Manganese Crusts and Nodules from the Hawaiian Ridge[1]

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ABSTRACT: Manganese stains, crusts, and nodules are widely distributed on the insular slopes of the Hawaiian ridge. The thickness of the manganese crusts depends on depth of water, water circulation, and the age and lithology of the substrate, and varies from absent to stains off the island of Hawaii to a maximum of 5 cm in the vicinity of Midway. Scanning electron microscope studies indicate that the internal structure of the manganese crusts is relatively featureless compared with that of deep-sea manganese nodules. Reconsideration of ages of manganese deposits from the Hawaiian archipelago indicates that the rates of accretion of manganese crusts are probably in the same range as those of deep-sea deposits and that the crusts do not accrete at a much faster rate than deep-sea deposits as previously suggested. Iron staining is observed in the volcanic substrates and becomes more apparent with the increasing age of the substrate. There appears, however, to be no evidence that iron oxide is a ubiquitous control factor in initiating manganese crustal growth. Because of the terrain and the rocky nature of the substrate, diagenetic processes within the sediment column probably play no major role in controlling the composition of manganese crusts on the flanks of the island ridge.

MANGANESE STAINS, crusts, and more rarely nodules have been recovered from submarine terraces and slopes throughout the Hawaiian archipelago on a variety of substrates, although dominantly on highly altered volcanic rock. The thickness of the crusts is variable even within a single dredge haul, but in general increases with increasing age of the substrate (i.e., toward the northwest, the older sector of the seamount chain). Maximum thicknesses of 5 cm are observed for the manganese crust in the vicinity of Midway, although thicknesses of up to 2 cm are more common. The crusts are found mainly between 400 and 2000 meters and occur dominantly on terraces. Seven major terraces are identified on the Hawaiian ridge (Stearns 1966, 1967, Mathewson 1971, Morgenstein 1974). These terraces act as traps to downward-moving rubble on which the manganese oxides accrete. The Waho Terrace at 1100 meters, which is generally recognizable throughout the archipelago, contains the most extensive crustal deposits.

The manganese deposits of the Hawaiian archipelago have recently attracted interest as a potential economic resource, particularly for cobalt, and a preliminary report on their distribution, mineralogy, and composition has been prepared (Frank et al. 1976). We present here a short account of the morphology, internal structure, and composition, and the role of iron oxides in initiating manganese crustal growth in these deposits. The samples described here are those collected from the Hawaiian chain southeast of Midway (Frank et al. 1976) and do not include those collected during the 1976 R/V Kana Keoki cruises to the leeward Hawaiian and Emperor Seamount chains, which are still being studied.
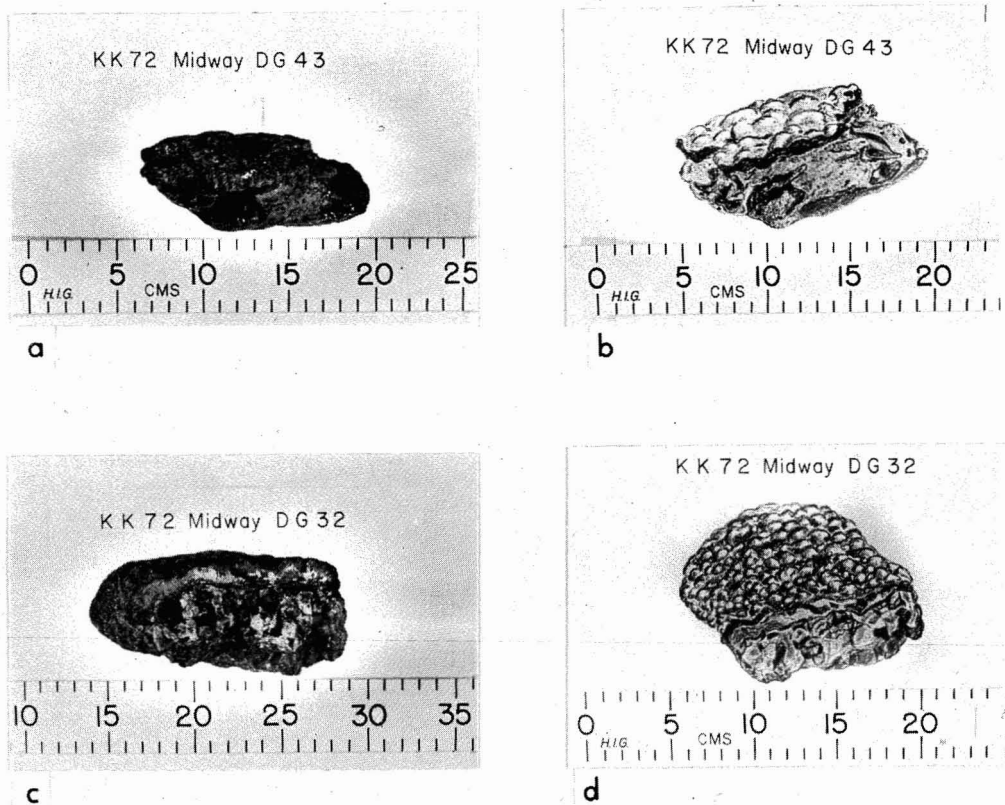
FIGURE 1. Comparison of photographs and charcoal and pastel drawings of manganese crusts from two localities in the Hawaiian archipelago. Drawings have the advantage that they can be used to highlight features of importance in the origin of the crusts. They are particularly useful in that perspective can be chosen to illustrate more facets of the object than is possible in photography, and the problems with depth of focus of the camera can be overcome (for example, where it becomes impossible to bring out microbotryoidal surface texture of the crust as well as the major morphological features of the crust). Photography does, however, remain superior for routine, accurate documentation of nodule collections and gives better results than drawings for many nodule shapes, particularly where the above points are less important. The drawings are by L. Fortin; we believe that this is the first time that drawings of this quality of manganese crusts have been produced since the classic drawings in the H.M.S. Challenger reports. The scale is in centimeters. The samples are: a, Manganese crust with botryoidal surface texture from station KK 72 Midway Dredge 43 (24°17.5′ N, 166°43.8′ W, 1060–1170 meters). The altered volcanic substrate is penetrated by manganese-encrusted bore tubes. Photograph. b, Drawing of sample shown in part a. c, Manganese-encrusted altered volcanic substrate or large, flattened manganese nodule (depending on definition of a manganese nodule) from station KK 72 Midway Dredge 32; present on upper surface. Upper manganese crust is thicker than lower crust. Contact between manganese crust and substrate is well defined, although some manganese-lined bore tube features are noted. Photograph. d, Drawing of sample shown in part c.

MORPHOLOGY

Manganese crusts from the Hawaiian archipelago display a variety of morphologies, but they commonly are flattened or angular crusts and may display thicker manganiferous coatings on the upper surfaces than on the lower surfaces. The crusts commonly have manganiferous botryoidal protuberances typically 5 to 15 mm in diameter, although sometimes larger on the upper surfaces. The substrates are generally highly altered volcanic debris, which in some cases has been replaced by manganese oxides

(Figure 1a, b). In other cases, the surface is covered with a smooth thin coating of manganese oxides. The crusts grade into nodule form in regions where the manganese crusts are thicker, but retain botryoidal surfaces. In general, for such nodules, the manganese crust is of similar thickness on all sides of the nodules (Figure 1c, d) and the nodules tend to be discoidal in shape. In some cases, the nuclei of these nodules, although composed of highly submarine-weathered volcanic material, show a sharp contact with the overlying manganese crust and are not interpenetrated to any significant extent by manganese oxides or manganese dendrites. The crusts and substrate have in many cases been bored by burrowing organisms. The resulting bore tubes are in the range of 2 to 40 mm in diameter. In some nodules, the bore tube is restricted to the substrate and does not penetrate into the overlying manganese crust. In such cases, the boring clearly predates the manganese accretion. The walls of these tubes are sometimes lined with a thin layer of ferric oxides, particularly when the bore is through the volcanic substrate. This mode of occurrence of the iron minerals suggests that the iron is derived principally by leaching of the substrate material. The bore holes are filled with carbonate material in some cases, and organic remains and tubes are also seen on the upper surfaces of some crusts. Light brown iron oxide and silicate minerals are commonly interlayered with the black manganese oxide matrix. As previously mentioned, the thickness of the crusts generally increases with increasing age of the substrate. For example, manganese oxide coatings are thin or absent on volcanic rocks dredged from around the island of Hawaii (Moore 1966), and increase in thickness along the chain to the northwest with increasing age of the volcanic islands and seamounts. Coral growth on the ridge obviously postdates the volcanic rock of the island, and manganese crustal thickness on coral is therefore generally less than that on volcanic rock from the same area, and often occurs as stains. Some of the manganese-encrusted rocks are extremely large and samples in excess of

50-cm diameter have been dredged. Presumably, even larger deposits occur in situ (e.g., Figures 4, 8, 9).

INTERNAL STRUCTURE

The internal structure of Hawaiian archipelagic manganese nodules and crusts, as studied by X-ray radiography and optical and scanning electron microscopy (SEM), is not as well developed as in deep-sea manganese nodules. The characteristic features of deep-sea nodules, such as concentric banding, growth cusps, columnar structure, and microlaminations, are either absent or subdued. X-ray radiographs of nodules from the Kauai channel (Kaieiewaho channel), for example, show diffuse banding in the manganese oxide layers and a sharp contact between the manganese crust and the associated nucleus (Figure 2). The account here is therefore of features observed in this relatively structureless iron–manganese oxide matrix.

Microlaminations of the order of 5 to 10 μm in width can be seen in parts of the manganese crustal matrix (Figure 3a). In contrast to those observed in deep-sea nodules (Margolis and Glasby 1973), however, these laminations cannot be traced over large distances and do not appear to be a major feature of manganese oxide accretion in this type of environment. Cusplike features can also be seen (Figure 3b), but these are rare and do not appear to be fundamental growth structures similar to those observed in deep-sea nodules (Dunham and Glasby 1974). Small worm tubes occur on the surface of some crusts (Figure 3d), but the outer walls tend to be composed of clay minerals rather than calcareous material as judged by X-ray analysis. The volcanoclastic material that commonly forms the nucleus of the nodules may contain abundant foraminifera (Figure 3e), but the outer walls of the foraminifera again tend to be composed of clay minerals or to be iron-cemented (Dudley 1976) rather than calcareous. The volcanoclastic material does, however, effervesce with dilute HCl, indicating that calcareous material must be present. Compared with those of
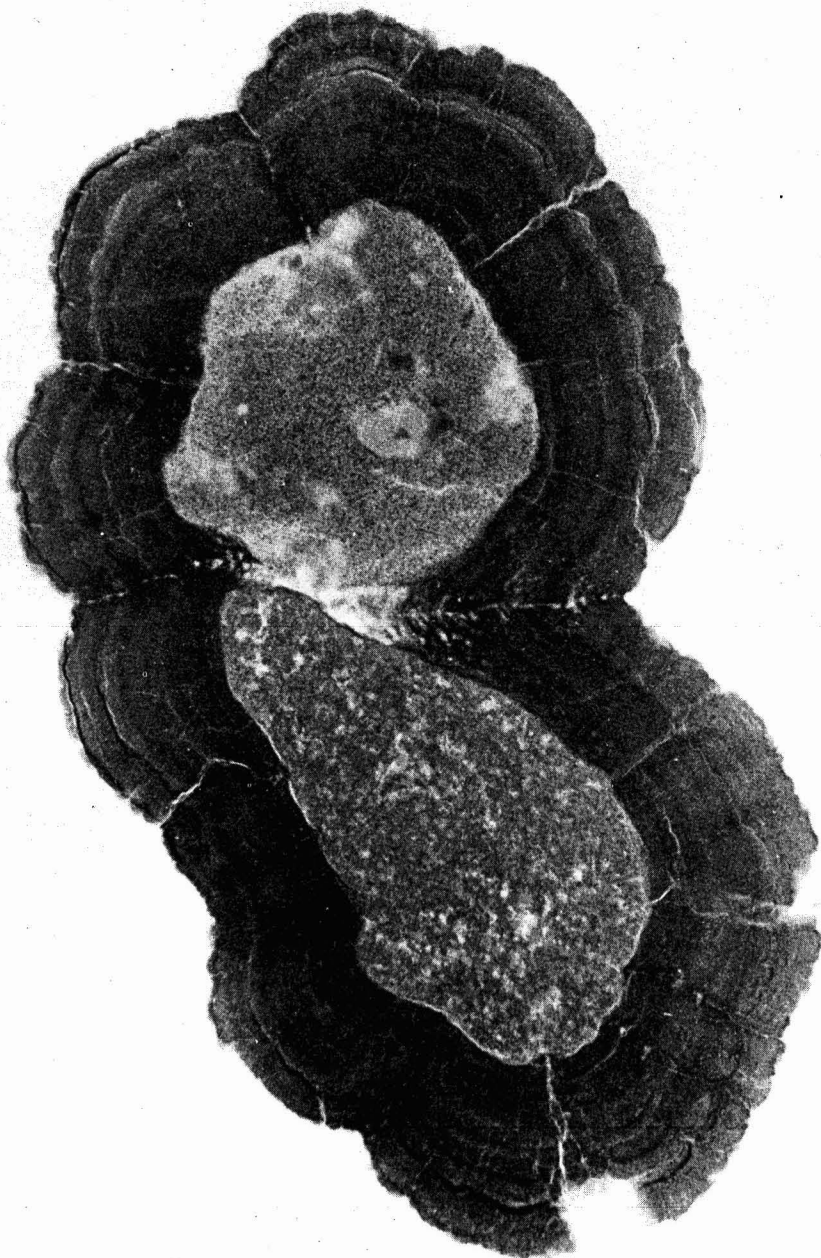
FIGURE 2. X-ray radiograph of a medium-sized nodule from the Waho shelf containing two discrete nuclei.
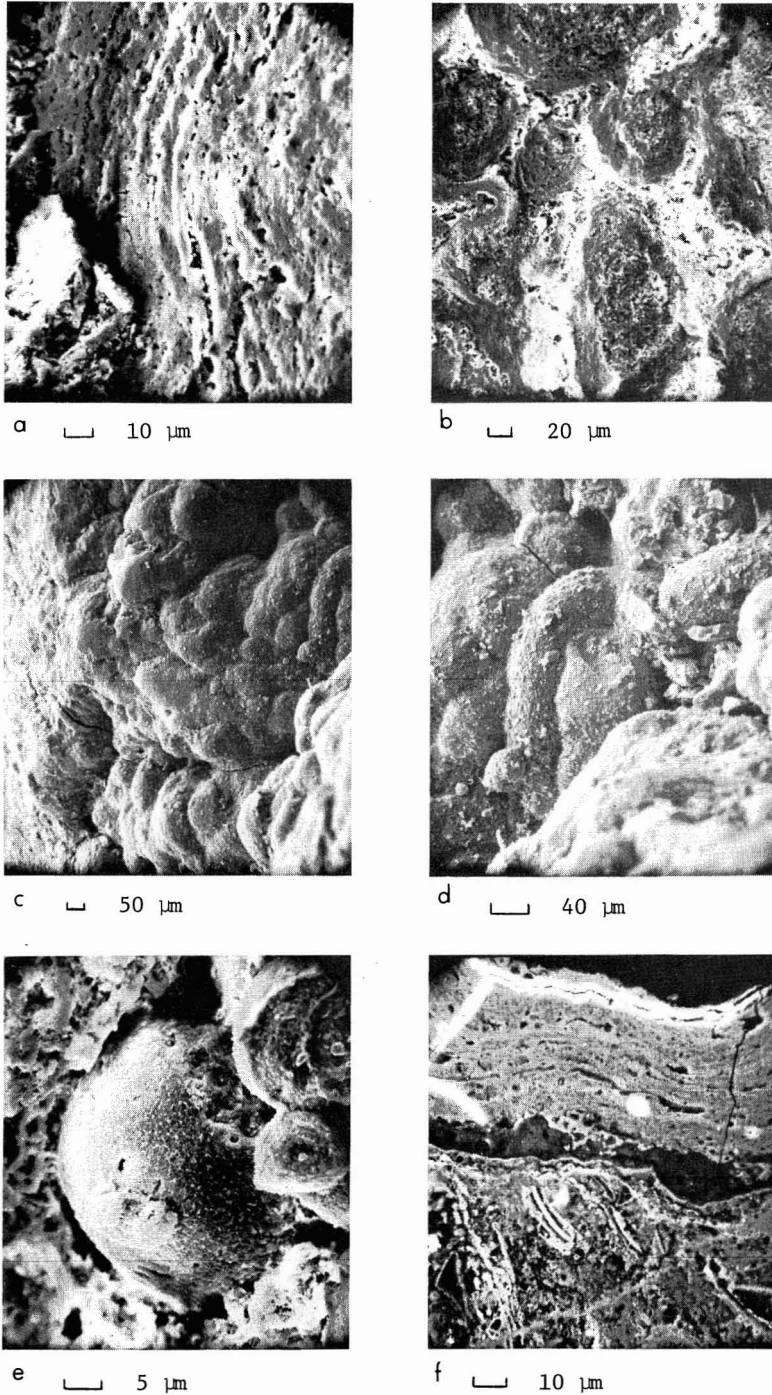
FIGURE 3. *a*, Laminations in a manganese crust from Midway 72-07-02 Dredge 47 (23°49.9′ N, 164°25.2′ W, 775–960 meters). *b*, Poorly defined growth cusps in a manganese crust from Midway 72-07-02 Dredge 47. *c*, Microbotryoids on surface of a manganese crust from Midway 72-07-02 Dredge 32 (25°40.5′ N, 168°41.8′ W, 1450–1570 meters). *d*, Worm tube on surface of a manganese crust from Midway 72-07-02 Dredge 32. *e*, Foraminifera in volcanoclastic material in nucleus of a manganese nodule from Midway 72-07-02 Dredge 32. *f*, Hydrated volcanic glass layer 10 μm thick separating manganese crust on right from basaltic nucleus on left in sample Mn 75-02 Station 11 Dredge 8 (20°08.2′ N, 156°15.9′ W, 1220–1660 meters), sample 3. Note the weak laminations in the manganese crust.

TABLE 1

MN 75–02

SAMPLE NUMBER	AREA	STATION NUMBER	DREDGE NUMBER	LOCATION	DEPTH (meters)	DESCRIPTION
1	Waho shelf	1	1	21°50′ N, 158°40′ W	1,265–1,320	Primarily a friable, yellow-brown, coarse sandy tuff with 0.5 to 2 mm ferromanganese encrustation displaying a smooth to botryoidal surface
2	Waho shelf	2	2	21°50′ N, 158°40′ W	1,265–1,320	Brown, coarse sandy tuff with Mn coating 3 to 10 mm thick and a smooth botryoidal surface
3	Alenuihaha channel (south side)	11	8	20°08′ N, 156°16′ W	1,220–1,660	Interbedded yellow-brown tuff and manganese crust*

*Dredge 8 also contained (a) friable, partially altered, mottled, coarse sandy tuff with crystalline tuff just below the Mn crust; (b) friable, yellow-brown, coarse sandy tuff with a 7-cm-long, 1.5 cm diameter manganese-lined bore tube; (c) gray porphyritic basalt with olivine phenocrysts; manganese oxides appear primarily as staining or crusts 1 to 2 mm thick, with smooth to low botryoidal surface textures.

deep-sea nodules, the manganese crusts of the Hawaiian archipelago display few well-defined structural features.

Of particular importance is the nature of the contact between the volcanic substrate and the overlying manganese crust. This is generally sharp. Figure 3f shows a layer of volcanic glass approximately 10 μm thick forming the contact between the outer manganese crust and the volcanic core (which is relatively unweathered) in a sample from the eastern end of the Hawaiian chain in the vicinity of Molokai. With increasing distance to the west along the island ridge, the nuclear material is observed to be progressively more highly altered, but the contact between oxide crust and nucleus remains sharp. At the extreme western end of the Hawaiian chain in the vicinity of Midway, interpenetration of manganese into the substrate in the form of dendrites becomes more common, and in the Emperor Seamount chain interpenetration and replacement of the substrate by manganese oxides becomes marked.

Botryoidal textures such as noted by Morgenstein (1972a, b) were not observed within the manganese crusts examined in this study using SEM techniques (cf. surface of the crusts in the size range 100–200 μm, Figure 3c; see also Fewkes 1976). Morgenstein (1972b) estimated the rates of accretion of manganese oxides in the Hawaiian archipelago to be of the order 10 to 20 mm/10⁶

yr (i.e., two to three times faster than normal deep-sea nodular formation). Interestingly, Burnett and Morgenstein (1976) subsequently presented hydration-rind and uranium-series accretion rates of nodules from a depth of 1230 meters on the Waho shelf of 3.5 and 3.6 mm/10⁶ yr, respectively, which suggests that manganese nodules and crusts from the Hawaiian archipelago have growth rates similar to those of deep-sea nodules. Although only a portion of the nodules originally collected from the Kauai channel are still available, it can be stated with some certainty that the manganese crustal thickness in the channel is typically in the range 3 to 4 mm, reaching 10 mm in only a few cases. Taking this thickness of manganese crusts in the Kauai channel and the age of the channel as less than 2.7 million years (based on the age of the Waianae volcano on Oahu, Macdonald and Abbott 1970), the minimum average accretion rate of Kauai channel manganese deposits is of the order of 1.5 mm/10⁶ yr. The actual rate is obviously more rapid, but again comparable with the deep-sea rates of accretion.

ELECTRON MICROPROBE ANALYSIS

Three samples of ferromanganese oxide crusts from the Hawaiian archipelago (Table 1) have been examined by electron microprobe for structure and chemical growth patterns. Two samples are from the Waho
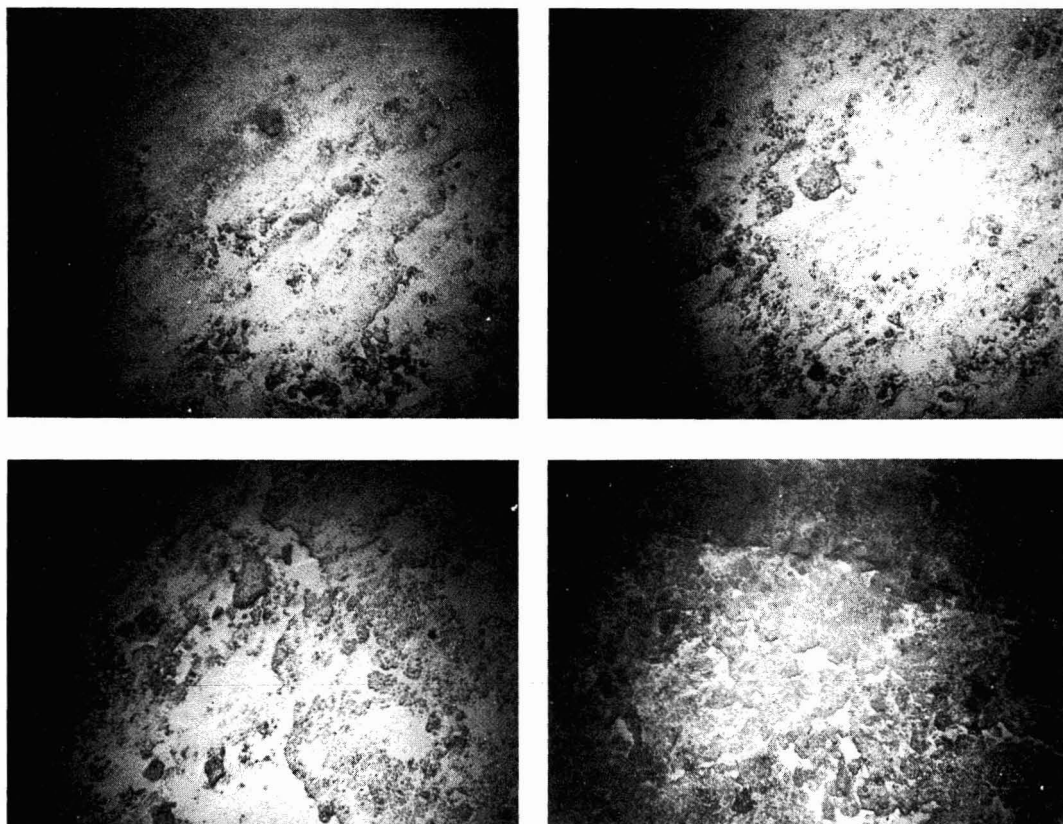
FIGURE 4. Bottom photographs of the Waho shelf, northwest of Oahu. Cruise Mn 75-02 Station 3 (21°54′ N, 158°40′ W, 1770 meters). Thin sediment cover on lithified bedded volcanoclastic substrate. Note fragmentation of edges of outcrops.

terrace level in the Kauai channel (Waho shelf) and one from the Alenuihaha channel on the northwest side of the island of Hawaii. In general, the nuclei of samples selected for electron microprobe studies have undergone less submarine weathering and have thinner manganese coatings than those studied by other methods.

Waho shelf samples 1 and 2 were recovered (Figure 4) about 6 km from the camera station on the north side of the shelf. Here the bottom slopes sharply to the north. Sediment cover is thin and patchy. The substrate consists of beds of lithified volcanogenic sediment encrusted with manganese oxides. These beds are eroding at the edges of the outcrops and the debris is migrating downslope.

Sample 1 is a manganese-encrusted agglomeration of micronodules. The micronodules consist of thin (0.1–0.8 mm) manganese oxide coatings on basalt nuclei up to 5 mm in diameter (Figure 5). The micronodules are held in a matrix of fine sediment and iron-rich cement. This lithified deposit is then encrusted by a 1-mm-thick manganese oxide layer. Microprobe analyses were carried out on the main crust of the sample and an adjacent underlying manganese coating of one of the micronodules. The main crust (outer, more recent manganese oxide layer) appears optically more reflective and less laminar than the inner micronodule manganese layer. It shows signs of fracture and erosion at the exposed outer surface. A 0.7-mm-long point traverse was made by microprobe across the outer manganese crust and inner micronodule manganese zone.
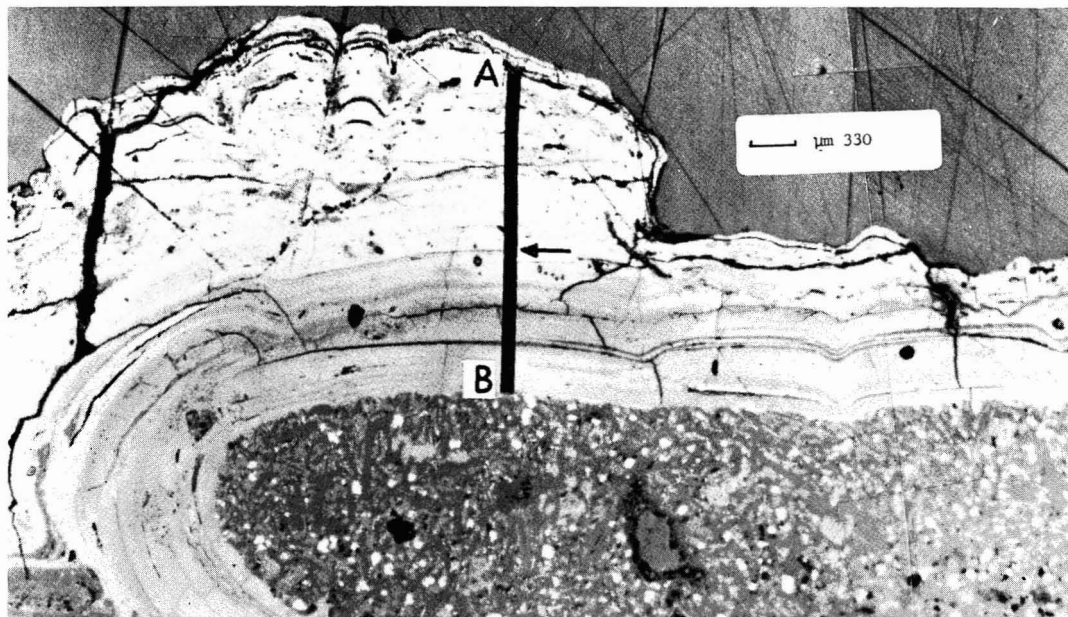
FIGURE 5. Optical photomicrograph of section of sample 1 showing a portion of the basaltic nucleus of a micro-nodule and the primary (micronodule) and secondary oxide layers. Point traverse (Figure 6) follows line A–B. Boundary between oxide layers is marked by arrow.

This traverse (Figure 6) shows the inner manganese layer (early micronodule coating) to be high in Fe and low in Mn (14–24 percent versus 14–16 percent Fe and 10 percent versus 22 percent Mn) compared with the outer layer. The Fe values of the inner layer are quite variable and the Mn values are fairly constant. In the outer layer, both Fe and Mn show little variability; only one area has a high Fe content (approx. 22 percent)—no low Mn content corresponds to this. High Mn values occur in two areas, one at the outer rim of the sample (approx. 30 percent Mn) and one at the outer edge of the boundary between the inner and outer manganese oxide layers (approx. 36 percent Mn).

The boundary between the inner and outer manganese layers is physically sharp but chemically has a transition zone 60 μm thick. Over this distance, a steady change in values of manganese and iron occurs. There is no abrupt change in composition at the physical boundary. This suggests that there has been migration of transition metals after formation

TABLE 2

POINT ANALYSES SAMPLE 1

ELEMENT	1	2	3	4
Mn	10.5	10.7	12.9	16.6
Fe	16.8	16.7	16.7	16.5
Ni	0.2	0.1	0.2	0.1
Co	0.3	0.2	0.1	0.2
Ti	1.9	1.9	1.6	2.0
Cu	0.1	0.1	0.1	0.1

NOTE: Points 1 to 4 are shown in Figure 7. Data are uncorrected weight percents.

of the two layers (or in the early stages of deposition of the outer layer). The Mn/Fe ratios in the inner layer range from 0.4 to 0.7. In the outer layer, the Mn/Fe ratios are 1.4 to 1.6.

In both layers, Ni covaries with Mn, and Co with Fe. Copper does not follow Mn. This may be due to the very low concentrations present. Table 2 shows the inner and outer oxide layer concentrations for Ti, Cu, Ni, and Co. Copper shows no variation across the two layers.
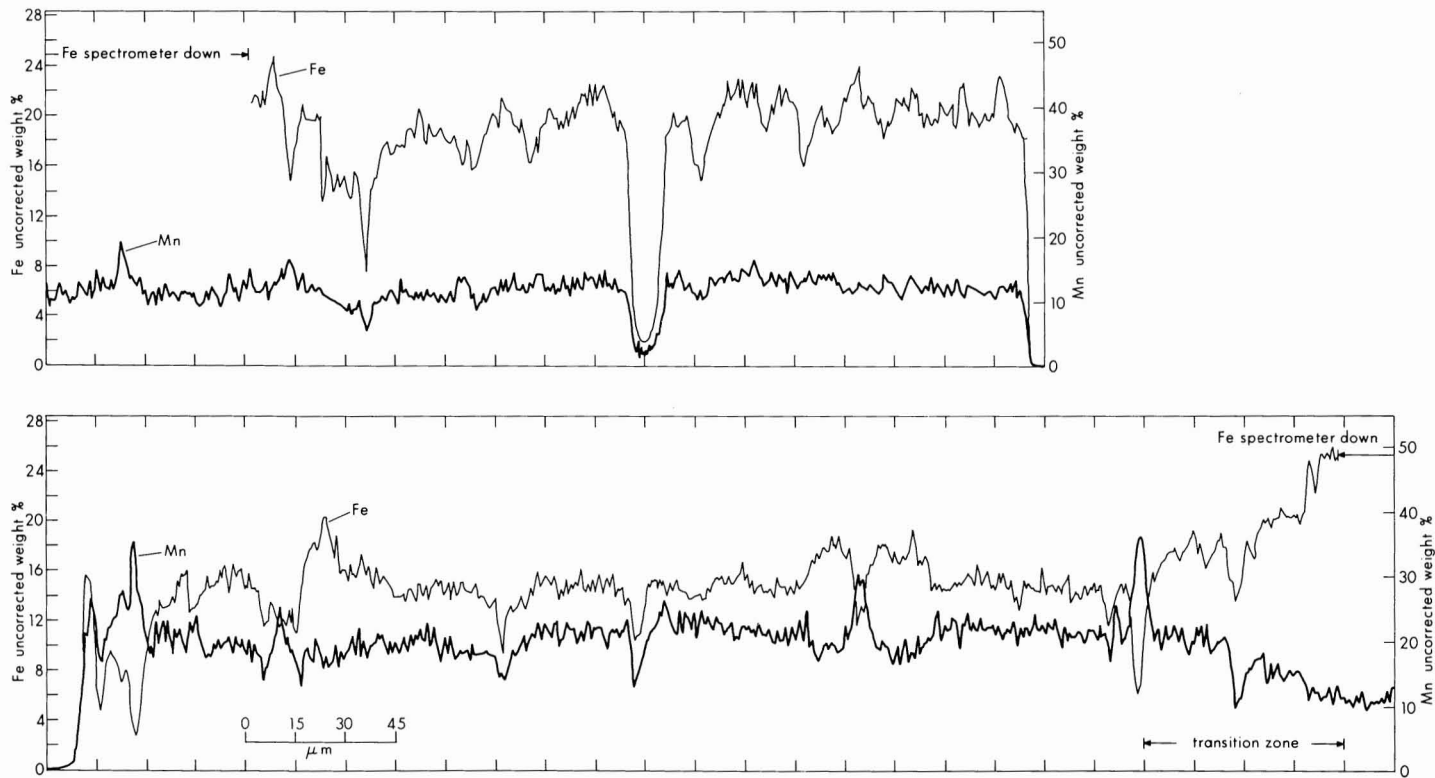
FIGURE 6. Electron microprobe traverse of micronodule oxide coating and the encrusting oxide layers of sample 1 for Mn and Fe. Boundary between the two oxide layers indicated by the arrow in Figure 5. Scales are in micrometers and percentages; separate scales for percent Fe and Mn. Each traverse consists of point analyses at 0.75-μm intervals.
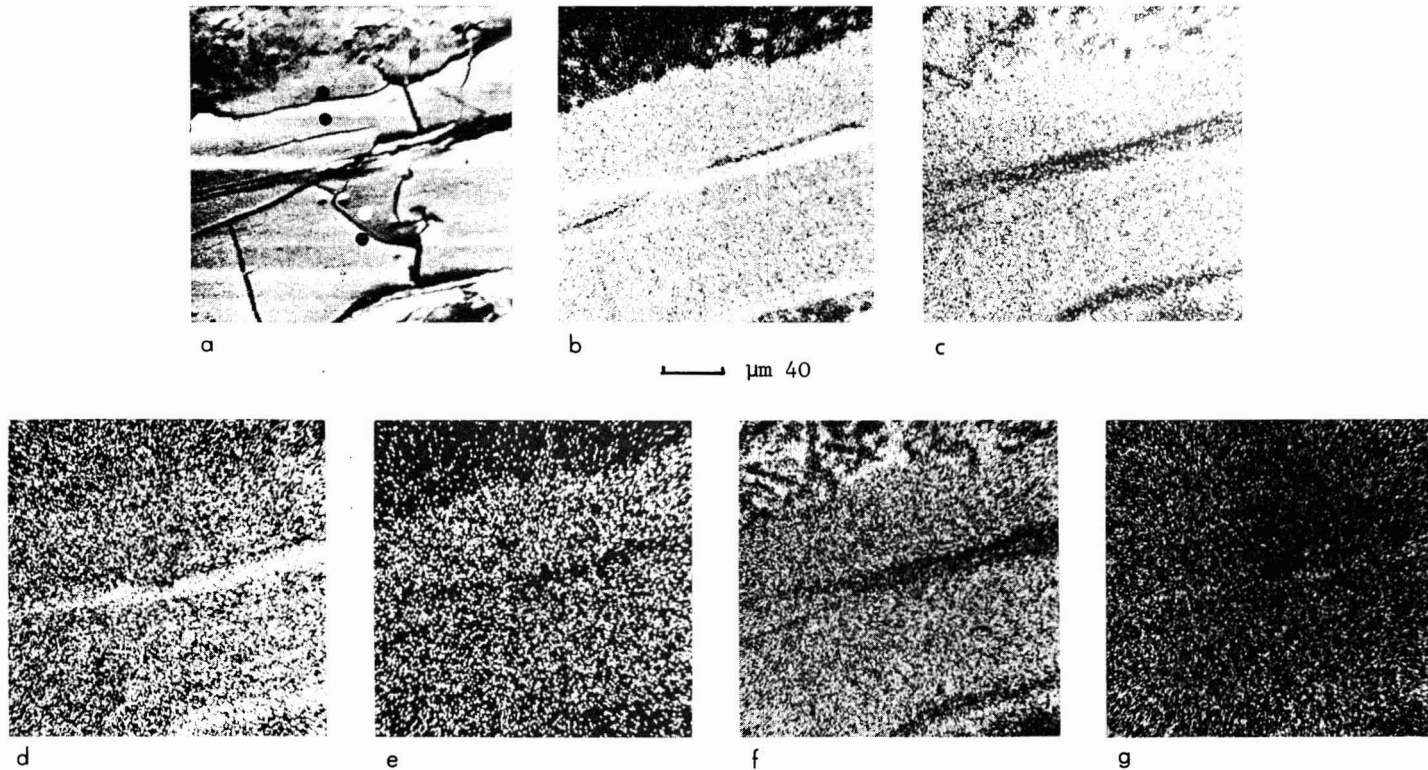
μm 40

FIGURE 7. Electron microprobe elemental distribution photographs of sample 1. *a*, Secondary electron photograph; points are top to bottom, numbers 1 to 4 of Table 2. *b*, Mn. *c*, Fe. *d*, Cu. *e*, Ni. *f*, Co. *g*, Ti.
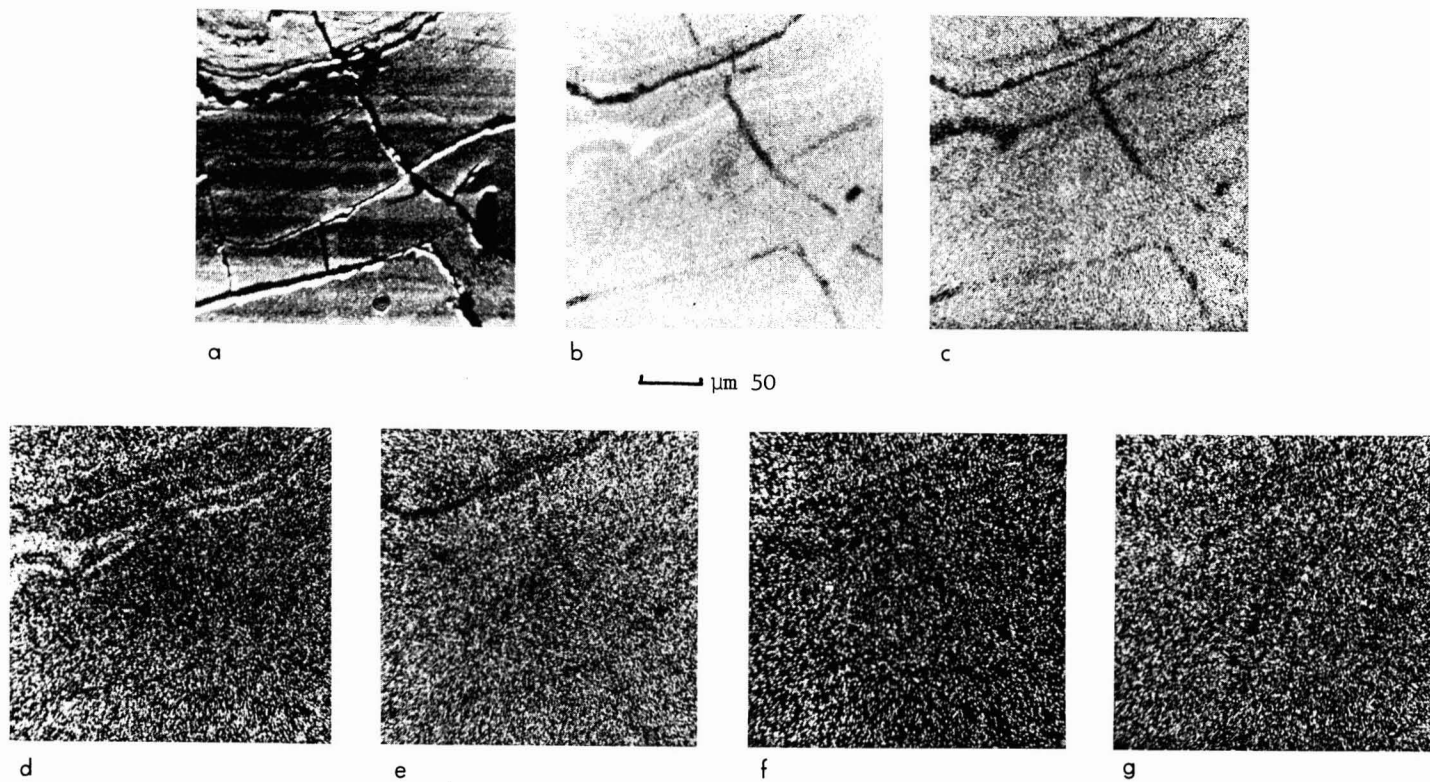
FIGURE 8. Electron microprobe elemental distribution photographs of sample 2. *a*, Secondary electron photograph; points are top to bottom, numbers 1 to 3 of Table 3. *b*, Mn. *c*, Fe. *d*, Cu. *e*, Ni. *f*, Co. *g*, Ti.

Figure 7 shows the elemental distribution in the inner manganese layer and nucleus. Manganese is almost exclusively in the oxide layer, while Fe has high values in the basalt nucleus and especially at the inner boundary between the nucleus and manganese oxide layer. Cobalt follows the Fe distribution in the oxide but is essentially absent in the nucleus. Titanium follows Fe in the oxide; it is abundant in the nucleus, where it is associated with discrete titanium-rich mineral grains, while iron is more evenly distributed. There is some minor enrichment of Cu in the regions of highest Mn values.

In this sample, Fe may well be leached from the interior to the surface of the substrate and play a role in initial accumulation of the ferromanganese oxides, as suggested by Burns and Brown (1972) and Morgenstein (1974). The Mn, Ni, and Co are supplied from seawater, whereas Ti appears to be derived from the substrate (nucleus). This is in keeping with the high Ti contents of the substrate and Hawaiian soils on land (Walker 1964). Copper values are too low to permit an interpretation of the source of this element, although it is presumed to be seawater.

Sample 2 is a coarse-grained volcanogenic sandstone with a 2-mm-thick manganese oxide crust. The Mn/Fe ratio varies from 0.78 to 1.36 from the base to outer surface of the crust. Table 3 presents point analyses for Mn, Fe, Cu, Co, Ni, and Ti. Two thin bands appear in the elemental distribution but not in the structure of the layer (Figure 8). These are higher in Mn and Ni, and lower in Fe than the bulk of the layer. Titanium is highest at the base of the crust. Cobalt shows no patterning in the element-distribution photographs, but the point analyses (Table 3) do show a small increase in Co in the outer part of the crust where Mn is highest and Fe is lowest. In contrast to sample 1 from the same station, no strong substrate influence is apparent for the manganese crustal composition in sample 2.

Sample 3, from the margin on the northwest side of the island of Hawaii, is entirely different from the Waho shelf material. The deposit as seen on the sea floor (Figure 9)

TABLE 3

POINT ANALYSES SAMPLE 2

ELEMENT	1	2	3
Mn	20.7	17.0	12.3
Fe	14.8	14.7	15.5
Ni	0.2	0.2	0.2
Co	0.6	0.5	0.5
Ti	0.7	0.6	0.9
Cu	0.1	0.1	0.1

NOTE: Points 1 to 3 are shown in Figure 8. Data are uncorrected weight percents.

has a rougher surface than that on the Waho shelf off Oahu (Figure 4) and as a result has a more patchy sediment cover. Ferromanganese oxides coat angular and rounded clumps of lava and tuffs in contrast to the bedded appearance of the outcrops off Oahu. Manganese coatings are thinner (1–2 mm) than off Oahu. However, in the sample examined by microprobe, there are extensive internal fillings of ferromanganese material (cement or micronodule agglomerations) up to 5 to 7 mm thick. The zone studied in this sample consists of micronodules in a manganese oxide groundmass, but unlike the micronodules of sample 1, these are smaller, do not have large nuclei relative to their total size, and show well-developed laminar structure. These micronodules form a mass that encloses larger fragments of altered volcanic rocks (Figure 10). The micronodules are 1 to 6 mm in diameter, with concentric laminae of 50 μm or less. Under the ore microscope, the oxides are highly reflective in vertical illumination. X-ray diffraction analyses of adjacent material show only δ-MnO$_2$ to be present. The sample studied with the microprobe appears to be somewhat anomalous. The micronodule nuclei are not identifiable, because they are either extremely small or have been completely replaced by ferromanganese oxides. The oxides are high in Mn (20–26 percent) and low in Fe (< 0.5 percent). In fact, within the well-defined laminar structures of the micronodules, Fe is almost absent. As seen in Figure 11, Fe is high only in the outer margin of the micronodule and in some of the spaces between nodules (in the amorphous cement). There is a slight
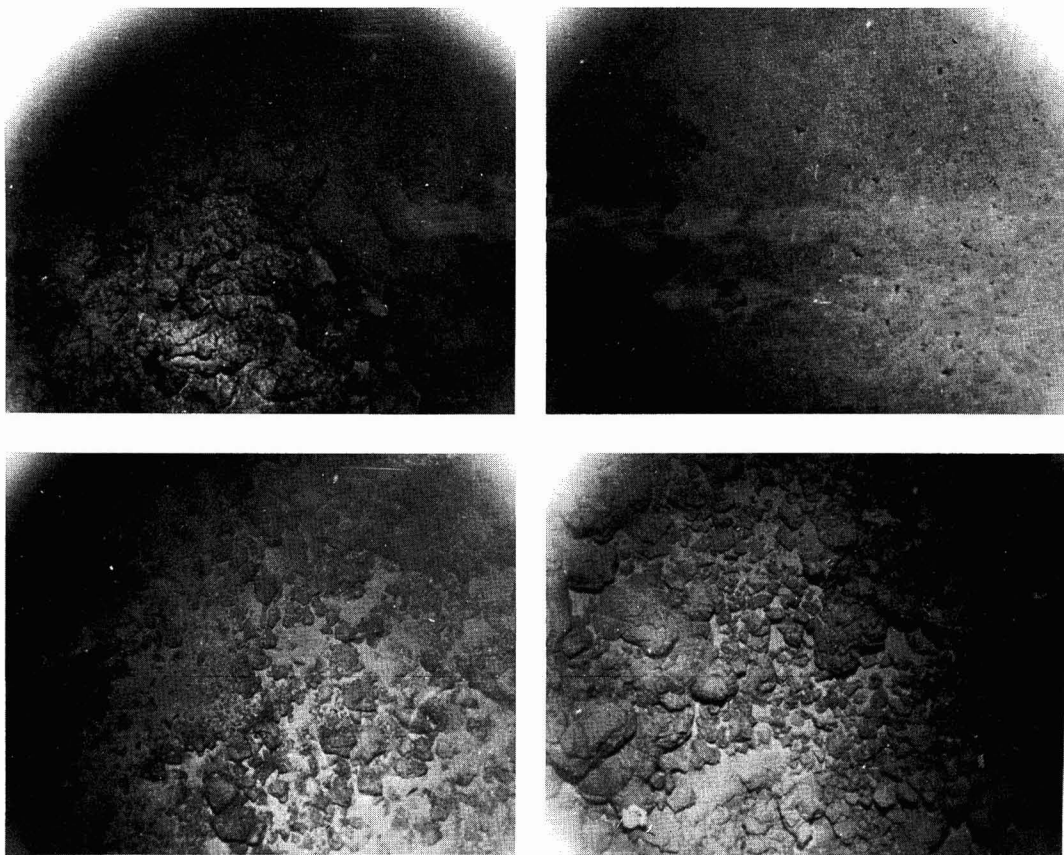
FIGURE 9. Bottom photographs from Station 12, Alenuihaha channel (20°05.7′ N, 156°15.8′ W, 1420 meters). Note lava surfaces and fragmentation of edge of outcrops.
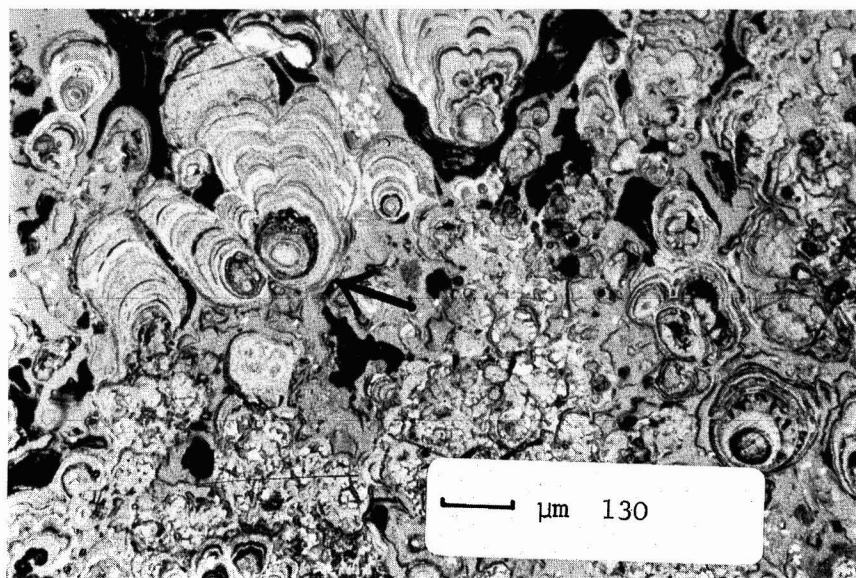

FIGURE 10. Optical photomicrograph of section of sample 3 from Station 11, Alenuihaha channel (20°08.2′ N, 156°15.9′ W, 1220–1660 meters). Micronodule groundmass. Arrow marks micronodule studied by microprobe.
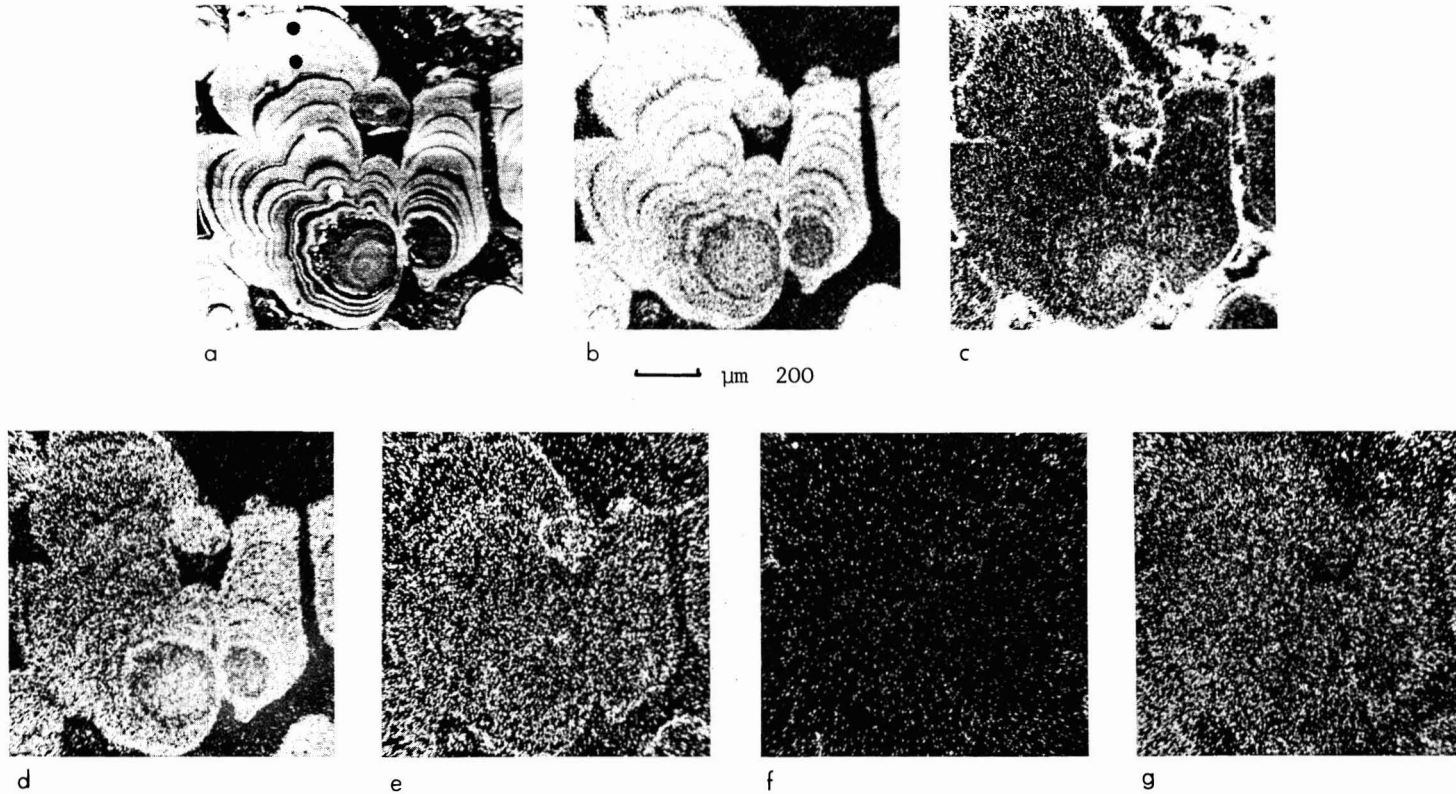
μm 200

FIGURE 11. Electron microprobe elemental distribution photographs of sample 3. *a*, Secondary electron photograph; points are top to bottom, numbers 1 to 4 of Table 4. *b*, Mn. *c*, Fe. *d*, Cu. *e*, Ni. *f*, Co. *g*, Ti. Note Fe distribution on outer margin.

TABLE 4

POINT ANALYSES SAMPLE 3

ELEMENT	1	2	3	4
Mn	26.0	25.7	22.5	17.0
Fe	0.5	0.3	0.3	0.3
Ni	1.0	1.0	0.6	0.7
Co	0.1	0.1	0.1	0.1
Ti	0.1	0.1	0.1	0.1
Cu	0.1	0.1	0.1	0.1

NOTE: Points 1 to 4 are shown in Figure 11. Data are uncorrected weight percents.

increase in Fe near the micronodule nucleus. In contrast, Mn is lowest near the nucleus and absent from the cement and zones between the micronodules. Nickel covaries with Mn. Cobalt is present in low concentrations (0.1 percent) throughout the micronodule and is also concentrated on the rim of the micronodules in the high Fe zone. Titanium is essentially absent from the sample. Copper values are low and, in general, follow Mn. As in samples 1 and 2, the concentrations of Cu are too low for a pattern to be clearly defined. Point analyses are given in Table 4.

ROLE OF IRON OXIDES IN MANGANESE ACCRETION

On the basis of the work of Burns and Brown (1972), Morgenstein (1974) suggested that the formation of iron oxide minerals is important in seeding manganese accretion in the Hawaiian archipelago and that the rate of iron oxide supply controls the rate of manganese accretion. Examination of a large number of hand specimens of manganese crusts from the archipelago does not support this contention, as there appears to be no evidence in most nodules of a discrete iron oxide layer at the contact between the volcanic substrate and the overlying manganese crust, which is necessary to initiate such a process. Where a discrete iron oxide layer is formed (as, for example, on the surface of a bore hole through the volcanic substrate), it is generally not coated with manganese oxides. The formation of discrete iron oxide minerals or layers in volcanic substrate does,

however, depend upon (among other conditions) the age and lithology of the substrate. Flecking of iron oxide minerals around vesicles, formation of discrete iron-rich bands, surface staining of the substrate by iron oxide layers, and the conversion to an iron-rich clay are all noted to varying degrees in the substrates of samples dredged from the western end of the Hawaiian chain and the Emperor Seamount chain. These iron oxide minerals are undoubtedly derived by halmyrolysis from the substrate material (Pasteur 1968, Cronan 1974). By virtue of the greater age of the substrate material from the western end of the Hawaiian chain, these substrates are characterized by the thickest manganese crusts and, because the iron is generally associated with the substrate rather than the manganese oxides, it stratigraphically underlies the manganese oxide layers. From visual observation, however, there appears to be no correlation between the occurrence of the iron oxides and the formation of manganese oxide layers. Surface staining of the substrate by iron oxides, for example, often occurs on parts of the rock where manganese oxides are absent. Further, the manganese and iron contents of manganese crusts from the Hawaiian chain (average 23.2 and 17.3 percent, respectively, Frank et al. 1976) are in the general range of deep-sea nodules (Cronan 1972), although the iron content is about a factor of two higher than in the equatorial North Pacific nodules. This suggests that enrichment of iron from the substrate into the crust does not take place on any more significant scale than in the deep sea, although some iron may be derived from local volcanic sources in deep-sea nodules (Cronan 1972). Although leaching and redeposition of iron is therefore important in the rocks of the Hawaiian chain, particularly in the volcanic rocks, no direct causal relationship between iron and manganese oxide deposition can be inferred in samples from this region.

By contrast, electron microprobe studies of the material from the archipelago show the presence of iron-rich basal layers in a number of cases. The absence of such layers as a general feature on the microscale sup-

ports the conclusion from the hand specimen examinations that iron oxides do not play a principal or necessary role in initiating manganese oxide growth. In those cases where such layers do exist, however, they do influence later manganese oxide growth. Such iron basal layers are derived directly from the substrate, and iron (as well as Ti) appear to be supplied to the oxide layers in part from the substrate. Other transition elements are supplied dominantly from seawater.

Where iron-rich basal layers do occur, it is observed that the immediately subsequent manganese oxide layer is compositionally different from the later manganese oxide growth and from manganese oxide growth where the iron layer is absent. These differences include higher Fe contents, lower Mn/Fe ratios, and higher Co and Ti values in the layers associated with iron basal layers. Under vertical illumination, the manganese oxides adjacent to iron basal layers are less reflective than those not associated with such layers. Sorem and Foster (1972) have suggested that zones of moderate reflectivity (gray, smooth appearance) are generally "amorphous Fe–Mn oxides" and zones of high reflectivity (white, dense appearance) are mixtures of crystalline Mn–Fe oxides and amorphous Fe–Mn oxides. Such differences observed in the present samples may be a result of the influence of the iron basal layer on the mineralogy of the manganese oxides.

ROLE OF DIAGENESIS IN MANGANESE ACCRETION

The fact that the lower surface of the volcanic substrate is commonly not coated by a manganese oxide layer suggests that upward diffusion of manganese through the sediment column and deposition at the sediment–water interface are not important in this type of environment. Seawater is probably the major source of ferride elements in the manganese crusts, although leaching of elements from the volcanic substrates (Fein and Morgenstein 1972) may also contribute to a lesser degree to the formation of the crusts. The sharp nature of the contact between the outer

manganese crust and the underlying nucleus, however, suggests that replacement of the volcanic core by manganese oxides is not a major phenomenon, particularly at the eastern end of the Hawaiian chain. At the western end of the Hawaiian chain and in the Emperor Seamount chain, replacement of the substrate by manganese oxides becomes more apparent.

LITERATURE CITED

BURNETT, W. C., and M. MORGENSTEIN. 1976. Growth rates of Pacific manganese nodules as deduced by uranium-series and hydration-rind dating techniques. Earth Planet. Sci. Lett. 33:208–218.

BURNS, R. C., and B. A. BROWN. 1972. Nucleation and mineralogical controls on the composition of manganese nodules. Pages 51–61 in D. R. Horn, ed. Ferromanganese deposits on the ocean floor. National Science Foundation, Washington, D.C.

CRONAN, D. S. 1972. Regional geochemistry of ferromanganese nodules in the world ocean. Pages 19–30 in D. R. Horn, ed. Ferromanganese deposits on the ocean floor. National Science Foundation, Washington, D.C.

———. 1974. Authigenic minerals in deep-sea sediments. Pages 491–525 in E. D. Goldberg, ed. The sea. Vol. 5. John Wiley & Sons, New York.

DUDLEY, W. C. 1976. Cementation and iron concentration in foraminifera on manganese nodules. J. Form. Res. 6:202–207.

DUNHAM, A. C., and G. P. GLASBY. 1974. Petrographic and electron microprobe investigation of some deep- and shallow-water manganese nodules. N. Z. J. Geol. Geophys. 17:929–953.

FEIN, C. D., and M. MORGENSTEIN. 1972. Microprobe analyses of manganese crusts from the Hawaiian Archipelago. Pages 41–58 in J. E. Andrews et al. Investigations of ferromanganese deposits from the central Pacific. Hawaii Inst. Geophys. Rept. HIG-72-23, Honolulu.

FEWKES, R. H. 1976. The origin of marine manganese nodules as determined by textural and mineralogical analysis. Ph.D. Thesis. Washington State University, Pullman. 169 pp.

FRANK, D. J., M. A. MEYLAN, J. D. CRAIG, and G. P. GLASBY. 1976. Ferromanganese deposits of the Hawaiian Archipelago. Hawaii Inst. Geophys. Rept. HIG-76-14, Honolulu. 71 pp.

MACDONALD, G. A., and A. T. ABBOTT. 1970. Volcanoes in the Sea: The geology of Hawaii. University of Hawaii Press, Honolulu. 441 pp.

MARGOLIS, S. V., and G. P. GLASBY. 1973. Microlaminations in marine manganese nodules as revealed by scanning electron microscopy. Bull. Geol. Soc. Am. 84:3601–3610.

MATHEWSON, C. C. 1971. Engineering analysis of subaerial and submarine geomorphology along the north coast of Molokai Island, Hawaii. Ph.D. Thesis. University of Arizona, Tucson. 123 pp.

MOORE, J. G. 1966. Rate of palagonitization of submarine basalt adjacent to Hawaii. U.S. Geol. Surv. Prof. Pap. 550D:163–171.

MORGENSTEIN, M. 1972a. Manganese accretion at the sediment–water interface at 400 to 2400 meters depth, Hawaiian Archipelago. Pages 131–138 in D. R. Horn, ed. Ferromanganese deposits on the ocean floor. National Science Foundation, Washington, D.C.

———. 1972b. Sedimentary diagenesis and rates of manganese accretion on the Waho shelf, Kauai Channel, Hawaii. Pages 1–40 in J. E. Andrews et al. Investigations of ferromanganese deposits from the central Pacific. Hawaii Inst. Geophys. Rept. HIG-72-23, Honolulu.

———. 1974. Sedimentary diagenesis and manganese accretion on submarine platforms, Kauai Channel, Hawaii. Ph.D. Thesis. University of Hawaii, Honolulu. 172 pp.

PASTEUR, T. P. 1968. Petrologic variations within submarine basalt pillows of the South Pacific–Antarctic Ocean. Contr. Sedimentol. Res. Lab. Fla. State Univ. 27. 108 pp.

SOREM, R. K., and A. R. FOSTER. 1972. Internal structure of manganese nodules and implications in beneficiation. Pages 167–181 in D. R. Horn, ed. Ferromanganese deposits on the ocean floor. National Science Foundation, Washington, D.C.

STEARNS, H. T. 1966. Geology of the State of Hawaii. Pacific Books, Palo Alto, California. 266 pp.

———. 1967. Geology of the Hawaiian Islands. Bull. No. 8. Dept. of Land and Natural Resources, State of Hawaii. Supplement by G. A. Macdonald.

WALKER, J. L. 1964. Pedogenesis of some highly ferruginous formations in Hawaii. Hawaii Inst. Geophys. Rept. HIG-64-10, Honolulu. 406 pp.