that a few free-fall grabs came back empty, although bottom photographs of an identical area taken by the free-fall-grab camera showed moderately high nodule density.

In order to examine the relationship between nodule characteristics and water depth

TABLE 1

Variation in Total Number of Nodules, by Number (Upper Line) and Weight (in Grams, Lower Line), Collected by Free-Fall Grab or Spade Corer, and Average Surface Density and Chemical Composition of Nodules with Water Depth

				SIZE CLASS (r	nm)			2.2	-		_
DEPTH RANGE (m)	NUMBER OF STATIONS	0-20	20-40	40-60	60-80	> 80	DENSITY (kg/m^2)	Mn (%)	Fe (%)	Ni (%)	Cu (%)
4700-4800	1	50 (57)	28 (32)	7 (8)	3 (3)		11	25.5	10.2	1.02	0.61
		80 (8)	420 (42)	260 (26)	240 (24)						
4800-4900	5	53 (27)	103 (53)	35 (18)	2 (1)	-	12.6	25.8	7.9	1.21	0.85
		81 (2)	1,708 (48)	1,351 (38)	400 (11)						
4900-5000	8	81 (21)	219 (58)	72 (19)	6 (2)	_	8.6	26.3	9.8	1.14	0.79
		173 (3)	2,466 (47)	2,050 (39)	595 (11)						
5000-5100	11	109 (20)	349 (64)	72 (13)	15 (3)	6 (1)	9.7	26.7	9.4	1.15	0.82
		214 (2)	3,907 (44)	2,395 (27)	1,215 (14)	1,165 (13)				1	
5100-5200	43	1,176 (53)	771 (35)	164 (7)	67 (3)	28 (1)	10.5	27.7	6.8	1.31	1.00
		2,029 (5)	9,401 (25)	7,628 (20)	9,218 (24)	9,950 (26)					
5200-5300	59	568 (37)	659 (43)	210 (14)	51 (3)	27 (2)	7.1	28.3	7.1	1.26	0.99
		1,227 (4)	7,862 (25)	8,041 (26)	7,078 (23)	6,871 (22)					
5300-5400	8	137 (48)	112 (39)	35 (12)	4 (1)	1 (0.3)	7.5	26.9	7.3	1.09	0.86
		239 (6)	1,656 (42)	1,220 (31)	480 (12)	300 (8)					
Manganese crusts	s 4					_		28.1	8.7	1.14	0.66

Note: Percentage values are given in parentheses. In cases where the free-fall grab returned empty, the station was ignored since bottom photographs showed some of these stations to be in areas of manganese encrustations. Dredge data were also ignored. Average analysis of manganese crusts also listed for comparison.

TABLE 2

Number of Stations with Polynucleate Nodules, Mononucleate Nodules, Mixed Assemblages of Polynucleate and Mononucleate Nodules, and Manganese Crusts as a Function of Water Depth

DEPTH RANGE (m)			MONONUCLEATE NODULES	MIXED ASSEMBLAGES	CRUSTS	
4700-4800	1	1 (11)	_	_	_	
4800-4900	5	1 (10)	1 (4)	3 (16)	4	
4900-5000	8	3 (6)	1 (0.3)	5 (11)	1	
5000-5100	11	8 (9)	3 (12)	_		
5100-5200	43	11 (ÌI)	20 (10)	12 (12)	1	
5200-5300	59	16 (9)	34 (5)	9 (11)	1	
5300-5400	8	2 (19)	4 (0.9)	2 (9)	_	

Note: Average surface densities of nodules (kg/m²) are given in parentheses.

more meaningfully, nodules from each station were divided into four main categories (mononucleate nodules, polynucleate nodules, a mixed assemblage of mononucleate and polynucleate nodules, and manganese crusts) and each station classified accordingly. The number of stations containing each nodule type is given as a function of water depth in Table 2. and the average surface density of nodules is given in parentheses. Of the stations that vielded nodules, 46 percent contained principally mononucleate nodules, 31 percent polynucleate nodules, and 23 percent a mixed assemblage of nodules. In terms of the total weight of nodules recovered, the percentages recovered in each category were 39, 30, and 31 respectively. More importantly, percent. Table 2 shows that the distribution of nodules with water depths differs somewhat from that proposed by Andrews and Friedrich (1979), who suggested that small polynucleate nodules in high density predominate on the flanks of the peaks whereas mononucleate nodules with lower density are the dominant facies on the low rolling abyssal hill topography between the peaks. In fact, polynucleate nodules are found throughout the entire depth range sampled, with 68 percent of the stations containing polynucleate nodules sampled below 5100 m whereas mononucleate nodules are found principally below 5000 m. Surface densities for polynucleate and mixed assemblage nodules are moderately high throughout the entire depth range sampled (although highly variable within each depth range) whereas for mononucleate nodules they are highest between 5000 and 5300 m, with some evidence of a fall off in abundance below 5300 m. Polynucleate nodules are therefore much more uniformly distributed with water depth than mononucleate nodules.

In order to pursue this matter further, the size distribution by number and by weight, surface density, and average weight of nodules in each nodule category has been calculated (Table 3). This shows that mononucleate nodules occur on average in somewhat lower abundance than polynucleate nodules but are larger and have a higher average weight. For example, 68 percent of mononucleate nodules are larger than 60 mm, compared to 15 percent for polynucleate nodules. These data taken together show that the classic "hamburger" nodule is found predominantly in a relatively restricted depth range of 5000-5300 m in this area. Manganese crusts are found predominantly above 5000 m, although a limited number were recovered below this depth (Table 1).

The data in Tables 2 and 3 show that a study of the depth distribution of various nodule parameters (such as chemical composition) in the *Valdivia* 13/2 area would be somewhat misleading because the three discrete populations of nodules involved (mononucleate nodules, polynucleate nodules and a mixture thereof, and crusts), each with markedly different morphological and size characteristics, have significantly different depth distributions. Nonetheless, it can be seen that polynucleate nodules are distributed throughout the sampled depth range, crusts in the elevated

TABLE 3

VARIATION IN TOTAL NUMBER OF NODULES, BY NUMBER (UPPER LINE) AND WEIGHT (IN GRAMS, LOWER LINE), FOR EACH NODULE TYPE

				D. ED. LOVETT				
NODULE TYPE	NUMBER OF STATIONS	0-20	20-40	40-60	60-80	> 80	(kg/m^2)	AVERAGE NODULE WEIGHT (g)
Mononucleate	63	323 (38)	253 (30)	141 (16)	90 (10)	49 (6)	6.6	
nodules		601 (2)	3,662 (10)	7,791 (20)	12,241 (32)	13,932 (36)	(0.2-23)	44.7
Polynucleate	42	676 (26)	1,266 (48)	243 (9)	27 (1)	5 (0.2)	9.9	
nodules		1,329 (4)	15,597 (53)	8,322 (28)	2,930 (10)	1,400 (5)	(0.2-24)	11.2
Mixed	31	1,145 (54)	720 (34)	216 (10)	29 (1)	8 (0.4)	11.4	
assemblage		2,118 (7)	12,286 (41)	7,827 (26)	4,570 (15)	3,410 (11)	(2-27)	14.3

Note: Percentage values are given in parentheses. Surface densities of nodules (kg/m², with range of densities given in parentheses) and average weight of nodules (g) for each nodule type are also given.

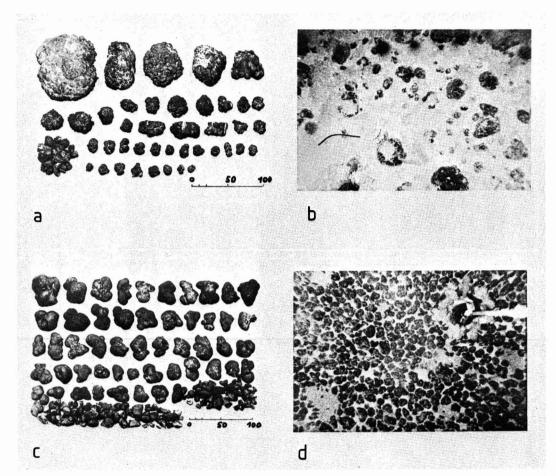


FIGURE 3. a, on board and b, in situ photographs of mononucleate nodules from station 67 GBH. c, on board and d, in situ photographs of polynucleate nodules from station 170 GBH. A scale of 0–100 mm is shown in the on board photographs. In situ photographs were taken by a camera attached to a free-fall grab approximately 1 m above the sea floor.

seamount areas, and mononucleate nodules predominantly in the depth range 5000-5300 m. From Table 1, it is seen that the nodule density is on average moderately high (> 7 kg/m²) at all water depths, but that the form in which the nodules occur changes with water depth (Table 2). The overall mass balance of the nodules therefore remains roughly independent of water depth, but the form of the nodules varies with water depth. From the data in Tables 1–3, it is therefore clear that the primary parameters by which we may describe the nodules (water depth, nodule size, and nodule morphology) are interlinked.

Comparison with other study areas in the equatorial north Pacific shows that mor-

phology and depth distribution of Valdivia 13/2 nodules is very similar to that observed in the Valdivia 13/1 area; the reader is referred to Halbach and Özkara (1979: 79-80) for a discussion of the distribution of nodules in the Valdivia 13/1 area. By contrast, polynucleate nodules were largely absent in area C studied during the ICIME Project, and the depth range there (170 m) was too small to permit any meaningful assessment of the relationship between nodule density and water depth. Within the three DOMES sites, polynucleate nodules such as those observed in the Valdivia 13/2 area were present principally in DOMES site A and to a lesser extent in site C (Piper et al. 1979:452-453). Within DOMES site C,

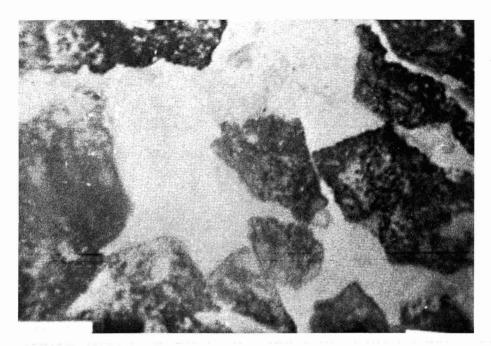


FIGURE 4. In situ photograph of manganese crusts from station 82 KA. In situ photograph taken by a camera attached to a spade corer approximately 1 m above the sea floor.

the larger mononucleate nodules are found principally in channels between abyssal hills whereas polynucleate nodules are restricted to the flanks of one of the abyssal hills (Piper et al. 1979: 463); this is similar to the distribution found here. No such relationship was observed for DOMES sites A or B.

In order to give a better idea of the nodule morphologies present, photographs of nodules representative of each morphological type are given in Figure 3. These samples were recovered by free-fall grab, and the photographs were taken in situ and on board ship to facilitate comparison. An in situ photograph of manganese crusts is given in Figure 4. The station data for each of these stations are listed in Table 4. Although these photographs represent only a small minority of the total nodules collected, they do give a reasonable indication of the principal nodule morphologies present.

Station 67 GBH represents dominantly mononucleate nodules taken on the south side of West Peak. The nodules are analogous to those taken from area C of the ICIME Project. The larger (> 40 mm) nodules are

discoidal-ellipsoidal nodules with equatorial rims and mammillated smooth to microbotryoidal surface texture on the upper surface and botryoidal or cavernous granular surface texture on the lower surface. The smaller nodules (< 40 mm) are faceted spheroidal to ellipsoidal with suppressed equatorial rims in the 20-40-mm size range. Surface texture is botryoidal to microbotryoidal. The smaller nodules also contain a number of polynucleate nodules. The in situ photographs show that the larger nodules are commonly covered with a thin layer of sediment as previously recorded for nodules from this region by Horn, Horn, and Delach (1973a:43, fig. 30) and Paul (1976) and lie deeper in the sediment than the polynucleate nodules (cf. Sorem et al. 1979a). The sediment shows evidence of bioturbation. including the possible occurrence of worm tubes. Biological tubes, possibly similar to those described by Dugolinsky (1976) and Dudley (1979), are frequently seen on the surface of this type of nodule.

Station 170 GBH represents dominantly polynucleate nodules up to 80 mm in diameter with smooth to microbotryoidal surface tex-

 $TABLE\ 4$ Principal Characteristics of Nodules from the Stations Illustrated in Figures 3 and 4

STATION			DEPART	SURFACE	LARGEST	SMALLEST		SIZE	CLASS (1	mm)		DDOVEN
STATION NUMBER	LATITUDE	LONGITUDE	DEPTH (m)	(kg/m^2)	(mm)	(mm)	0-20	20-40	40-60	60-80	> 80	BROKEN NODULES
67 GBH	9°16.45′ N	146°4.4′ W	5189	14	100 × 80 × 50	12 × 10 × 9	20	15	4	2	1	
170 GBH	9°20.0′ N	146°45′ W	5292	20	(400 g) $60 \times 50 \times 40$	(1 g) 15 × 15 × 15	50	150 24	250 16	400	400	50
170 OBH	9 20.0 IN	140 43 W	3292	20	(85 g)	(1.5 g)	10	450	550	90	_	700
82 KA	9°19.4′ N	146°3.4′ W	4828	_		_	-	_	_		_	

Note: In the section on size class, the upper line refers to the number of nodules in each size class at each station and the lower line to the weight of nodules (g) in each size class.

ture taken on the northwest side of West Peak. In the larger nodules, the surface texture differs on the upper and lower surfaces. Septarian cracks can be seen on the surfaces of a number of nodules. The in situ photographs show extremely close packing of nodules on the sea floor, and the nodules appear to lie on the sediment surface. Several zones of bioturbation are observed where nodules have either been pushed aside or buried. Extensive bioturbation in equatorial north Pacific sediments has previously been reported by Ryan and Heezen (1976), Paul et al. (1978), Thiel (1978), Dudley (1979), Hecker and Paul (1979), and Ruppert (1979).

Station 82 KA (Figure 4) shows the in situ occurrence of manganese crusts at the crest of West Peak.

The above description shows that the nodules sampled here are very similar to those described by Halbach and Özkara (1979) for the *Valdivia* 13/1 area, although we do not accept the arbitrary classification scheme of nodules into A, B, and AB types used by these authors (cf. Halbach, Özkara, and Hense 1975).

NODULE COMPOSITION

The nodules were chemically analyzed on board ship for Mn, Fe, Ni, and Cu by X-ray fluorescence spectroscopy following grinding and drying of the samples at 110°C for 24 hr (Friedrich et al. 1976); the elements Co, Zn, Al. Si. and Ba were analyzed in selected samples by atomic absorption spectrophotometry in Aachen (Thijssen et al. 1981). In addition, the percent lithogenous fraction of selected samples was determined following treatment of the sample by 25 percent HCl. Element composition in these nodules was then computed on a lithogenous-free basis to make allowance for the effects of variation in the silicate contents of the nodules. This represents an analysis of the hydrolyzate fraction of the nodules. The procedure follows that described by Glasby and Thijssen (in press, a).

Considering only the four principal transition elements in nodules (Mn, Fe, Ni, and Cu), nodules from the *Valdivia* 13/2 area dis-

play a marked variability in the bulk composition. The following ranges for the average bulk composition of the nodules from each station are observed: Mn, 22.8–33.3 percent; Fe, 2.8–14.0 percent; Ni, 0.72–1.67 percent; and Cu, 0.47-1.35 percent. These correspond to variations of a factor of 1.5 for Mn. 5.0 for Fe. 2.3 for Ni. and 2.9 for Cu. These variations are comparable to or greater than those observed in area 4c on the Carlsberg Ridge (Glasby et al. 1974) in the Wahine area (Calvert et al. 1978) and in area C of the ICIME Project and detract from the assertion of Dugolinsky (1976) that nodules display relatively consistent chemical compositions over broad regions of the equatorial north Pacific (cf. Craig 1979b). It should be pointed out, however, that the Valdivia 13/2 area was specifically selected to display topographic variability where variability in nodule composition might be expected. More specifically, the bulk analyses presented here indicate that the Mn/Fe ratio and Ni and Cu contents of the nodules increase with water depth below 5100 m (Table 1), although there is some evidence that this increase is not sustained below 5300 m.

Three factors may be responsible for the observed variation in nodule composition with water depth (water depth itself, nodule size, and nodule morphology). In order to clarify this situation, the average nodule composition at each station was calculated as a function of water depth for each size class (Table 5), as a function of nodule size (Table 6), and as a function of morphology (Table 7). Table 5 shows that increasing water depth leads to an increase in the Mn/Fe ratio and Ni and Cu content of the nodules, although this is not always systematic. This is illustrated in Figure 5 (cf. Calvert et al. 1978:173, fig. 3), although this relationship is not precise, particularly in the west side of West Peak. Table 6 shows that these parameters also increase with nodule size class (cf. Heve 1979, Sorem et al. 1979b). In the depth ranges 5100–5200 m and 5200-5300 m, for example, there is an increase in the Mn/Fe ratio and Ni and Cu content of the nodules with increasing nodule size (compare Table 5). However, the data in Table 7 show a marked variation in com-

TABLE 5

VARIATION IN COMPOSITION OF NODULES WITH WATER

DEPTH (ALL ANALYSES IN PERCENT)

DEPTH RANGE (m)	NUMBER OF ANALYSES	Mn	Fe	Ni	Cu
					10000
a. 0-20 mm si					
4700-4800	1	24.2	11.1	0.92	0.57
4800-4900	4	28.1	7.5	1.26	0.94
4900-5000	1	27.7	7.0	1.45	1.02
5000-5100	4	25.4	8.8	1.14	0.86
5100-5200	15	25.5	7.7	1.23	0.96
5200-5300	16	24.5	6.0	1.17	0.99
5300-5400	5	27.6	5.4	1.17	1.02
b. 20-40 mm s	size class				
4700-4800	1	24.3	10.5	1.01	0.59
4800-4900	6	26.5	8.1	1.23	0.87
4900-5000	6	25.9	9.4	1.17	0.82
5000-5100	9	27.5	9.4	1.18	0.71
5100-5200	24	26.8	7.4	1.32	1.00
5200-5300	34	26.8	7.3	1.24	0.99
5300-5400	5	25.9	8.6	1.12	0.84
c. 40-60 mm s	size class				
4700-4800	1	29.7	8.0	1.15	0.74
4800-4900	6	21.9	8.1	1.02	0.68
4900-5000	5	26.7	10.5	1.10	0.74
5000-5100	7	26.1	10.4	1.08	0.75
5100-5200	29	28.0	6.9	1.31	0.75
5200-5300	36	28.4	7.6	1.25	0.99
5300-5400	3	26.1	11.0	1.01	0.63
d. 60–80 mm s	ina alasa	-9.1			
4700–80 mm s		26.2	10.1	1 12	0.64
4800-4900	1 2			1.13	
		26.0	7.4	1.19	0.76
4900-5000	1	29.9	6.5	1.27	0.95
5000-5100	5	25.2	8.8	1.18	0.85
5100-5200	20	29.8	6.4	1.34	1.04
5200-5300 5300-5400	24 2	29.8 26.9	6.6 8.5	1.35 1.02	0.74
	_	20.9	0.3	1.02	0.72
e. > 80 mm si	ze class				
4700-4800		20.6	11.5	0.04	0.01
4800-4900	1	20.6	11.5	0.94	0.81
4900-5000	1	28.3	5.8	1.36	1.00
5000-5100				_	_
5100-5200	7	30.1	6.0	1.39	1.01
5200-5300	12	29.8	6.1	1.30	0.98
5300-5400			-	_	

position between mononucleate and polynucleate nodules (which was shown to be statistically significant at the 99 percent confidence level using the Student *t* test) as well as manganese crusts; in fact, the manganese crusts appear to be on average similar in composition to the polynucleate nodules (cf.

TABLE 6

VARIATION OF NODULE COMPOSITION WITH SIZE CLASS
FOR THE TOTAL NODULE POPULATION (ALL WATER
DEPTHS: ALL ANALYSES IN PERCENT)

SIZE CLASS (mm)	NUMBER OF ANALYSES	Mn	Fe	Ni	Cu
0-20	46	25.7	6.7	1.20	0.96
20 - 40	85	26.7	7.9	1.24	0.94
40-60	87	27.5	7.9	1.22	0.92
60 - 80	55	29.0	6.9	1.31	1.11
> 80	21	29.4	6.3	1.31	0.98

TABLE 7

AVERAGE BULK ANALYSES AND STANDARD
DEVIATIONS FOR MONONUCLEATE NODULES,
POLYNUCLEATE NODULES, MIXED ASSEMBLAGE OF
MONONUCLEATE AND POLYNUCLEATE NODULES, AND
MANGANESE CRUSTS (ALL ANALYSES IN PERCENT)

MORPHOLOGY	NUMBER OF ANALYSES	Mn	Fe	Ni	Cu
Mononucleate	62	29.5	5.7	1.40	1.15
nodules		± 2.1	± 1.0	± 0.16	± 0.14
Polynucleate	37	25.8	10.2	1.06	0.71
nodules		± 1.8	± 2.5	± 0.20	± 0.22
Mixed	27	26.6	7.7	1.19	0.89
assemblage		± 2.1	± 2.1	± 0.19	± 0.18
Manganese crusts	4	18.6	10.9	1.04	0.70

Friedrich and Schmitz-Wiechowski 1980). From a consideration of all these data, it was concluded that nodule composition is related principally to nodule morphology and this results in the secondary relationship between nodule composition and water depth or size class (cf. Halbach and Özkara 1979:80). Halbach and Özkara (1979) concluded that absolute depth does not control the composition of nodules directly. To test this hypothesis, the composition of the polynucleate nodules alone was calculated as a function of water depth (Table 8), and no systematic trend was observed. Similarly, only a minor change in the composition of mononucleate nodules with increasing size was noted (Table 9). It may therefore be concluded that the bulk composition of nodules in the Valdivia 13/2 area is primarily related to nodule morphology and that the variation in composition

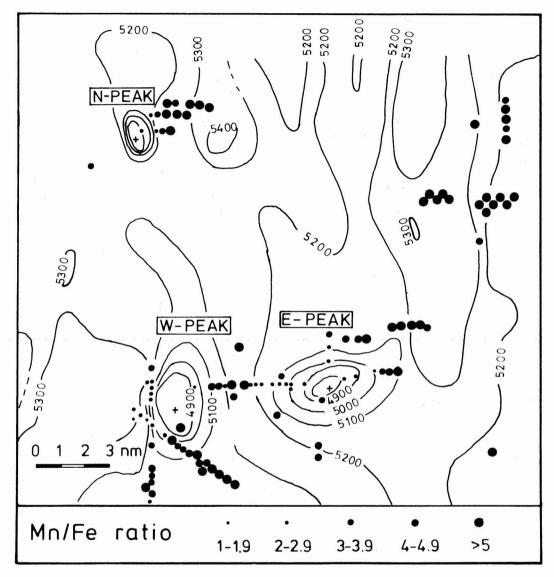


FIGURE 5. Schematic diagram showing the variation in the Mn/Fe ratios of the nodules with location in the Valdivia 13/2 area. The dot size is a measure of the Mn/Fe ratio.

of the total nodule population with water depth and nodule size is an artifact (or secondary feature) resulting from considering a mixed population of nodules. The importance of morphology in controlling nodule composition has previously been noted by Meyer (1973) and Glasby et al. (1974).

In assessing the influence of nodule morphology on composition, it is noted that the

differences in the Mn/Fe ratios of the mononucleate and polynucleate nodules is more the result of the Fe content of the polynucleate nodules being higher than the Mn content lower (cf. Calvert et al. 1978, Dugolinsky 1976). This greater variability in the Fe contents of the nodules led Friedrich et al. (1976) to describe the nodules from the area as Fe-rich polynodules and Fe-poor mononod-

TABLE 8

VARIATION IN COMPOSITION OF POLYNUCLEATE
NODULES WITH WATER DEPTH
(ALL ANALYSES IN PERCENT)

DEPTH RANGE (m)	NUMBER OF ANALYSES	Mn	Fe	Ni	Cu	
4700-4800	1	25.5	10.2	1.02	0.61	
4800-4900	1	23.4	9.5	1.08	0.64	
4900-5000	1	23.5	12.8	0.88	0.50	
5000-5100	6	26.3	10.7	1.06	0.71	
5100-5200	11	26.6	8.5	1.23	0.86	
5200-5300	15	25.8	10.4	0.98	0.67	
5300-5400	2	25.2	12.0	0.92	0.53	

TABLE 9

VARIATION IN COMPOSITION OF MONONUCLEATE NODULES WITH SIZE (ALL ANALYSES IN PERCENT)

NUMBER OF ANALYSES	Mn	Fe	Ni	Cu	
18	26.1	5.2	1.27	1.11	
28	28.4	5.9	1.43	1.21	
35	29.6	5.7	1.43	1.18	
37	30.3	5.8	1.42	1.12	
18	30.0	5.9	1.35	1.01	
	18 28 35 37	ANALYSES Mn 18 26.1 28 28.4 35 29.6 37 30.3	ANALYSES Mn Fe 18 26.1 5.2 28 28.4 5.9 35 29.6 5.7 37 30.3 5.8	ANALYSES Mn Fe Ni 18 26.1 5.2 1.27 28 28.4 5.9 1.43 35 29.6 5.7 1.43 37 30.3 5.8 1.42	

TABLE 10

AVERAGE BULK COMPOSITION OF NODULES FROM Valdivia 13/2 AREA (9°25′ N, 146°00′ W, 5400–4740 m), Wahine AREA (8°20′ N, 153° W, c. 5000 m with 280 m relief; Calvert et al. 1978), AND AREA C (11°30′ N, 134° W, 4656–4916 m; Friedrich et al. in press)

	Mn (%)	Fe (%)	Ni (%)	Cu (%)
Valdivia 13/2	27.8	7.4	1.26	0.97
Wahine	24.6	6.8	1.08	1.14
Area C	29.1	5.4	1.29	1.19

ules. However, for the development of ideas on the mode of element supply to nodules, it is better to consider the Mn/Fe ratio of the nodules rather than the Fe content as the distinguishing criterion (cf. Calvert et al. 1978, Friedrich, Kunzendorf, and Plüger 1973, Hein et al. 1979, Lyle, Dymond, and Heath 1977). In fact, the variation in the Mn/Fe ratio of the nodules in the *Valdivia* 13/2 area (1.7–10.0; see Figure 5) is greater than that reported by

Calvert et al. (1978) for nodules from the Wahine area.

For comparison, the average bulk compositions of the nodules from three areas in the equatorial north Pacific high-productivity belt are listed in Table 10. The data show the same overall patterns in composition, although some differences are apparent. Whether these are related to differences in nodule morphology cannot be established on the basis of the limited data available. However, nodules from the *Valdivia* 13/2 area are similar to those of area C in having a Ni/Cu ratio greater than unity.

The previous discussion has dealt with the bulk composition of the four principal transition elements in nodules. Analysis of the bulk composition of selected nodules for nine substances (Table 11) shows that on average mononucleate nodules have higher contents of Mn, Ni, Cu, and Zn and lower contents of Fe and Co than the polynucleate nodules. The Si, Al, and Ba contents appear to be similar. A correlation matrix of the data shows the typical element associations found in deep-sea nodules: Mn-Ni-Cu-Zn-Ba?, Fe-Co, and Al-Si (Table 12). The unusual association of Ba may reflect its occurrence as barite in the nodules. Analysis of a few nodules on a lithogenous-free basis (Table 13) shows that, in general, smaller nodules contain a much higher proportion of lithogenous material than larger nodules at the same station; this may reflect the relatively larger size of silicatebearing nuclei in the smaller nodules and the fact that larger nodules frequently have broken fragments of older nodules as nodule nuclei. There appears to be no marked difference on average in the proportion of lithogenous material in mononucleate and polynucleate nodules. The hydrolyzate fraction of the nodules (expressed on a lithogenous-free basis) shows higher contents of Mn, Ni, Cu, and Zn and lower contents of Fe and Co in the mononucleate nodules than in the polynucleate nodules. This confirms that these differences in composition between mononucleate and polynucleate nodules reflect real differences in the composition of the nodules and not the effect of dilution by silicate material (cf. Calvert et al. 1978).

TABLE 11

BULK ANALYSES OF NODULES FROM SELECTED STATIONS DISPLAYING DIFFERENT MORPHOLOGIES (ALL ANALYSES IN PERCENT)

STATION NUMBER	MORPHOLOGY	SIZE CLASS (mm)	Mn	Fe	Co	Ni	Cu	Zn	Ва	SiO_2	Al_2O_3
66 KA	Mononucleate	< 20	28.3	5.5	0.240	1.54	1.20	0.130	0.21	18.31	8.16
		20 - 40	30.3	5.1	0.196	1.66	1.34	0.152	0.21	14.59	7.60
		40-60	18.5	2.6	0.110	1.17	0.91	0.115	0.15	8.56	4.78
67 GBH	Mixed assemblage	20-40	25.3	6.6	0.222	1.40	1.12	0.121	0.28	21.59	9.18
		40 - 60	30.9	6.3	0.181	1.43	0.99	0.180	0.23	12.64	6.46
		60 - 80	27.5	6.8	0.185	1.29	0.89	0.121	0.23	20.47	8.99
73 GBH	Polynucleate	< 20	23.3	10.0	0.279	1.13	0.68	0.080	0.24	25.33	9.79
		20 - 40	22.2	8.5	0.254	1.08	0.64	0.096	0.24	18.98	6.16
		40-60	27.8	9.3	0.268	1.15	0.74	0.121	0.26	12.64	9.22
83 KA	Mixed assemblage	20 - 40	29.8	6.6	0.252	1.47	1.04	0.097	0.27	18.61	8.28
		40-60	23.7	10.2	0.222	0.97	0.59	0.096	0.23	17.49	9.07
103 GBH	Mixed assemblage	< 20	20.0	7.4	0.162	1.10	0.91	0.086	0.17	30.84	10.86
		20 - 40	24.3	7.3	0.212	1.32	1.07	0.112	0.14	25.59	9.35
		40-60	25.4	7.7	0.260	1.32	1.02	0.118	0.28	19.19	8.65
		60 - 80	25.0	11.0	0.290	0.96	0.61	0.097	0.21	17.11	7.82
120 GBH	Polynucleate	20 - 40	27.0	12.5	0.293	0.98	0.58	0.102	0.21	11.98	5.14
		40-60	25.5	13.3	0.202	0.86	0.46	0.091	0.21	12.43	4.93
140 GBH	Mononucleate	< 20	24.8	5.2	0.200	1.27	1.18	0.165	0.28	30.85	11.62
		40-60	33.0	5.7	0.195	1.54	1.24	0.181	0.23	12.43	5.76
		> 80	31.5	6.3	0.192	1.42	1.09	0.183	0.23	12.43	5.67
155 KA	Polynucleate	< 20	22.9	10.4	0.267	0.98	0.57	0.090	0.18	23.96	8.84
		20 - 40	25.6	10.6	0.295	1.03	0.60	0.100	0.19	16.47	7.05
		40-60	29.7	8.0	0.285	1.15	0.74	0.160	0.24	12.79	5.59
		60 - 80	26.2	10.1	0.300	1.13	0.64	0.116	0.22	17.01	6.03
165 GBH	Mononucleate	< 20	27.1	5.4	0.188	1.51	1.20	0.125	0.19	21.97	8.64
		40 - 60	31.3	4.8	0.243	1.67	1.31	0.125	0.19	14.70	7.20
		60 - 80	31.1	5.0	0.171	1.58	1.21	0.188	0.30	12.41	6.35
		> 80	30.1	5.8	0.192	1.49	0.99	0.172	0.28	13.56	6.58
167 GBH	Polynucleate	< 20	28.0	8.1	0.249	1.32	0.94	0.135	0.17	8.30	7.33
		20 - 40	27.8	8.5	0.158	1.30	0.91	0.168	0.27	7.51	6.63
Average m	ononucleate nodule		28.6	5.1	0.193	1.54	1.17	0.154	0.23	15.98	7.24
	olynucleate nodule		26.6	9.9	0.259	1.10	0.68	0.114	0.22	15.22	6.88

	Mn	Fe	Со	Ni	Cu	Zn	SiO_2	Ba	Al_2O_3
Al ₂ O ₃	-0.32	-0.07	0.04	0.01	0.17	-0.29	0.82	0.07	1.00
Ba	0.38	-0.07	0.03	0.22	0.14	0.41	-0.06	1.00	
SiO ₂	-0.47	0.00	0.10	-0.13	0.04	-0.41	1.00		
Zn	0.71	-0.56	-0.43	0.64	0.60	1.00			
Cu	0.49	-0.86	-0.49	0.94	1.00				
Ni	0.67	-0.81	-0.38	1.00					
Co	0.02	0.63	1.00						
Fe	-0.25	1.00							
Mn	1.00								

TABLE 13

ANALYSIS OF PERCENT LITHOGENOUS MATERIAL AND THE CONTENT OF Mn, Fe, Co, Ni, Cu, and Zn in the Hydrolyzate Fraction (Calculated on a Lithogenous-Free Basis) of Nodules from Selected Stations Displaying Different Morphologies (All Analyses in Percent)

STATION NUMBER	MORPHOLOGY	SIZE CLASS (mm)	LITHOGENOUS MATERIAL	Mn	Fe	Co	Ni	Cu	Zn
66 KA	Mononucleate	< 20	21.3	35.96	6.99	0.30	1.96	1.52	0.17
		20-40	17.5	36.73	6.18	0.24	2.01	1.62	0.18
		40-60	10.3	20.62	2.90	0.12	1.30	1.01	0.13
103 GB	Mixed assemblage	< 20	34.5	30.53	11.30	0.25	1.68	1.39	0.13
		20-40	28.6	34.03	10.22	0.30	1.85	1.50	0.16
		40-60	21.5	32.36	9.81	0.33	1.68	1.30	0.15
		60-80	21.4	31.81	13.99	0.37	1.22	0.78	0.12
155 KA	Polynucleate	< 20	24.1	30.17	13.70	0.35	1.29	0.75	0.12
		20-40	17.1	30.88	12.79	0.36	1.24	0.72	0.12
		40-60	15.1	34.98	9.42	0.34	1.35	0.87	0.19
		60 - 80	19.7	32.63	12.58	0.41	1.41	0.80	0.16
165 GBH	Mononucleate	< 20	26.1	36.67	7.31	0.25	2.04	1.62	0.17
		60 - 80	15.4	36.76	5.91	0.20	1.86	1.43	0.22
		< 80	16.2	35.92	6.92	0.23	1.78	1.18	0.21

NODULE MINERALOGY

X-ray diffraction analysis of 33 untreated nodule samples selected from a range of stations and including all size classes and morphologies showed the crusts and nodules in all cases to contain δ -MnO₂ and todorokite as the principal manganese minerals, with quartz and zeolite and/or plagioclase as the principal silicate minerals (Table 13) (cf. Calvert et al. 1978). Barite was noted in one sample. However, in detail, it was noted that the polynucleate nodules contain relatively higher abundances of δ -MnO₂ than todorokite whereas monoucleate nodules contain higher abundances of todorokite than δ -MnO₂. Mineralogical differences, although minor, are therefore apparent and related to morphology.

INTERNAL STRUCTURE

The internal structure of *Valdivia* 13/1 nodules has been described by Halbach and Özkara (1979) and of *Valdivia* 13/2 nodules by Kiggen (1979) and von Stackelberg (1982). Von Stackelberg (1982: fig. 3) has published photographs showing the principal internal structures of *Valdivia* 13/2 nodules. As noted by Halbach and Özkara, the polynucleate nod-

ules have several nuclei of weathered basaltic fragments whereas the nuclei of larger discoidal mononodules are composed predominantly of broken fragments of older nodules (cf. Kiggen 1979, Meyer 1973, Ruppert 1979). In the ferromanganese oxide layers, Kiggen (1979) has noted the occurrence of massive zones, compact zones, columnar zones, and mottled structure as defined by Sorem and Fewkes (1977) as well as the colloform texture noted by Halbach and Özkara (1979: fig. 6).

In the case of the polynucleate nodules, the cores are irregularly shaped and consist essentially of zeolitic clays with variable concentrations of microfossils; the zeolites probably result from the alteration of palagonite of volcanic origin (Nayudu 1964). Minor to trace quantities of palagonite, chlorite, calcite, apatite, rutile, ilmenite, plagioclase, barite, and sphene occur dispersed in the cores. Barite may occur in high concentrations in the core material (up to 0.97 percent Ba in the total nodule sample analyzed at station 87 GBH). The volcanic cores are usually strongly replaced by manganese oxides. Radial fractures in the outer manganese oxide layers of the nodules are common in polynucleate nodules, reflecting the occurrence of septarian cracks. Fracturing of the cores and interpenetration by manganese oxides is also noted (cf.

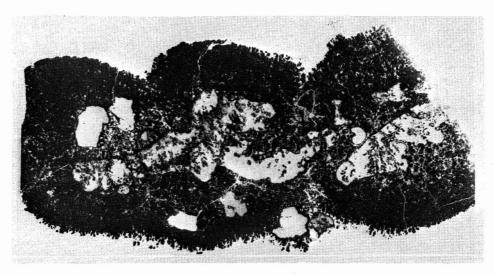


FIGURE 6. Photograph of a cross section of a polynucleate nodule from station 91 GBH showing the nucleus characteristics.

Heye 1975). Such interpenetration can lead to the effective fragmentation of the cores. A photograph of a core of a polynucleate nodule is given in Figure 6.

DISCUSSION

From the preceding sections, it can be seen that nodule composition is related principally to nodule morphology, and this leads to a secondary relationship between nodule composition and water depth or nodule size class. Nodule mineralogy also appears to be related to nodule morphology. The data show that mononucleate nodules are characterized by higher Mn/Fe ratios, higher Ni and Cu contents, and higher abundances of todorokite compared to polynucleate nodules. Crusts are more similar in composition (and mineralogy) to polynucleate nodules, although large variations in composition may occur within individual crusts (Friedrich and Schmitz-Wiechowski 1980). The depth distribution of these nodule types is different, with mononucleate nodules found principally in the depth range 5000-5300 m in the abyssal regions, polynucleate nodules found throughout the depth range sampled, and crusts found on the crests and flanks of seamounts.

It is believed that these features can be best interpreted in terms of the diagenetic supply of the transition elements Mn, Ni, Cu, and Zn to the nodules resulting from the dissolution of siliceous tests in situ within the sediment column. While this process occurs throughout the equatorial north Pacific nodule belt where siliceous oozes make up the principal sediment type, it appears to be more pronounced in the abvssal regions rather than on the flanks of seamounts and has been shown to take place in the Valdivia 13/2 area (von Stackelberg 1979). The enhanced supply of transition elements from the sediment column would lead to the enrichment of these elements in the nodules and the resultant stabilization of todorokite. This relationship between the diagenetic supply of elements and nodule morphology, growth rate, composition, and mineralogy is discussed in detail by Glasby and Thijssen (in press, b).

On this hypothesis, such a diagenetic supply would be most pronounced in larger mononucleate nodules embedded at the sediment—water interface in the abyssal environment (cf. Sorem et al. 1979a) and would account for their compositional and mineralogical characteristics. In the case of manganese crusts and polynucleate nodules, such diagenetic supply takes place on a more limited scale,

although it occurs (average Mn/Fe ratio of polynucleate nodules is 2.5); this explains the lower Mn/Fe ratios and Ni and Cu contents and lower todorokite abundances in these nodules. Such a process is almost certainly related to the nature of the underlying sediments since it is becoming clear that nodule abundance and character are related to the nature and thickness of the underlying sediment sequence even on a local scale (Calvert et al. 1978, Mizuno 1981, Moore and Heath 1966, Tamaki, Honza, and Mizuno 1977, von Stackelberg 1982). Piper and Williamson (1977), for example, have shown that nodules with high Mn/Fe ratios are associated with low sedimentation rates. Calvert et al. (1978) have extended this idea and suggested that the compositional characteristics of the nodules in the Wahine area are related to the thickness of the Quaternary sediments; nodules associated with thinner Quaternary sediments being more diagenetic in character. Data for the Wahine area show that the thickness of the Ouaternary sediments is greater on the slopes of the seamounts than in the depressions; this could be due to ponding of the sediment on small topographic steps. Craig (1979a), working on the Valdivia 13/1 area, has shown that sediment thickness is greater in the depressions than on the slopes. In the Valdivia 13/2 area, von Stackelberg (1979:580, table 5) has shown that sedimentation rates are indeed higher on the flanks of the seapeaks, and von Stackelberg (1982) has deduced that the polynucleate nodules are formed under conditions of higher sedimentation rates than mononodules. Recent evidence has shown that the deep flow varies around seamounts (Gould et al. 1981, Kenyon 1978), and this would affect sedimentation characteristics (Johnson and Johnson 1970, Normark and Spiess 1976). Sedimentation rate therefore appears to be a critical factor in controlling nodule characteristics (including nodule composition and mineralogy) in the Valdivia 13/2 area. Part of the difference in the character between the polynucleate and mononucleate nodules (particularly the thickness of the outer layer of manganese oxides) (cf. von Stackelberg 1982) may be related to the accretion rates of the manganese nodules (as measured by the

Mn/Fe ratio) in the posthiatus period which would be related to this enhanced diagenetic supply of elements in the basinal areas. This factor has been particularly well demonstrated by Heye and Marchig (1977), Piper and Williamson (1977), and Heye (1978). Alternatively, the polynucleate nodules may be more juvenile than the mononucleate nodules (cf. Craig and Andrews 1978).

A second factor involved in nodule formation in the Valdivia 13/2 area is the seeding of nodules as first proposed by Glasby (1973) and Horn, Horn, and Delach (1973b). On this hypothesis, polynucleate nodules are nodules formed in regions where abundant potential nucleating agents are available. Such an area could well be on the flanks of seamounts where fragmentation of outcrop and downward movement of sediment would take place to supply such seeds. Trapping of such seeds on topographic steps could facilitate this process. Mononucleate nodules, on the other hand, would tend to form in more stable sedimentary environments away from such conditions. Finally, nodule characteristics in the Valdivia 13/2 area are thought to be related to sedimentary hiatuses. This theme was developed in some detail by von Stackelberg (1979, 1982) and enables some deduction of the growth period and relative maturity of the nodules to be made. The morphology of the nodules is therefore controlled by a combination of sedimentation rate and seeding processes which in turn influence the nodule composition and mineralogy. Polynucleate nodules are therefore envisaged to form in regions of higher sedimentation rate where abundant seeds are available whereas mononucleate nodules are thought to form in stable abyssal environments characterized by lower sedimentation rates. These two types of environment tend to overlap in the Valdivia 13/2 area as shown by the occurrence of mixed populations of mononucleate and polynucleate nodules. The distribution, morphology, and composition of polynucleate nodules are therefore functions of sedimentation rate and seeding effects and are related to topography and water depth only indirectly. Below 5300 m, the occurrence and density of mononodules tends to decrease (Table 2). The reason for this

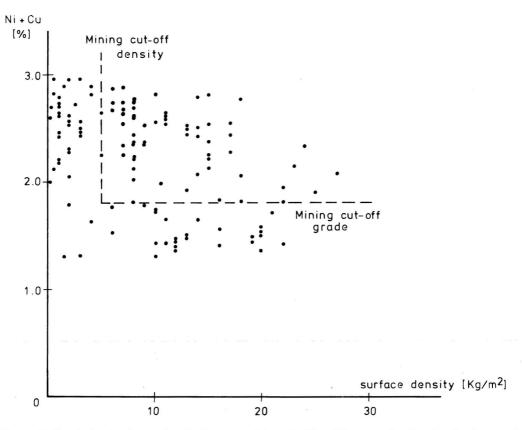


FIGURE 7. Graph showing the relationship between nodule grade (Ni and Cu content) and surface density at each station. The dotted line gives the values of nodule grade and density for the mining cut-off grade.

is not understood, although it may again be related to the sedimentation conditions at this depth.

The ideas developed here are very similar to those of Halbach and Özkara (1979) to account for the distribution of nodules in the Valdivia 13/2 area. However, we disagree with Halbach and Özkara's division of nodules into the "A and AB categories" as defined by these authors. It is believed that the difference in the characteristics of these nodule types is merely one of size and reflects the rolling characteristics of the nodules on the sea floor as a function of size. Smaller nodules tend to be spheroidal with uniform surface texture on all sides; with increasing size, the nodules become progressively flatter and have different surface texture on the upper and lower surfaces. This reflects the fact that the rolling characteristics of the nodules are related to

approximately the third power of nodule diameter. Smaller nodules therefore tend to have the characteristics of being deposited in a uniform milieu because their rate of rolling on the sea floor is faster than their growth rate; larger nodules, which are more static on the sea floor, have characteristics that indicate deposition of elements from seawater on the upper surface and from pore water on the lower surface, respectively. This suggests that the division of the *Valdivia* 13/1 nodules into A and AB types is arbitrary.

Finally, Menard and Frazer (1978) have suggested that manganese nodule grade (percent Ni and Cu) and abundance (kg/m²) of manganese nodules are negatively correlated both regionally and locally in the Pacific; on a local scale, this is thought to be related to topography (cf. Mizuno 1981). Data for the *Valdivia* 13/2 area (Figure 7) show only a

weak relationship between these two parameters when plotted graphically, although they give a correlation coefficient of -0.40 (for 121 data points), which is statistically significant at the 99.9 percent confidence level. In spite of the high level of statistical significance, it is believed that the graphical plot of the data gives only tenuous support of Menard and Frazer's assertion for this area. However, the data do show that approximately half the stations fall in the field of potential economic interest. A more rigorous analysis of the economic potential of the nodules from this area is therefore required.

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