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# Relationship between ferromanganese nodule compositions and sedimentation in a small survey area of the equatorial Pacific

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## ABSTRACT

The bulk chemical compositions of ferromanganese nodules recovered from 14 of 38 sediment cores collected from a 230 km² area of abyssal hill topography in the northern equatorial Pacific (8°20'N; 153W; regional depth 5000m) vary nonrandomly between fairly wide limits. The nodules have Mn/Fe ratios ranging from 2.60 to 5.38 and all samples contain todorokite and $\delta -MnO_2$. The variation in the Mn/Fe ratio is governed by the total Fe contents of the nodules; Mn varies to a much smaller extent. Cu and Ni contents average about 1% and vary independently of the Mn contents.

The compositional variation in the nodules is related to two features of the associated sediments, which are siliceous pelagic clays. The total Fe contents correlate positively with the oxalate-soluble Fe contents of the surface (0-2 cm) sediments; and their Mn/Fe ratios correlate negatively with the accumulation rates of the sediments. We suspect that the composition of the nodules is influenced to a considerable extent by diagenetic reactions in the sediments, the clearest manifestation of this being the transformation of oxyhydroxide Fe into an insoluble form, possibly by the formation of smectite. This in turn leads to the formation of relatively Fe-poor ferromanganese nodules. Such nodules occur on slowly accumulating sediments where relatively more diagenetic reaction in the sediments has taken place.

## 1. Introduction

The chemical composition of ferromanganese concretions is known to be regionally variable on several scales. Mero (1962), Cronan and Tooms (1969) and Price and Calvert (1970) have discussed inter- and intra-ocean variations, while variability within much smaller areas has been described by Cronan and Tooms (1967) and Glasby *et al.* (1971; 1974). Over areas of irregular topography on the Carlsberg Ridge, for example, the Ni and Cu contents of concretions varied by factors of up to 5 and 7 (Cronan and Tooms, 1967), or 3 and 5, respectively (Glasby *et al.,* 1974). In addition, Cronan and Tooms (1967) found large compositional differences between concretions of different sizes from a single sampling site.

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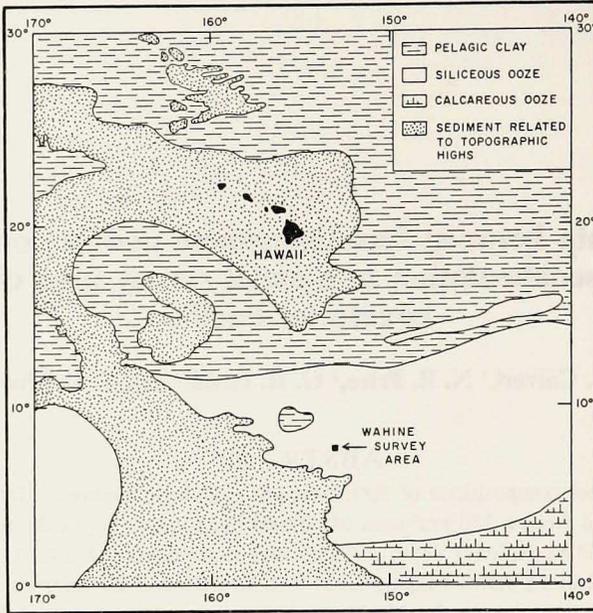
Figure 1. Location of WAHINE survey area. Lithology of sediments after Horn *et al.* (1972).

Cronan and Tooms (1967) ascribed such local variability to different volcanic or hydrothermal metal sources, or to the existence of two or more nodule populations whose compositions reflect formation under different conditions at different times. On the other hand, Glasby (1973) has suggested that the high degree of variability in many sets of analyses may also arise from the inclusion of some aluminosilicate or other nonoxide material in the nodule samples analysed; such components would dilute the oxide phases to different extents.

These observations and suggestions should be reassessed in the light of recent work on large-scale regional variations in the bulk composition and mineralogy of abyssal ferromanganese nodules (Piper and Williamson, 1977; Calvert and Price, 1977). These studies largely confirm previous observations and have been used to frame working hypotheses for the formation of ferromanganese concretions in the deep sea.

In this paper we report the chemical composition and mineralogy of a suite of ferromanganese nodules from a 230 km² area of the north equatorial Pacific collected during an intensive study of the sedimentation and stratigraphy in a region of abyssal hill topography. Heath and Moore (1965) and Moore and Heath (1966; 1967) have described the survey conducted during WAHINE Expedition of the Scripps Institution of Oceanography. Moore (1970) has described the pattern of sedimentation in the area, based principally on a micropalaeontological examination of sediment cores.
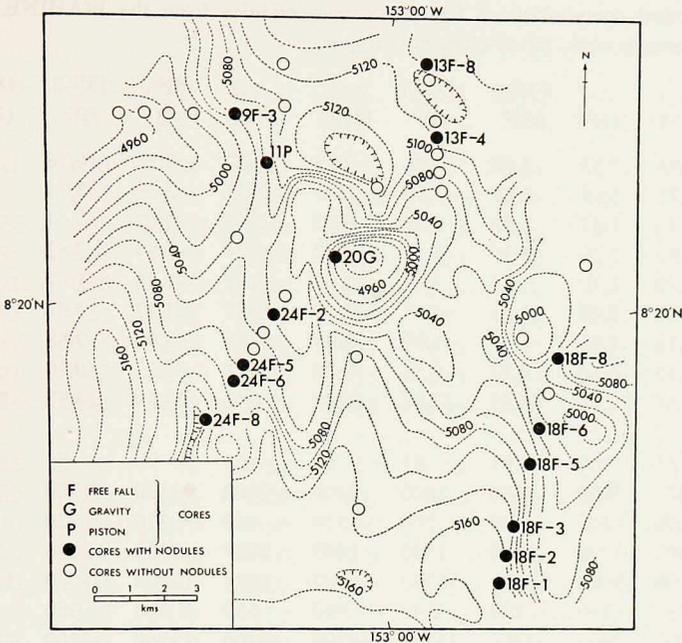
Figure 2. Core locations and bathymetry in the WAHINE area. Contours in meters.

*a. Description of the area.* The area surveyed (Fig. 1), which lies within the "normal" part of the central Pacific Basin (Menard, 1964), is characterized by a northwest-southeast trending ridge composed of three separate abyssal hills (Fig. 2). The total relief is 280m and slopes are generally 2-3°. Sub-bottom acoustic profiling over the area shows the presence of between 100 and 440m of sediment above a prominent reflector. This layer of sediment is thin on the hills and thickest in depressions such that the topography of the first reflector has been smoothed.

In spite of the rather simple distribution of sediment revealed by acoustic methods, the stratigraphic data from the 38 cores collected in the area (Fig. 2) show that the thickness of Quaternary sediment, i.e. sediment above the deepest occurrence of Quaternary microfossils, is greater on the slopes than in the depressions. This could be due to local ponding of sediment on small topographic steps possibly produced by faulting (Moore, 1970).

The sediment sampled by coring consists of siliceous pelagic clay. An upper section of yellow-brown, mottled clay, 1 to greater than 169 cm thick, contains Quaternary and Tertiary Radiolaria and is Quaternary in age. A lower section of darker brown, more distinctly mottled clay contains only Tertiary Radiolaria and is middle Tertiary in age. The contact between the two sections is quite distinct and may be sharp. Manganese micronodules are common here and siliceous microfossils are more heavily corroded.

Table 1. Chemical composition of ferromanganese nodules from the WAHINE survey area. Major elements in wt%, minor elements in ppm.

| Sample | 9F-3 | 11P | 13F-4 (A)* | 13F-4 (B) | 13F-8 | 18F-1 | 18F-2 (A) | 18F-2 (B) | 18F-3 (1A) | 18F-3 (1B) |
|---|---|---|---|---|---|---|---|---|---|---|
| Si | 6.58 | 7.33 | 7.10 | 6.96 | 7.19 | 6.07 | 6.12 | 6.16 | 6.07 | 10.51 |
| Al | 2.76 | 3.05 | 2.81 | 2.60 | 2.60 | 2.57 | 2.68 | 2.76 | 2.41 | 4.40 |
| Ti | 0.46 | 0.57 | 0.42 | 0.39 | 0.33 | 0.68 | 0.62 | 0.64 | 0.59 | 0.52 |
| Fe | 5.98 | 7.59 | 5.35 | 5.53 | 4.97 | 9.24 | 7.94 | 7.63 | 7.45 | 5.14 |
| Ca | 1.80 | 1.79 | 1.84 | 1.79 | 1.97 | 1.82 | 1.84 | 1.67 | 1.83 | 2.18 |
| Mg | 2.11 | 2.08 | 1.81 | 1.75 | 1.90 | 1.87 | 1.27 | 1.93 | 1.81 | 1.69 |
| K | 1.38 | 1.01 | 1.01 | 1.00 | 0.95 | 0.88 | 0.80 | 0.88 | 0.85 | 1.21 |
| P | 0.15 | 0.16 | 0.30 | 0.15 | 0.20 | 0.16 | 0.23 | 0.20 | 0.23 | 0.22 |
| Mn | 25.88 | 22.47 | 25.85 | 25.96 | 26.74 | 24.02 | 24.49 | 24.33 | 24.80 | 16.89 |
| | | | | | | | | | | |
| As | 55 | 100 | 65 | 65 | 50 | 105 | 95 | 55 | 90 | 45 |
| Ba | 2300 | 1900 | 3800 | 2800 | 2400 | 2000 | 1500 | 1700 | 2000 | 1950 |
| Ce | 230 | 300 | 200 | 200 | 160 | 410 | 310 | 320 | 340 | 290 |
| Co | 1400 | 1700 | 1300 | 1300 | 1100 | 2000 | 2100 | 2000 | 1800 | 1200 |
| Cu | 12100 | 9000 | 17600 | 15300 | 12700 | 8600 | 12000 | 13000 | 11900 | 8200 |
| Mo | 380 | 330 | 390 | 380 | 390 | 330 | 360 | 380 | 340 | 280 |
| Ni | 11200 | 9400 | 13200 | 12300 | 10500 | 10100 | 11700 | 12200 | 12100 | 8200 |
| Pb | 430 | 520 | 400 | 340 | 310 | 600 | 590 | 620 | 560 | 440 |
| Rb | 15 | 20 | 20 | 20 | 15 | 15 | 20 | 20 | 15 | 20 |
| Sr | 440 | 510 | 450 | 430 | 420 | 470 | 480 | 510 | 470 | 500 |
| Th | 15 | 20 | 15 | 10 | 10 | 25 | 20 | 20 | 20 | 20 |
| Y | 95 | 110 | 105 | 100 | 85 | 125 | 115 | 120 | 115 | 120 |
| Zn | 980 | 830 | 830 | 850 | 1050 | 780 | 860 | 870 | 850 | 670 |
| Zr | 280 | 310 | 235 | 220 | 185 | 410 | 375 | 410 | 320 | 420 |

*b. Manganese nodules.* Manganese nodules were recovered in 15 of the cores collected (Fig. 2). Most of the nodules were at, or close to, the top of the sediment cores, but in core 24F-8, nodules were found at ~17cm and ~59cm depth as well as at the surface.

The WAHINE nodules range from spheroidal to discoidal to ellipsoidal in shape. The nodule from core 11P is dumbell-shaped, as a result of the fusion of two 1 cm spheroidal nodules. The volume of individual concretions ranges from less than 1 cm³ to 150 cm³, with a median value of 5 cm³. Neither the shape nor the volume of the nodules is correlated with their compositions or depositional setting (thickness of underlying Quaternary sediment). As Moore and Heath (1966) have discussed previously, however, nodules are most likely to be recovered on steep slopes where Quaternary sediments are thickest. Neither the spheroidal nor flattened nodules show the smooth tops and rough bottoms described by Raab (1972).

| 18F-3 (2) | 18F-5 | 18F-6 (1) | 18F-6 (2) | 18F-8 | 20G | 24F-2 | 24F-5 | 24F-6 | Average | 24F-8** |
|---|---|---|---|---|---|---|---|---|---|---|
| 6.26 | 6.21 | 6.35 | 7.00 | 6.77 | 7.38 | 6.16 | 6.68 | 6.58 | 6.81 | — |
| 2.62 | 2.49 | 2.62 | 2.91 | 2.76 | 2.97 | 2.65 | 2.76 | 2.78 | 2.80 | — |
| 0.52 | 0.62 | 0.49 | 0.50 | 0.40 | 0.59 | 0.48 | 0.55 | 0.53 | 0.52 | 0.56 |
| 7.10 | 7.94 | 6.47 | 6.58 | 5.74 | 7.49 | 6.37 | 7.28 | 6.93 | 6.77 | 7.31 |
| 1.79 | 1.91 | 1.86 | 1.89 | 1.79 | 1.68 | 1.72 | 1.86 | 1.82 | 1.83 | — |
| 2.05 | 1.87 | 2.23 | 1.87 | 2.05 | 1.93 | 1.99 | 1.96 | 2.08 | 1.91 | — |
| 0.99 | 0.87 | 0.95 | 1.00 | 0.92 | 1.19 | 0.93 | 1.00 | 0.96 | 0.99 | — |
| 0.17 | 0.21 | 0.17 | 0.16 | 0.14 | 0.16 | 0.15 | 0.17 | 0.15 | 0.18 | — |
| 25.42 | 24.64 | 26.35 | 24.18 | 26.43 | 23.25 | 25.57 | 24.41 | 26.58 | 24.64 | 24.89 |
| | | | | | | | | | | |
| 85 | 85 | 60 | 75 | 50 | 75 | 65 | 75 | 85 | 73 | — |
| 1900 | 1750 | 2050 | 2150 | 2000 | 2000 | 1850 | 2100 | 2000 | 2113 | — |
| 270 | 330 | 270 | 270 | 190 | 330 | 280 | 310 | 270 | 278 | — |
| 1700 | 1800 | 1500 | 1400 | 1400 | 1800 | 1700 | 1600 | 1600 | 1600 | 2530 |
| 9500 | 9300 | 10300 | 13000 | 12000 | 9900 | 10500 | 9900 | 10900 | 11353 | 16460 |
| 380 | 350 | 370 | 350 | 370 | 330 | 370 | 380 | 370 | 359 | 570 |
| 10000 | 10800 | 9000 | 12200 | 11100 | 10200 | 10500 | 9200 | 10700 | 10768 | 18550 |
| 500 | 570 | 470 | 450 | 390 | 530 | 460 | 490 | 510 | 483 | 420 |
| 20 | 15 | 15 | 20 | 15 | 20 | 15 | 20 | 15 | 18 | — |
| 450 | 510 | 440 | 490 | 410 | 490 | 490 | 500 | 470 | 470 | — |
| 15 | 20 | 20 | 15 | 10 | 20 | 20 | 20 | 20 | 18 | — |
| 115 | 120 | 100 | 105 | 90 | 105 | 95 | 100 | 105 | 106 | — |
| 870 | 840 | 930 | 840 | 980 | 810 | 940 | 850 | 880 | 869 | — |
| 310 | 340 | 310 | 340 | 235 | 360 | 310 | 360 | 340 | 319 | — |

* Samples designated (1) and (2) represent samples from separate nodules from a single core. Samples designated (A) and (B) represent subsamples from a single nodule.
** From Somayajulu *et al.* (1971).

Whether this reflects repeated overturning, or burial of the nodules by a thin layer of sediment is unclear. In any case, there is no significant fractionation of elements between opposed surfaces of the nodules.

The WAHINE nodules have accreted around lumps of sediment or, less commonly, fragments of older nodules. Again, the nature of the nucleus is independent of the composition or depositional setting of a nodule. Samples for chemical and mineralogic analysis were obtained by quartering the nodules through their minor axes. An attempt was made to partition the nuclei and outer layers into the samples in the proportions found in the original nodules.

## 2. Analytical methods

The nodules were sectioned with a clean hacksaw and divided into small sub-

Table 2. Bulk chemical composition and oxalate-soluble Mn and Fe ($Mn_{ex}$ and $Fe_{ex}$) contents of sediments from the WAHINE Survey area. Major elements in wt. %, minor elements in ppm.

| Sample (cm) | 9F-3 (1-3) | 9F-3 (10-12) | 11P (0-2) | 11P (9-11) | 13F-4 (0-2) | 13F-4 (2-4) | 13F-4 (10-12) |
|---|---|---|---|---|---|---|---|
| Si | 24.05 | 25.08 | 24.89 | 23.07 | 24.98 | 25.26 | 24.14 |
| Al | 6.41 | 6.57 | 6.84 | 7.42 | 6.52 | 6.73 | 6.52 |
| Ti | 0.37 | 0.38 | 0.39 | 0.42 | 0.38 | 0.40 | 0.37 |
| Fe | 4.41 | 4.58 | 4.55 | 4.90 | 4.48 | 4.58 | 4.58 |
| Ca | 1.12 | 1.14 | 1.18 | 1.26 | 1.25 | 1.16 | 1.14 |
| Mg | 1.93 | 1.96 | 2.05 | 2.29 | 1.93 | 1.99 | 1.96 |
| K | 2.06 | 2.11 | 2.09 | 2.20 | 2.07 | 2.12 | 2.03 |
| P | 0.23 | 0.20 | 0.23 | 0.28 | 0.27 | 0.25 | 0.23 |
| Mn | 0.33 | 0.43 | 0.67 | 0.60 | 0.43 | 0.24 | 0.22 |
| As | 10 | 10 | 20 | 10 | 15 | 15 | 10 |
| Ba | 3750 | 3900 | 4000 | 4600 | 3600 | 3950 | 3800 |
| Ce | 70 | 50 | 80 | 80 | 70 | 90 | 70 |
| Co | 170 | 300 | 290 | 270 | 215 | 205 | 180 |
| Cu | 480 | 490 | 530 | 630 | 570 | 500 | 330 |
| Mo | 5 | 5 | 10 | 10 | 5 | 5 | 5 |
| Ni | 205 | 210 | 270 | 370 | 270 | 165 | 155 |
| Pb | 35 | 45 | 45 | 40 | 45 | 40 | 40 |
| Rb | 100 | 100 | 100 | 95 | 100 | 105 | 105 |
| Sr | 235 | 245 | 240 | 265 | 245 | 255 | 240 |
| Th | 20 | 20 | 15 | 10 | 20 | 20 | 15 |
| Y | 180 | 165 | 170 | 215 | 205 | 190 | 190 |
| Zn | 190 | 170 | 200 | 230 | 210 | 190 | 190 |
| Zr | 145 | 170 | 180 | 175 | 140 | 145 | 155 |
| $Mn_{ex}$ | 0.27 | | 0.55 | 0.49 | 0.37 | 0.19 | 0.17 |
| $Fe_{ex}$ | 0.57 | | 0.57 | 0.60 | 0.48 | 0.88 | 0.86 |

samples for analysis. In addition to the visually representative subsamples taken from individual nodules, more than one subsample was taken from some nodules from parts that clearly contained more or less aluminosilicate. Sediment samples were taken from the immediate vicinity of the nodules and at horizons approximately 10cm from the core surfaces.

Nodule and sediment subsamples were dried to constant weight at 100°C and ground to pass 200 mesh in agate. The chemical compositions were determined by X-ray emission spectroscopy using methods described by Calvert and Price (1977). Briefly, the major elements were determined on fusion beads ($Li_2B_4O_7$ and $La_2O_3$) in pellet form, and the minor elements were determined on loose powders. The standards for the sediments consisted of a wide range of international geochemical standards, while the nodule standards were synthetic mixtures of Specpure

| 13F-8 (0-2) | 13F-8 (9-11) | 18F-1 (0-2) | 18F-1 (9-11) | 18F-2 (0-2) | 18F-2 (9-11) | 18F-3 (0-2) | 18F-3 (8-10) | 18F-5 (0-2) |
|---|---|---|---|---|---|---|---|---|
| 25.73 | 24.00 | 25.03 | 24.56 | 25.22 | 25.22 | 25.17 | 25.08 | 24.56 |
| 6.81 | 6.49 | 6.41 | 6.65 | 6.44 | 6.65 | 6.33 | 6.41 | 6.68 |
| 0.39 | 0.37 | 0.37 | 0.38 | 0.38 | 0.38 | 0.37 | 0.38 | 0.38 |
| 4.55 | 4.48 | 4.51 | 4.41 | 4.34 | 4.51 | 4.41 | 4.62 | 4.41 |
| 1.29 | 1.21 | 1.11 | 1.07 | 1.11 | 1.07 | 1.21 | 1.14 | 1.16 |
| 1.81 | 2.08 | 1.96 | 1.96 | 1.96 | 2.02 | 1.96 | 1.99 | 1.69 |
| 2.06 | 2.03 | 2.07 | 2.07 | 2.07 | 2.12 | 2.02 | 2.12 | 2.17 |
| 0.30 | 0.24 | 0.21 | 0.20 | 0.20 | 0.18 | 0.24 | 0.22 | 0.28 |
| 0.31 | 0.23 | 0.37 | 0.45 | 0.32 | 0.31 | 0.58 | 0.63 | 0.53 |
| | | | | | | | | |
| 15 | 10 | 10 | 15 | 10 | 15 | 10 | 10 | 15 |
| 3900 | 4150 | 3650 | 3800 | 3600 | 4000 | 3900 | 4150 | 4050 |
| 70 | 60 | 90 | 70 | 70 | 60 | 70 | 60 | 70 |
| 130 | 190 | 185 | 255 | 130 | 230 | 200 | 255 | 200 |
| 490 | 530 | 490 | 550 | 450 | 500 | 520 | 570 | 500 |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 10 | 5 |
| 210 | 155 | 190 | 190 | 210 | 170 | 330 | 300 | 295 |
| 40 | 40 | 30 | 35 | 35 | 40 | 35 | 40 | 30 |
| 100 | 95 | 95 | 100 | 100 | 100 | 100 | 105 | 95 |
| 270 | 245 | 230 | 250 | 250 | 250 | 255 | 255 | 235 |
| 20 | 15 | 10 | 20 | 10 | 10 | 10 | 20 | 15 |
| 220 | 210 | 165 | 160 | 160 | 150 | 170 | 170 | 155 |
| 190 | 180 | 170 | 190 | 180 | 170 | 210 | 180 | 180 |
| 145 | 170 | 140 | 165 | 160 | 175 | 145 | 145 | 145 |
| | | | | | | | | |
| 0.24 | 0.17 | 0.28 | 0.33 | | 0.25 | 0.49 | 0.52 | 0.44 |
| 0.51 | 0.43 | 0.88 | 0.89 | | 0.96 | 0.90 | 0.60 | 0.63 |

oxides. Precisions of the major and minor element determinations are less than 5% for concentrations greater than 10 ppm.

Separate splits of the sediment samples were leached with a mixed solution of 0.2M ammonium oxalate and 0.2M oxalic acid (Schwertmann, 1964) for 4 hrs in the dark in order to remove amorphous Fe and Mn oxyhydroxides but without attacking goethite or iron-rich smectite (see Heath and Dymond, 1977). After filtration, the leachates were analyzed for Fe and Mn by atomic absorption spectrophotometry.

The mineralogy of the bulk nodule and sediment samples was determined on separate subsamples dried at room temperature by conventional X-ray diffraction techniques using Cu radiation and a curved graphite monochromator. The terminology of the manganese phases follows Burns and Burns (1976).

Table 2 (continued)

| 18F-5 (9-11) | 18F-6 (0-2A) | 18F-6 (0-2B) | 18F-6 (7-9) | 18F-8 (0-2A) | 18F-8 (0-2B) | 18F-8 (9-11) | 19F-3 (0-1) | 20G (0-2) | 20G (9-11) |
|---|---|---|---|---|---|---|---|---|---|
| 25.59 | 24.89 | 24.19 | 24.84 | 25.50 | 25.12 | 25.08 | 24.28 | 24.38 | 23.44 |
| 6.57 | 6.23 | 6.57 | 6.78 | 6.36 | 6.47 | 6.54 | 6.62 | 6.25 | 6.94 |
| 0.37 | 0.37 | 0.39 | 0.39 | 0.37 | 0.37 | 0.39 | 0.40 | 0.37 | 0.39 |
| 4.48 | 4.16 | 4.48 | 4.55 | 4.48 | 4.37 | 4.51 | 4.48 | 4.20 | 4.62 |
| 1.11 | 1.61 | 1.26 | 1.29 | 1.21 | 1.21 | 1.14 | 1.18 | 1.97 | 1.61 |
| 1.93 | 1.90 | 1.75 | 1.57 | 1.96 | 1.93 | 1.87 | 1.33 | 1.87 | 1.57 |
| 2.07 | 1.97 | 2.17 | 2.19 | 2.06 | 2.03 | 2.12 | 2.21 | 2.00 | 2.24 |
| 0.21 | 0.42 | 0.31 | 0.31 | 0.25 | 0.24 | 0.21 | 0.30 | 0.19 | 0.25 |
| 0.28 | 0.54 | 0.53 | 0.63 | 0.43 | 0.50 | 0.40 | 0.45 | 0.48 | 0.43 |
| | | | | | | | | | |
| 10 | 10 | 10 | 10 | 10 | 10 | 10 | 15 | 15 | 10 |
| 3900 | 3950 | 3900 | 3900 | 3750 | 3750 | 3650 | 3700 | 4150 | 3800 |
| 80 | 70 | 80 | 60 | 70 | 90 | 70 | 80 | 60 | 80 |
| 170 | 210 | 240 | 240 | 230 | 250 | 210 | 210 | 195 | 340 |
| 430 | 500 | 500 | 520 | 510 | 560 | 500 | 470 | 450 | 520 |
| 5 | 5 | 5 | 10 | 5 | 5 | 5 | 5 | 5 | 5 |
| 160 | 295 | 300 | 290 | 220 | 265 | 210 | 270 | 250 | 215 |
| 30 | 30 | 40 | 35 | 45 | 30 | 45 | 35 | 35 | 30 |
| 105 | 95 | 100 | 100 | 100 | 100 | 105 | 100 | 95 | 100 |
| 250 | 270 | 250 | 250 | 250 | 270 | 255 | 230 | 270 | 255 |
| 15 | 15 | 20 | 15 | 20 | 10 | 15 | 15 | 15 | 15 |
| 165 | 180 | 175 | 185 | 190 | 180 | 170 | 165 | 140 | 155 |
| 190 | 200 | 200 | 200 | 190 | 190 | 190 | 180 | 220 | 190 |
| 180 | 140 | 165 | 165 | 160 | 175 | 170 | 150 | 135 | 160 |
| | | | | | | | | | |
| 0.21 | 0.44 | 0.43 | 0.49 | 0.33 | 0.43 | 0.31 | | 0.39 | 0.33 |
| 0.59 | 0.67 | 0.67 | 0.61 | 0.67 | 0.67 | 0.62 | | 0.72 | 0.60 |

## 3. Results

The chemical data for nodules and sediments are given in Tables 1 and 2, respectively. These data may be compared with partial analyses of three nodules from Core 24F-8 (Fig. 2) reported by Somayajulu et al (1971) (Table 1). The two sets of analyses are similar except in the case of Cu and Ni which are consistently lower in the data reported here (Table 1).

*a. Bulk compositions.* Based on the Si and Al contents, the aluminosilicate content of the nodules is estimated to be 25% by weight. From the XRD data, this material consists of quartz, feldspar, phillipsite and a mixture of clay minerals dominated by smectite. Sample 18F-3(1B) differs markedly in composition from the other nodules in containing approximately 45% aluminosilicate impurities. This material has increased the Si, Al, Ca, K, Sr and Zr contents and lowered the

| 24F-2 (0-2A) | 24F-2 (0-2B) | 24F-2 (9-11) | 24F-5 (0-2) | 24F-5 (9-11) | 24F-6 (0-2) | 24F-6 (3-5) | 24F-6 (19-21) | Average |
|---|---|---|---|---|---|---|---|---|
| 25.03 | 24.94 | 24.38 | 24.94 | 25.73 | 23.26 | 25.12 | 20.27 | 24.63 |
| 6.49 | 6.41 | 6.76 | 6.49 | 6.33 | 5.56 | 6.36 | 5.30 | 6.49 |
| 0.37 | 0.37 | 0.38 | 0.37 | 0.38 | 0.32 | 0.37 | 0.25 | 0.37 |
| 4.41 | 4.27 | 3.22 | 4.34 | 4.41 | 3.74 | 4.41 | 4.44 | 4.41 |
| 1.09 | 1.09 | 1.22 | 1.09 | 1.19 | 1.21 | 1.29 | 2.32 | 1.25 |
| 1.95 | 1.95 | 2.05 | 1.93 | 2.05 | 1.75 | 2.02 | 2.17 | 1.93 |
| 1.99 | 2.01 | 2.03 | 1.98 | 2.06 | 1.78 | 1.95 | 1.37 | 2.04 |
| 0.21 | 0.23 | 0.23 | 0.23 | 0.24 | 0.26 | 0.29 | 0.33 | 0.25 |
| 0.53 | 0.53 | 1.05 | 0.53 | 0.35 | 0.58 | 0.58 | 1.17 | 0.49 |
| | | | | | | | | |
| 10 | 10 | 20 | 15 | 15 | 15 | 15 | 10 | 12 |
| 4050 | 3800 | 4250 | 3950 | 3800 | 4100 | 4550 | 8400 | 4074 |
| 60 | 60 | 80 | 70 | 70 | 60 | 70 | 50 | 70 |
| 195 | 215 | 280 | 220 | 155 | 200 | 205 | 175 | 216 |
| 490 | 500 | 730 | 510 | 450 | 510 | 530 | 710 | 532 |
| 5 | 60 | 25 | 5 | 5 | 5 | 5 | 60 | 10 |
| 280 | 295 | 460 | 290 | 210 | 300 | 320 | 530 | 260 |
| 45 | 40 | 35 | 45 | 30 | 35 | 35 | 45 | 38 |
| 95 | 95 | 100 | 95 | 100 | 90 | 95 | 45 | 97 |
| 240 | 255 | 265 | 230 | 235 | 260 | 275 | 390 | ,255 |
| 20 | 15 | 20 | 15 | 15 | 10 | 10 | 5 | 15 |
| 150 | 115 | 175 | 115 | 175 | 175 | 180 | 240 | 174 |
| 190 | 190 | 210 | 180 | 180 | 190 | 200 | 260 | 194 |
| 145 | 135 | 160 | 150 | 145 | 140 | 145 | 135 | 155 |
| | | | | | | | | |
| 0.49 | 0.51 | 0.93 | 0.41 | 0.30 | 0.49 | 0.49 | 1.06 | 0.41 |
| 0.57 | 0.74 | 0.52 | 0.58 | 0.54 | 0.60 | 0.57 | 0.59 | 0.65 |

Mn, Fe, Mg, As, Ce, Co, Cu, Mo, Ni, Pb and Zn contents of the sample compared with the adjacent sample 18F-3(1A) from the same nodule. The concentrations of Ti, P, Ba, Rb, Th and Y in the two samples do not appear to be significantly different. This comparison distinguishes groups of elements whose variations are controlled by the aluminosilicate and the oxide fractions in a nodule, as well as pointing to a third group of elements which are present in both of these components. Note that the Fe content of sample 18F-3(1B), although lower than that of sample 18F-3(1A), still falls within the range of Fe contents of the entire suite of nodule samples. On the other hand, the Mn content of sample 18F-3(1B) is significantly lower than that of any other sample. This contrast reflects the relatively large amount of Fe and very small amount of Mn in the aluminosilicate material.

The Si/Al ratio in the nodules ranges from 2.23 to 2.76. In the sediments

(Table 2), the Si/Al ratio is consistently higher than it is in the nodules, ranging from 3.11 to 4.18. This is due to the presence of biogenous siliceous debris which has the effect of increasing the Si content of the bulk sediment and, therefore, the Si/Al ratio above a value of ~2.5 which is typical of pelagic clays.

Calvert and Price (1977) showed that the Si/Al ratios in nodule and associated sediment samples from a larger area of the Pacific were not consistently different and interpreted this as a reflection of the incorporation of aluminosilicate debris in the nodules of roughly similar composition to that of the associated sediment. In the present case, the clear difference in the Si/Al ratio probably indicates that siliceous biogenous material is absent from the nodules, either because any incorporated microfossil opal has dissolved from the nodules during the long residence at the sediment surface or because the nodules formed on sediments which contained less biogenous debris, but are now associated with a different type of substrate. Support for the former possibility comes from the composition of the surface and subsurface sediments (Table 2). The surface sediment sample in 11 out of 14 cases has a higher Si/Al ratio than the underlying sample. Assuming a constant opal supply rate to the bottom sediments, this is consistent with a slow solution of biogenous opal during the period represented by the section sampled.

The Mn/Fe ratio in the nodules ranges from 2.60 to 5.38, a remarkably wide range for an area of only 230 km². That this variation is not caused by the presence of variable quantities of aluminosilicate material is shown by a comparison of the bulk chemical composition in Table 1 and by the differences between samples 18F-3(1A) and 18F-3(1B) discussed above.

The survey area lies at the margin of an extensive east-west zone in the northern equatorial Pacific where ferromanganese nodules have Mn/Fe ratios higher than 2 (Price and Calvert, 1970, Fig. 1; Piper and Williamson, 1977, Fig. 1). The variation in this ratio in the WAHINE nodules results from variations in the total Fe content, which ranges from 4.97 to 9.24%. In contrast, the Mn content, omitting sample 18F-3(1B), has a much narrower range, from 22.47 to 26.74%.

*b. Comparison of nodules from the same core.* Cores 13F-4, 18F-2, 18F-3 and 18F-6 contain two nodules at the sediment surface. The compositions of the pairs are very similar, differences probably being due largely to slight variations in the amount and composition of the aluminosilicate and other nonoxide material incorporated into the fragments that were analyzed. In most cases, the differences between individual element concentrations are close to the analytical precision. The largest differences are shown by Cu and Ni, the elements which have highly variable concentrations in nodules from the Carlsberg Ridge, as discussed earlier.

*c. Mineralogy of the nodules.* X-ray diffraction reveals the presence of todorokite and δ-MnO₂, together with aluminosilicates, in all samples. The presence of both todorokite and δ-MnO₂ was deduced from a comparison of the peak heights of the

9.6, 2.44 and 1.44Å reflections, following suggestions by Burns and Burns (1976). Both the 2.44 and 1.44 Å reflections, which are common to todorokite and $\delta$-MnO$_2$, have peak heights of comparable intensity to that of the 9.6Å reflection. A peak at ~7Å, which would indicate the presence of birnessite, the more ordered form of $\delta$-MnO$_2$ (Burns and Burns, 1976), could not be detected, but may have been masked by the sharp reflections of phillipsite in this region.

*d. Minor elements.* The concentrations of Cu and Ni in the nodules average 1.13 and 1.08%, respectively (Table 1). These high values are consistent with the location of the survey area in a region of minor-metal-enriched nodules bounded by 5N and 10N, and 120W and 160W (Horn *et al.*, 1973). The WAHINE nodules also have relatively high concentrations of Ba, Mo and Zn, which, like Cu and Ni, are closely correlated with the Mn content of abyssal ferromanganese nodules from the Pacific Ocean generally (Calvert and Price, 1977). The correlation coefficient matrix in Table 3 shows, however, that only Mo and Zn are significantly correlated with the Mn content. On the other hand, the Cu and Ni contents are significantly correlated.

Calvert and Price (1977) showed that the relationship between the Cu, Mo, Ni, Zn and Mn contents of abyssal Pacific nodules depends upon the mineralogy of the Mn-bearing phase, corroborating the earlier conclusions of Barnes (1967) and Cronan and Tooms (1969). In todorokite-bearing nodules, the concentrations of the minor metals are higher than in nodules without todorokite, and they vary widely, whereas the Mn content is much more uniform. In the WAHINE area, the mineralogy of the nodules is more or less constant and the divalent minor metals are much less dependent on the total Mn content. Similar variability is evident in electron-microprobe analyses of the anisotropic (todorokite) phase of Pacific nodules reported by Banning (1975) which show widely varying Cu and Ni contents (up to 2.95 and 3.6%, respectively) at a more or less fixed Mn content.

The concentrations of As, Ce, Co, Pb, Th and Ti are significantly correlated with the Fe content of the WAHINE nodules (Table 3); and in addition, Y and Zr are correlated with the Ce, Pb and Ti contents and Sr is correlated with the Ce and Ti contents. As already discussed the Fe content is much more variable than the Mn content in the suite of samples analyzed here. The associated group of minor elements shows a similar degree of variability. Calvert and Price (1977) showed that the concentrations of these minor elements (apart from Ce, Co and Th) were correlated in a simple way with the Fe content in a suite of nodules from a large area of the Pacific, pointing to a lack of mineralogical control on variations in the concentration of this group of elements in ferromanganese nodules.

*e. Areal variations in composition.* Although the bulk chemical composition of the ferromanganese nodules from the WAHINE survey area shows some variability, the variation is much smaller than that shown by suites of nodules from detailed survey

Table 3. Spearman rank correlation coefficient matrix for the nodule data. Significance levels, corrected for multiple pair-wise tests: $r = 0.78$ ($p < 0.01$); $r = 0.73$ ($p < 0.05$); $r = 0.70$ ($p < 0.10$); $r = 0.68$ ($p < 0.15$). In other cases a positive or a negative coefficient is indicated.

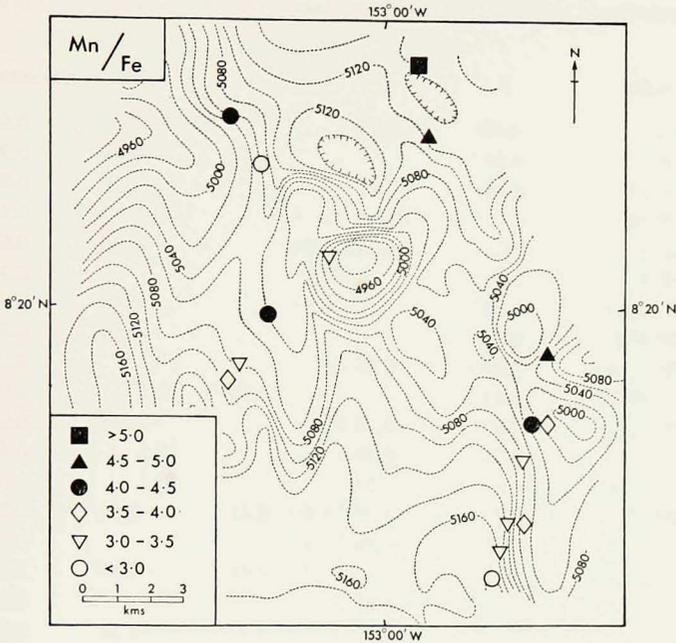| | Si | Al | Ti | Fe | Ca | Mg | K | P | Mn | As | Ba | Ce | Co | Cu | Mo | Ni | Pb | Rb | Sr | Th | Y | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | 0.69 | | | | | | | | | | | | | | | | | | | | | |
| Ti | − | − | | | | | | | | | | | | | | | | | | | | |
| Fe | − | − | 0.93 | | | | | | | | | | | | | | | | | | | |
| Ca | + | − | − | − | | | | | | | | | | | | | | | | | | |
| Mg | + | + | − | − | − | | | | | | | | | | | | | | | | | |
| K | 0.79 | 0.69 | − | − | − | + | | | | | | | | | | | | | | | | |
| P | − | − | + | + | + | − | − | | | | | | | | | | | | | | | |
| Mn | − | − | − | − | + | + | − | − | | | | | | | | | | | | | | |
| As | − | + | + | 0.77 | − | − | − | + | − | | | | | | | | | | | | | |
| Ba | + | + | − | − | + | + | + | − | + | − | | | | | | | | | | | | |
| Ce | − | − | 0.93 | 0.84 | − | − | − | + | −0.71 | + | − | | | | | | | | | | | |
| Co | −0.69 | − | 0.89 | 0.94 | − | − | − | + | − | 0.68 | 0.73 | 0.82 | | | | | | | | | | |
| Cu | + | − | − | − | − | − | − | − | + | − | + | − | + | | | | | | | | | |
| Mo | − | − | − | − | − | − | + | − | 0.68 | − | + | − | − | + | | | | | | | | |
| Ni | − | − | − | − | − | − | − | + | + | − | + | − | − | 0.84 | + | | | | | | | |
| Pb | − | − | 0.98 | 0.95 | − | − | − | + | − | + | −0.71 | 0.89 | 0.94 | − | − | − | | | | | | |
| Rb | + | + | + | + | − | − | + | + | − | + | − | + | + | + | + | + | + | | | | | |
| Sr | − | + | 0.68 | + | − | − | − | + | −0.78 | + | − | 0.70 | + | − | − | − | + | + | | | | |
| Th | − | − | 0.82 | 0.70 | − | − | − | − | − | + | − | 0.86 | 0.70 | + | − | − | 0.81 | − | + | | | |
| Y | − | − | 0.81 | + | + | − | − | + | − | + | − | 0.73 | + | − | − | − | 0.76 | + | + | + | | |
| Zn | − | − | − | − | − | + | − | − | 0.79 | − | + | − | − | + | + | + | − | − | − | − | − | |
| Zr | − | + | 0.82 | + | + | − | − | + | −0.74 | + | − | 0.79 | + | − | − | − | 0.73 | + | 0.71 | 0.78 | 0.73 | − |

Figure 3. Mn/Fe ratios of nodules in the survey area.

areas of similar size on the Carlsberg Ridge (Cronan and Tooms, 1967). More-over, it is possible to recognize a clear areal pattern to the variation in the analyses reported here. Figure 3 shows that the bulk Mn/Fe ratio in the nodules is highest (>4) in the northern part of the area and decreases somewhat irregularly to values <3 in the south. Other major and minor elements that covary with Mn and Fe show this same subtle areal variation. A factor analysis of the total analytical data provides a summary of inter-element associations and allows an objective mapping of the compositional variations over the area (Tables 4 and 5). Factor 1, dominated by Fe, Ti, As, Ce, Co, Pb, Sr, Th, Y and Zr, has highest loadings in the southern part of the area and these decrease to the north (Fig. 4). Factor 2, representing Mn, Mg, K, Mo and Zn, has highest loadings where the Mn/Fe ratios of the nodules are highest (Fig. 5). Factor 3, dominated by Si, Al, Ca, K, Rb, Sr and Zr, simply represents aluminosilicate debris incorporated into the nodules and the factor loadings show no systematic trend. Factor 4 has high scores for Ba, Cu, Ni and Rb, confirming the observations made earlier that the Cu and Ni contents of the nodules vary independently of the total Mn contents. The loadings for this factor are distributed, however, in a pattern similar to, but less clear than, that of the Factor 2 loadings.

Friedrich and Plüger (1974) have described compositional variations in ferro-

Table 4. Varimax factor loadings for the nodule data.*

| Sample | Factors | | | | Communality |
| | 1 | 2 | 3 | 4 | |
|---|---|---|---|---|---|
| 9F-3 | 0.47 | −0.78 | | | 0.94 |
| 11P | 0.75 | | 0.46 | −0.34 | 0.94 |
| 13F-4(A) | 0.31 | −0.52 | | −0.70 | 0.92 |
| 13F-4(B) | | −0.58 | | −0.72 | 0.98 |
| 13F-8 | | −0.91 | | −0.30 | 0.95 |
| 18F-1 | 0.93 | | | | 0.97 |
| 18F-2(A) | 0.80 | | | −0.48 | 0.95 |
| 18F-2(B) | 0.77 | | | −0.43 | 0.94 |
| 18F-3(1A) | 0.85 | −0.36 | | | 0.94 |
| 18F-3(1B) | 0.35 | | 0.89 | | 0.96 |
| 18F-3(2) | 0.69 | −0.40 | | −0.45 | 0.93 |
| 18F-5 | 0.87 | −0.33 | | | 0.96 |
| 18F-6(1) | 0.68 | −0.67 | | | 0.97 |
| 18F-6(2) | 0.59 | −0.40 | 0.41 | −0.54 | 0.97 |
| 18F-8 | 0.38 | −0.86 | | | 0.96 |
| 20G | 0.73 | | 0.46 | −0.36 | 0.95 |
| 24F-2 | 0.75 | −0.58 | | | 0.96 |
| 24F-5 | 0.70 | −0.36 | 0.43 | −0.38 | 0.95 |
| 24F-6 | 0.77 | −0.55 | | | 0.98 |
| Cumulative Variance (%) | 43.91 | 69.46 | 81.04 | 95.46 | |

\* Loadings less than 0.30 omitted.

manganese nodules from an area close to the WAHINE survey area and of similar size which resemble those reported here. Nodules from the northern part of their area have average Mn/Fe ratios of 4.8 and high concentrations of Cu and Ni, whereas nodules from the southern part have average Mn/Fe ratios of 2.4 and lower concentrations of Cu and Ni. The two types of nodules studied by Friedrich and Plüger are also morphologically distinct, in contrast to the Wahine nodules; the northern ones are discoidal and have smooth upper and rough lower surfaces, whereas the southern ones are more nearly spherical and smooth on all surfaces.

*f. Relationship between the nodules and the sediments.* The sediment samples analyzed in this study are, with a single exception, near-surface Quaternary siliceous clays (Table 2). The bulk major element data show that there is very little compositional variation over the area and there appears to be no relationship between the areal variations in the composition of the nodules and their associated sediments. The Tertiary sample, 24F-6 (19-21 cm), however, has significantly higher Mn, Ba, Cu, Mo, Ni, Sr, Y and Zn contents compared with the Quaternary sediments.

Table 5. Varimax factor scores for the nodule data.*

| | | Factors | | |
|---|---|---|---|---|
| Variable | 1 | 2 | 3 | 4 |
| Si | −0.63 | | 1.86 | |
| Al | | | 1.80 | |
| Ti | 1.51 | | | |
| Fe | 1.53 | | | |
| Ca | | −0.85 | 1.51 | |
| Mg | | −2.01 | | 0.68 |
| K | | −1.05 | 1.73 | |
| P | | | | −0.93 |
| Mn | 0.71 | −2.15 | −0.62 | |
| As | 1.42 | | | −0.63 |
| Ba | | −0.76 | | −1.02 |
| Ce | 1.35 | | | |
| Co | 1.68 | | | |
| Cu | | −0.82 | | −1.68 |
| Mo | | −2.00 | | −0.98 |
| Ni | | −0.74 | −0.85 | −1.80 |
| Pb | 1.66 | | | |
| Rb | | 1.14 | 1.73 | −3.41 |
| Sr | 1.20 | | 1.33 | |
| Th | 1.45 | | | 0.71 |
| Y | 1.16 | | | |
| Zn | | −2.11 | | |
| Zr | 1.20 | | 1.29 | |

* Values less than 0.60 omitted.

The concentrations of oxalate-soluble Mn and Fe in the sediments are also given in Table 2. An average of 84% (range 73-90%) of the total Mn and 15% (range 9-20%) of the total Fe are present as amorphous oxyhydroxides. In the case of Fe, the total concentrations remain relatively constant so that the relative proportions of soluble and insoluble Fe vary significantly between the samples. Figure 6 shows that, in spite of considerable scatter, the total Fe contents of the nodules (which are probably 90% oxyhydroxide) are positively correlated with the oxalate-soluble Fe contents of the surface (0-2cm) sediments, each variable varying by a factor of roughly two. Hence, Fe-poor nodules occur on sediments with a smaller proportion of the total Fe present in a readily-extractable form. This may be a smectite phase; Lyle *et. al.* (1977) suggest that a diagenetic reaction between biogenous Si and amorphous Fe oxyhydroxides to form an Fe-rich smectite in surface sediments is responsible for the formation of Fe-poor nodules in the Bauer Basin. On the other hand, nodules associated with sediments having a
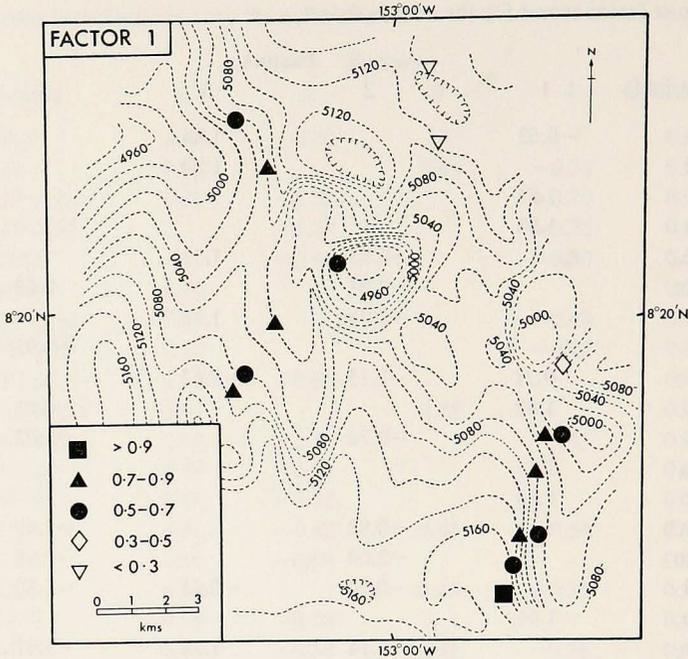
Figure 4. Distribution of Factor 1 loadings of nodule compositions.

greater proportion of Fe oxyhydroxides appear to contain more total Fe and, consequently, have lower Mn/Fe ratios.

A second relationship between the nodules and the sediments is revealed by an examination of the stratigraphy of the cores. As pointed out earlier, the cores collected during the survey contain two distinct sections of fossiliferous sediment, an upper Quaternary or late Tertiary section overlying a middle Tertiary section. The thickness of the Quaternary section does not appear to vary randomly over the area (Fig. 7). To the north of the NW-SE trending ridge, the section is generally less than 20cm thick. South of the ridge, the section is much thicker, some cores not having penetrated to the base.

Comparison of Figure 7 and Figures 3-5 shows that the composition of the nodules is related to the pattern of sedimentation; nodules with high Mn/Fe ratios and high concentrations of Ba, Cu, Mo, Ni, Zn, Mg and K tend to be found in areas with relatively thin Quaternary sections. Nodules with low Mn/Fe ratios and high concentrations of As, Ce, Co, Pb, Sr, Ti, Th, Y and Zr, on the other hand, are found in areas where the Quaternary section is quite thick. Samples 11P and 20G, from the ridge, which have relatively low Mn/Fe ratios, appear anomalous, relative to nearby samples in Figures 3-5. However, the correlation between the nodule compositions and the sedimentation pattern accounts for this apparent
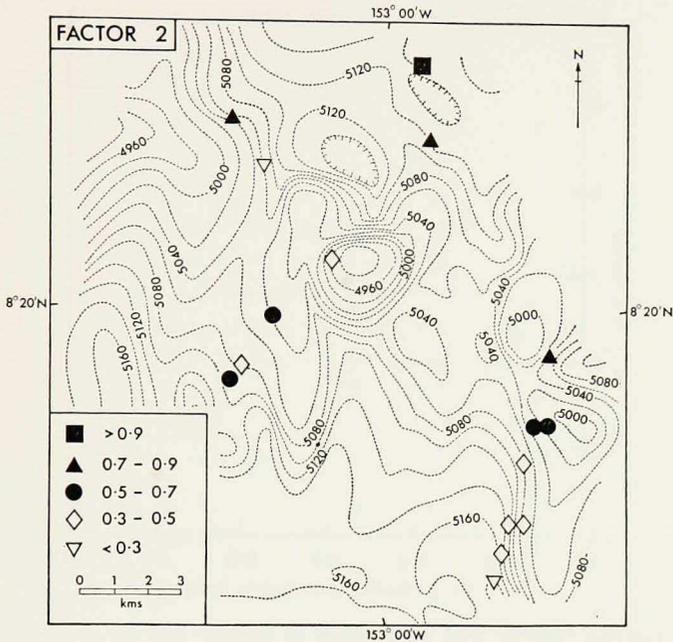
Figure 5. Distribution of Factor 2 loadings of nodule compositions.

anomaly in as much as the Quaternary section is much thicker at these two locali-
ties than at the core locations on the slopes to the north and south.

Figure 8 shows that the Mn/Fe ratio in the nodules and the thickness of the
Quaternary sediment section are significantly correlated; nodules having low ratios
are associated with variably thick Quaternary sections whereas nodules with high
ratios generally are underlain by less than 50cm of Quaternary sediment.

## 4. Discussion

Three factors appear to be responsible for most of the variability in the chemical
composition of abyssal ferromanganese nodules: 1) the relative proportions of the
detrital and oxide fractions (Glasby, 1973); 2) the mineralogy of the manganese
phases (Barnes, 1967; Cronan and Tooms, 1969; Price and Calvert, 1970); and
3) the total Mn and Fe contents (Calvert and Price, 1977).

The data presented in this paper show that the variability in the bulk composi-
tion of nodules from a small area of abyssal sea floor is not due to large differ-
ences in the amounts or the composition of the detrital component of the nodules.
In addition, the Mn-phase mineralogy of the nodules appears to be constant. Both
todorokite and $\delta$-$MnO_2$ can be detected in all samples.

The variability in the bulk composition of the WAHINE nodules seems to reflect
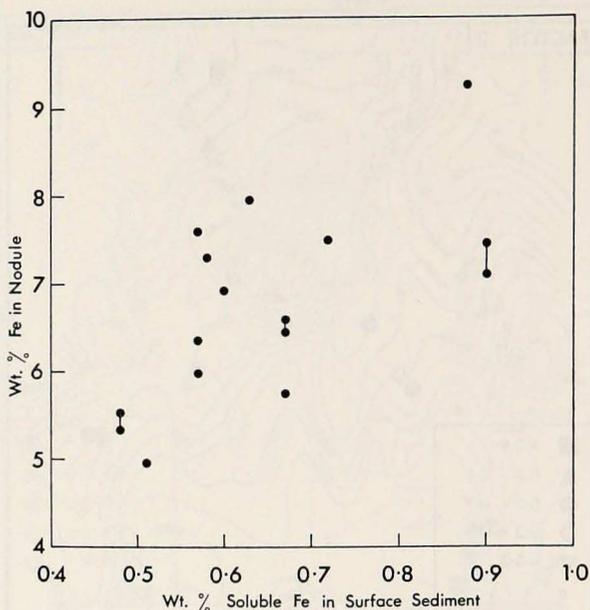
Figure 6. Relationship between total Fe contents of nodules and the oxalate-soluble Fe content of the surface (0-2cm) sediments.

two distinct phenomena: (1) The concentrations of a number of minor elements that are highly correlated with total Mn in nodules from a broad area of the Pacific show large variations despite an almost constant Mn content in the WAHINE nodules. It is unclear whether this reflects variable availability of these elements during primary deposition (Banning, 1975), or variable uptake by todorokite during authigenic growth of this phase within the nodules (R. G. Burns, oral comm., 1976). (2) The Fe content of the Wahine nodules is highly variable relative to the Mn content. Elements associated with the Fe-rich phase show parallel variations. It is not obvious why this variability is so great over such a small area.

The separation of Mn and Fe during diagenetic reactions in Recent sediments, and the enrichment of Mn relative to Fe in surface oxides formed from migrating pore solutions, have been extensively documented (Bezrukov, 1960; Hartmann, 1964; Manheim, 1965; Lynn and Bonatti, 1965; Cheney and Vredenburg, 1968; Li *et al*, 1969; Bonatti *et al*, 1971; Duchart *et al*, 1973). Such processes are known to be important in near-shore areas and in regions of hemipelagic sedimentation where the sediment accumulation rates are high, and where reducing conditions are found below a thin surface oxidized layer. In these environments, some iron accumulates as oxyhydroxides in the surface layers, but more is retained in the subsurface reduced sediments as ferrous sulphides. Manganese, on the other hand, is not retained to the same degree in the subsurface layers and so is more enriched
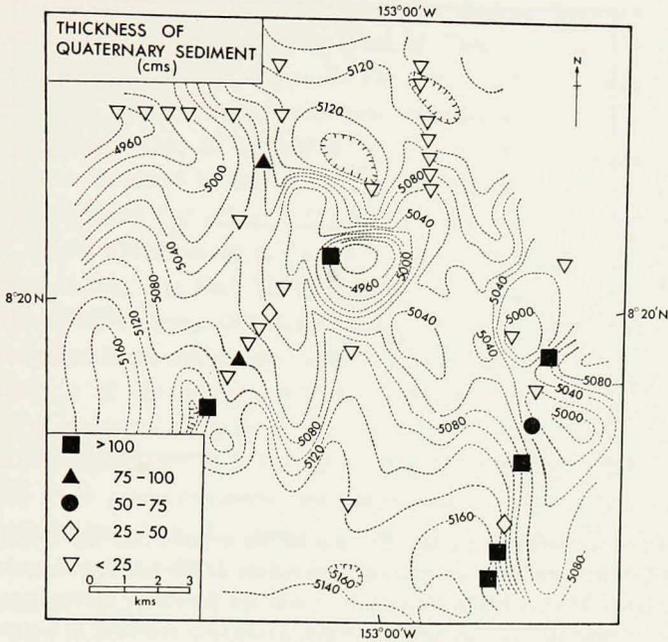
Figure 7. Thickness of Quaternary sediment in the survey area.

in the surface sediment. The resulting precipitates have Mn/Fe ratios much greater than unity, whether they are present as dispersed oxides (Bonatti *et al*, 1971) or as nodules (Calvert and Price, 1970; Price and Calvert, 1970).

The continuation of an area of Mn-enriched nodules westward from central America to the northern tropical Pacific led Price and Calvert (1970) to suggest that post-depositional migration of Mn also occurs in abyssal sediments containing relatively rapidly accumulating biogenous material. They also suggested that the Mn/Fe ratio of abyssal nodules provides a measure of the relative importance of seawater and diagenetic metal sources and that a marked regional variation in these two sources is related to the pattern of sedimentation throughout the Pacific.

Piper and Williamson (1977) have re-examined the regional compositional variations of Pacific nodules using more recent data, and find that abyssal nodules with high Mn/Fe ratios occur in areas of *slow* sediment accumulation rates. This is the converse of the relationship proposed by Price and Calvert (1970). It is, however, supported by our data from the WAHINE area. If we assume that the thickness of the Quaternary sediment section is proportional to the mean sedimentation rate, and that the nodules formed where they were collected, Figure 8 suggests that nodules with high Mn/Fe ratios formed in areas of low sedimentation rate. Piper and Williamson (1977) contend that diagenetic reactions, as they influence the fractionation of elements between nodule and sediment phases, are
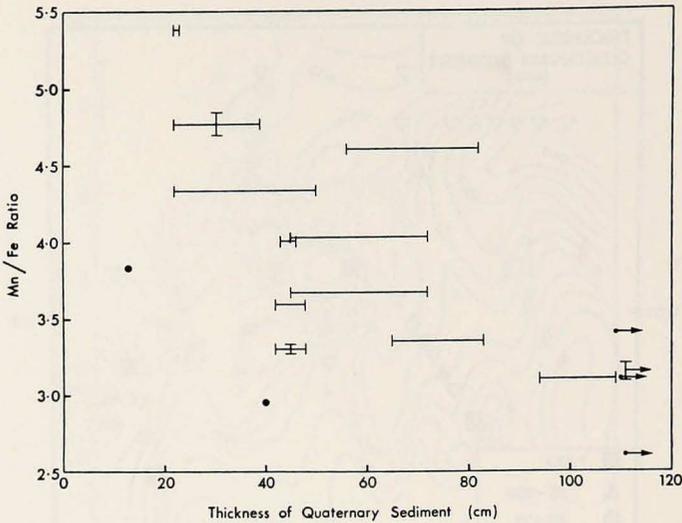
Figure 8. Relationship between the Mn/Fe ratio of the nodules and the thickness of Quaternary sediment. Horizontal bars indicate the uncertainty in the last appearance of Quaternary Radiolarians (after Moore, 1968). Vertical bars indicate the range of duplicate analyses of a single nodule. Arrows indicate the absence of pre-Quaternary sediment in a core.

restricted to the very surface sediment. Our observations suggest that the most marked result of such reactions is the retention of Fe relative to Mn in the sediment. This could be due to the formation of an Fe-rich smectite, as outlined by Lyle *et al.* (1977), by the reaction between biogenous opal and Fe oxyhydroxides which also includes Mn. In any case, the resultant nodules forming at the sediment surface are high in Mn, but are low, and variably so, in Fe.

Some further evidence bearing on these observations is provided by the discovery by Raab (1972) that nodules from the northern tropical Pacific are frequently discoidal in shape and that the compositions of the upper and lower surfaces are different. Smooth upper surfaces, exposed to the bottom water, have more Fe, Co and Pb, whereas lower, irregular surfaces, which represent that part of the nodules buried in the sediment, contain more Mn, Cu, Mo, Ni and Zn. These contrasting compositions are summarized in Calvert and Price (1977, Figs. 12-14).

Raab (1972) interpreted these observations as a consequence of the leaching of Mn and associated minor metals from the exposed upper surfaces of the nodules while accretion takes place predominantly on the lower surface. It seems more likely, however (Calvert and Price, 1976; Piper and Williamson, 1977), that the upper parts of the nodules were formed by precipitation from bottom water, whereas the lower parts were formed diagenetically from remobilized metals in the surface sediment.

In the WAHINE survey area, the ferromanganese nodules have bulk compositions and mineralogies which serve to identify them as diagenetic nodules, following the scheme outlined by Calvert and Price (1977) and Piper and Williamson (1977). Thus it appears that we are dealing with two types of diagenetic Mn and Fe oxyhydroxide precipitates. One is formed in rapidly accumulating sediments where surface oxides are enriched in Mn due to migration and depleted in Fe due to fixation in the sedimest. The other is formed in areas of very slow sedimentation where surface oxides are depleted in Fe due to reaction in the surface sediment and slightly enriched in Mn due both to an additional supply from settling particulate debris (Piper and Williamson, 1977) and from a small amount of migration within the surface sediment horizons. If this interpretation is correct, systematic variations in the composition of the nodules within the survey area can be interpreted as variations in the extent of diagenetic influence on the growth of the nodules, and this in turn is clearly related to the pattern of sedimentation. Thus, nodules associated with the most rapidly accumulating sediments, which have more Fe in the form of oxyhydroxides, show the greatest seawater influence, whereas nodules from thin Quaternary sections, where more Fe has been immobilized diagenetically, are more diagenetic in character. This pattern is certainly not intuitively obvious, but is consistent with the recent suggestions of Piper and Williamson (1977) and Lyle *et al* (1977).

In conclusion, it appears from recent work that ferromanganese oxide precipitates derived from sea water on the one hand, and from diagenetic reactions in bottom sediments on the other, can be recognized over the Pacific Ocean as a whole, over small area surveys and on the scale of an individual nodule. More detailed sampling of nodules and associated sediments in well-surveyed areas of sea floor in other areas of the Pacific, as well as other ocean basins, followed by the determination of the composition and accretion/accumulation rates of nodules and sediments, will be required to test the generality of these conclusions.

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