MANGANESE NODULES FROM THE CHALLENGER EXPEDITION AT REDPATH MUSEUM

JOHN S. STEVENSON AND LOUISE S. STEVENSON

*Department of Geological Sciences, and Redpath Museum,
McGill University*

ABSTRACT

Manganese nodules from Stations 252 and 281 of the Challenger Expedition, collected in 1875, have recently been discovered in the Redpath Museum. The nodules have been found to be quite typical specimens of two areas in the Central Pacific Ocean except for dehydration and other changes that have taken place during storage. The principal resolvable manganese mineral in nodules from Station 252 proved to be 10 Å manganite; there was a very thin surface coating of birnessite. δ manganite was the only manganese mineral found in nodules from Station 281.

Through electron microprobe studies, findings from chemical, optical and x-ray crystallographic work were correlated with the detailed picture of the occurrence and quantities of the different elements within the nodules. In all cases it was found that the iron and manganese had an antithetical relationship, and that nickel and copper were associated with the manganese. Special study was given to a 300-micron-square area in a nodule from Station 252 which included a segregation of 49.39% Mn, 5.31 % Ni, and 1.64% Cu. Crystallization of the manganese phases is thought to have provided a mechanism for formation of segregations which were further enriched through chemical scavenger action as long as ocean floor conditions permitted.

INTRODUCTION

During recent renovations of the Redpath Museum, McGill University, manganese nodules from two stations of the Challenger Expedition were discovered. It appears that these specimens, which had been stored in an obscure part of the Pleistocene and Recent Paleontology Collection, were a gift to our first Museum Director, Sir William Dawson, from the leader of the expedition, Sir John Murray.

As far as we know, these are the only nodules from "the Voyage of H.M.S. Challenger during the Years 1873–76" in Canada, and, in view of their historical interest, we have studied them in order to record as complete a description of the nodules as possible. This has also given us a unique opportunity to study unusually desiccated material, since these nodules had been stored in a very hot, dry location near steampipes in our building, interspersed with very humid periods during the summers, since 1882. As this is, of course, the exact opposite of the type of care given modern oceanographic specimens, where materials are sealed in waterproof plastic bags and carefully stored until they are analyzed, interesting differences from newly-collected nodules have been observed.

DESCRIPTION OF THE NODULES

From Challenger Station 252 (Lat. 37 52 N., Long. 160 17 W., 2740 fathoms) we have two nodules: an ovoid nodule about 9 cm long (Fig. 1) now weighing approximately 200 grams, and a second, broken nodule which appeared to have been about 7 cm long. A note found with the broken nodule read, "This specimen was broken for examination some time after it was dredged". The specimens from Station 252 were col-
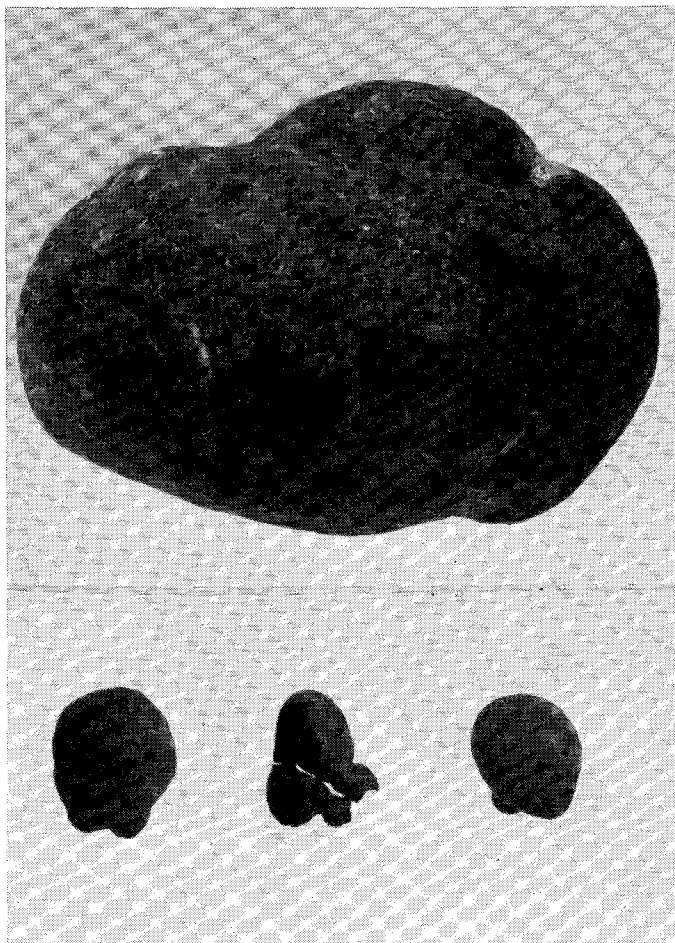

FIG. 1. (top) Nodule from Challenger Station 252, Redpath Museum, ×1.
FIG. 2. Nodules from Challenger Station 281, Redpath Museum, ×1.

lected on July 12, 1875. In the original Challenger Report nodules from this station were described as being in size and shape "pretty much like potatoes" (Murray & Renard 1891), a description that applies very well to our specimens.

From Station 281 (Lat. 22 21 S., Long. 150 17 W., 2385 fathoms) we have 45 small nodules, which were collected on October 6, 1875. The nodules from this station were described originally as being the size of marbles. Ours vary in diameter from 0.7 to 2.5 cm, with most of our "marbles" having a diameter of about 1.5 cm, and an average weight at the present time of slightly less than 2 grams. Although the nodules are roughly spheroid, most have smaller concretionary masses attached to the main mass (Fig. 2). A number of the nodules have a portion of the crust broken off, so that the onion-like structure is revealed.

Although the two stations represented are widely separated in latitude, both are in the Red Clay area of the Central Pacific Ocean and both represent rather deep stations (5011 m for Station 252 and 4362 m for Station 2810). Mero (1962, 1965) has mapped the manganese nodule stations of the Pacific Coast and divided them according to zones. In the Mero map, "Compositional Regions of Manganese Nodules", Station 252 is in the C-1 region, and Station 281 in the A-5 region, although very near the boundary.

Nodules from both stations showed numerous similarities and, in general, could be considered typical of manganese nodules from the ocean depths. The nodules from Station 281 are a slightly darker brownish black than those from Station 252. However, the nodules from Station 252 showed a thin black coating in places. All the Redpath nodules seem to be somewhat lighter in colour and much lighter in weight than most recently-collected nodules; this would be expected in view of their long storage under the museum conditions.

CHEMISTRY OF THE NODULES

Many theories for the origin of manganese nodules and their chemical formation have been presented, and generally it seems agreed that, although biological factors may contribute to the formation, inorganic processes are of principal significance (Arrhenius 1963; Goldberg 1954; Bonatti & Nayudu 1965; Rossman & Callender 1968; Cronan & Tooms 1968; and others). As the result of his studies following the Challenger voyage, Sir John Murray felt that submarine decomposition of manganese-rich basic eruptives was probably of greatest importance (Murray & Renard 1891).

However, from time to time the importance of biological processes has

been emphasized (Dieulafait 1883; Holmes 1965; and others). Perhaps some of the earlier writing stressing organic factors influenced former curators of the Redpath Museum in deciding to catalogue the nodules with the fossils rather than with the rocks and minerals in the geology collections. Furthermore, since a number of animal remains, such as the *Carcharodon* sharks' teeth found at Challenger Station 252, formed nuclei for some manganese nodules, it may have been thought at the time that the chief scientific interest of the Redpath nodules lay in their possible organic nuclei.

Manganese is added to ocean water by rivers, submarine volcanic eruptions, submarine springs, and the decomposition of igneous rocks and igneous detrital material on the ocean floor. Once on the bottom of the ocean, colloids of iron and manganese appear to find favourable localities for their agglomeration, and a suitable detrital material may accelerate nodule formation. It is thought that manganese is removed from bottom water by catalytic oxidation of the manganous ion by colloidal ferric hydroxide at the sediment-water interface. δMnO_2 may itself then act as a catalyst for more δMnO_2 precipitation. Hydrated oxides of iron and manganese have been found to act as chemical scavengers in removing specific ionic species such as copper, nickel and cobalt from solution in sea water and this is thought to account for their relatively high concentrations in manganese nodules (Goldberg 1954; Krauskopf 1956; Price 1967).

The chemical analyses of the major constituents of the Redpath Museum nodules from Stations 252 and 281 are given in Table 1. It will be seen that the nodules from both stations are typical in chemical composition of average manganese nodules from the ocean floors (Mero 1965,

TABLE 1. CHEMICAL ANALYSES
OF MAJOR CONSTITUENTS,
REDPATH NODULES

	L	S
SiO_2	23.0	23.0
Al_2O_3	5.7	8.2
Fe_2O_3	16.8	16.9
MgO	2.3	4.3
CaO	3.3	5.4
Na_2O	1.7	2.7
K_2O	1.4	1.3
H_2O	5.5	4.0
TiO_2	0.75	0.69
P_2O_5	0.16	0.17
MnO	31.6	28.3
CO_2	2.6	4.2

L: Large nodule, Station 252; S: Small nodule, Station 281.

TABLE 2. BULK SPECTROSCOPIC
ANALYSES OF MINOR ELEMENTS,
REDPATH NODULES

	L	S
Be	n.f.	n.f.
B	<.02	<.02
Sc	.015	.015
Ti	.56	.48
V	.048	.061
Cr	n.f.	n.f.
Co	.16	.13
Ni	.33	.56
Cu	.20	.22
Zn	n.f.	n.f.
Ge	.007	.009
Sr	.068	.068
Y	.018	.018
Zr	.089	.059
Ag	.0016	.0023
Sn	.039	.036
Sb	n.f.	n.f.
Ba	.16	.12
La	n.f.	n.f.
Yb	.0019	.0014
Pb	.050	.031

L: Large nodule, Station 252; S:
Small nodule, Station 281 n.f. = none
found.

Table XXVII), except for the decidedly lower water content of the Redpath specimens.

Minor elements were sought by bulk spectroscopic analysis of specimens "as is", and the results are given in Table 2. Although nodules from both stations appear to be high in scandium, nickel and copper, while the cobalt content is average, it is inadvisable to make direct comparisons with other published material because of the conditions under which the Redpath material had been stored for so long (F. Aumento, personal communication).

It is interesting to recall that analysts working on the Challenger material for the original report noted a "trace" of copper and a "good trace" of nickel for specimens from Station 252, and a "good trace" of copper and nickel and a "trace" of cobalt for the "dark brown" nodule analyzed from Station 281 (Murray & Renard 1891).

The chemical composition of the Redpath specimen from Station 252 confirms its assignment to the C-1 or high copper-nickel region of the Pacific Ocean (Mero 1962, 1965). However, the Station 281 analysis suggests that, although geographically this nodule is assignable to the A-5 or high-iron region, and is adjacent to the D-2 high-cobalt region, chemically it is not typical of these zones, but rather an example of the

many variations from the norm seen in detailed study of nodule distribution. Cronan & Toombs (1967), for example, have recorded interesting variations in their Northwest Indian Ocean studies, where considerable differences were seen in the composition of morphologically similar nodules from sites only a few miles apart.

PETROGRAPHY OF THE NODULES

Nodules from both stations were seen to be composed of concentric layers of manganese-iron oxides with fewer and thinner discontinuous layers of fine-grained silicates in amorphous manganese-iron oxides. Nodules from both stations also showed that the layers in much of the samples had been severely contorted on a small scale resulting in the silicate layers and the harder manganese-iron layers being brecciated and compressed into irregular folds, and there were many radial cracks in the nodules. Since this contortion is less conspicuous in new material, it is thought that it was caused, at least in part, by the heating and desiccation of the nodules in the Museum following their collection, a process somewhat similar to low-grade thermal metamorphism. An interesting contrast may be seen in the Challenger Report, where a nodule from Station 252, very similar to ours in size and shape, is well illustrated in its "unmetamorphosed" state by Murray & Renard (1891, Plate IX, 7).

This desiccation caused problems in nearly every phase of the study. In making thin sections and polished sections it was found that the specimens readily absorbed water and formed a muddy surface, and in the laboratory it was difficult to record the true weight of the nodules, since they were so hygroscopic that the weight differed greatly from day to day according to the atmospheric humidity.

No organic remains could be observed as nuclei in any of the nodules that were cross-sectioned, although Y-shaped pieces of apatite about 2 mm long were observed in a section from Station 281; these were presumed to be eroded particles derived from sharks' teeth. In the nodule sectioned from Station 252 no nucleus was seen for the nodule as a whole; the centre of the core appeared to be an agglomeration of micro-nodules. However small detrital minerals and fragments of altered volcanic rock appeared to furnish nuclei for small concentric areas throughout the nodule. Some, but not all, nodules studied from Station 281 had nuclei of highly altered volcanic rock fragments. Detrital material also formed nuclei for concentric areas within the various layers of the nodules from this station.

In thin section and polished section the nodules were seen to possess characteristic colloform layering. However, the layering is by no means

uniform throughout the nodules. The nodules consist of an inner or core zone and, concentric around this, an outer zone. In the larger nodule, from Station 252, the core zone comprises one-half to one-third the radius, whereas in the smaller nodules from Station 281, it comprises at least two-thirds the radius.

In all the nodules the outer zone consists of well-defined but highly crenulated laminations concentric to the whole nodule. The inner or core zone consists of laminations concentric about local centres, suggesting that in the cores we have closely packed coalescing sub-nodules. However similar local centres are occasionally seen between laminations in the outer zones.

Most of the laminations consist of Mn–Fe oxides, but between them occur discontinuous layers of clastic material, principally quartz, but with some feldspar noted.

The Mn–Fe oxide laminations vary considerably in hardness and reflectivity, both from lamination to lamination and within the laminations themselves. This has always been assumed to be a manifestation of variations in composition of different Mn–Fe layers, but it was necessary to study this question in greater detail with the electron microprobe.

MINERALOGY OF THE NODULES

Although the nodules consist largely of amorphous material, several of the constituents were found to be resolvable by x-ray powder photograph studies made in the British Museum (Natural History), Department of Mineralogy, by Dr. R. J. Davis.

Because of the possible association of high-nickel nodules with todorokite, special attention was given to this possibility, but no todorokite was present in the Redpath nodules studied.

Layer-by-layer studies were made, and the specimen from Station 252 was seen to have a thin outer layer of birnessite in the form of black spherules protruding at the surface. There were also traces of quartz and feldspar in this material. Scrapings of pale brown crystalline surface crust contained quartz and a trace of feldspar. Fragments of the porous outer core, layered, contained quartz and traces of feldspar and 10 Å manganite. The main resolvable manganese mineral of this nodule was, in fact, 10 Å manganite, and the brownish black solid inner core was largely composed of 10 Å manganite, with traces of quartz and feldspar. The iron-rich portions were amorphous. Illite, with quartz and feldspar, was seen in a buff, thick crust on a radial fracture and a brownish thick crust on a circumferential fracture; the clay seemed to be confined to in-filling of cracks in the core.

The nodule from Station 281 was studied in five layers: scrapings from pale brown powdery surface; brownish black massive outer crust; pale brown powdery material on inner surface; pale brown powdery material on fracture of core; brownish black massive core. Mineralogically the nodule was quite homogeneous, as all parts showed δMnO_2 with traces of quartz and feldspar.

In optical studies quartz was, again, seen to be the principal silicate mineral present, with lesser amounts of small plagioclase grains, in specimens from both stations. Much of the silicate material consisted of small broken grains of quartz and plagioclase with unresolved matter thought to be altered volcanic material. In nodules from Station 281 a number of nearly euhedral plagioclase crystals (An 30) were seen in silicate phases throughout the nodule. These appear to have been of phenocrystic origin. The following detrital minerals were also seen in nodules from Station 281: a 1 mm grain of magnetite and numerous small grains; small grains of ilmenite; and a few small grains of rutile.

ELECTRON MICROPROBE ANALYSIS

Electron microprobe techniques

An Acton MS64 (Cameca) instrument was used in the microprobe studies.

Sections of the nodules were cut, fine ground, mounted in epoxy-resin and polished. Because the nodules readily absorb water and form a "muddy" surface layer when wet-polished, they were dry-polished only. The polished specimens were coated with a thin layer of carbon (≈ 200 Å). The operating conditions of the equipment were 15 kv beam voltage and 50 na sample current.

Point analyses

Several areas were carefully selected for quantitative analyses for Fe, Mn, Si, Ni, Co, P, Cu and Ti. The areas were selected on the basis of colour, reflectivity, shape and spectrometer outputs on strip-chart recorders. It was thought that analyses of these areas would account for the principal compositional variations within the nodules.

The analyses were made by taking six 10-second readings within a small area, about 10 microns in diameter. Five consecutive 10-second readings were made on the standards, both before and after the above readings. Background readings were taken on either side of the spectral line position, three readings on either side, both on the standard and unknown. An electron beam diameter of approximately 1 micron was used.

A computer programme containing corrections for drift, deadtime, background, absorption, fluorescence and atomic number was used for the reduction of the data.

Through the use of the microprobe, it has been possible to show that differences in composition between layers do indeed exist, and to correlate layers and segregations of different reflectivities.

Most layers consist of medium hard, light grey to brownish grey oxide. This oxide occurs in both the core and outer zone of the larger nodule of Station 252 and the smaller nodules of Station 281, and serves as a groundmass for the variations to be described (A in Figs. 3 and 4). Three analyses of these layers are given in Columns 1, 4 and 5 of Table 3. This material is all low in Ni (0.24, 0.74 and 0.91) and high in Fe. It is to be noted, however, that, on traversing across these layers, the iron, relative to manganese, gradually and then more quickly decreased as one moved
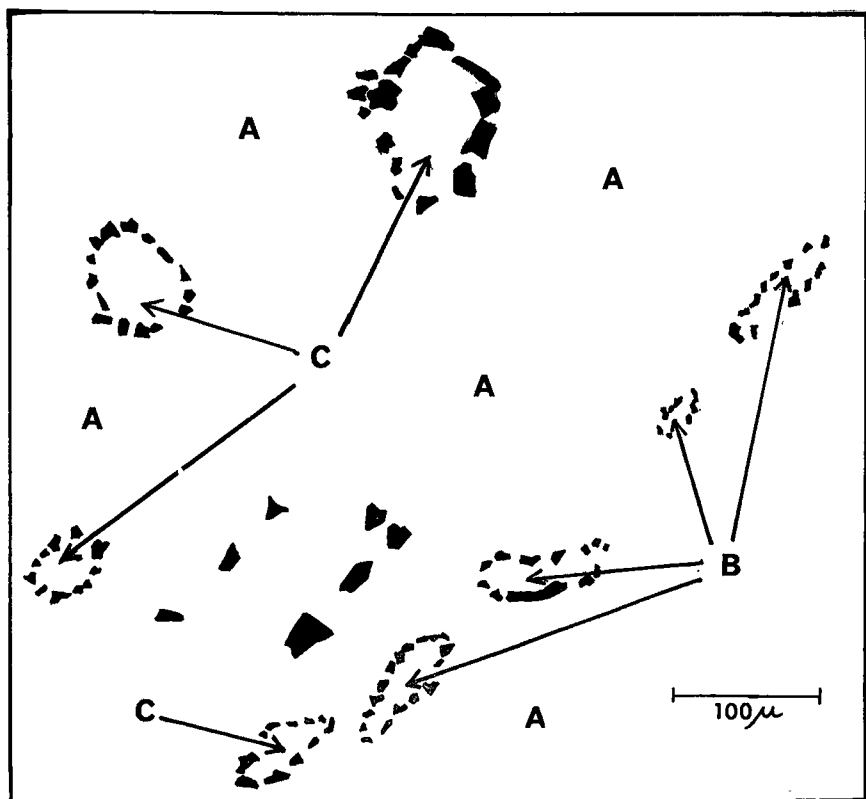
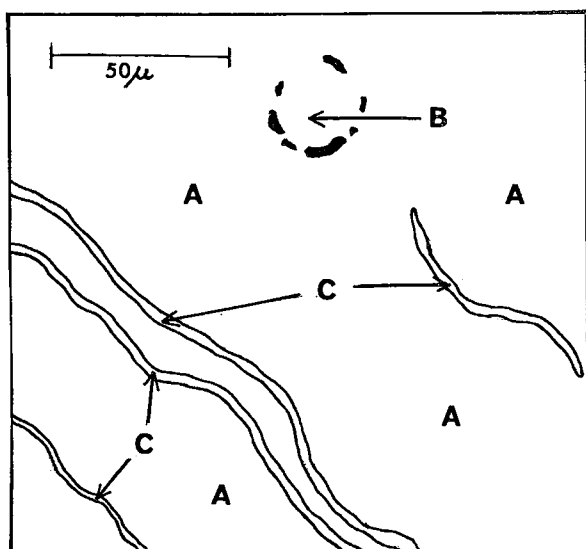FIG. 3. Sketch from polished section of portion of outer zone of large nodule from Station 252.

FIG. 4. Sketch from polished section of portion of small nodule from Station 281.

TABLE 3. COMPOSITIONS OF FE-MN LAMINATIONS AND SEGREGATIONS

	1	2	3	4	5	6	7	8
Fe	17.66	3.59	1.55	14.32	13.68	5.68	3.00	29.59
Mn	25.01	37.40	49.39	28.49	34.69	38.21	35.74	18.20
Si	2.98	0.47	0.78	2.20	1.13	0.57	0.34	2.97
Ni	0.24	1.78	5.31	0.74	0.91	2.26	2.56	0.18
Co	0.38	0.34	0.04	0.47	0.43	0.29	0.22	0.13
P	0.30	0.05	0.03	0.27	0.38	0.19	0.34	0.60
Cu	0.83	1.43	1.64	0.28	0.40	1.00	1.05	0.19
Ti	0.83	0.23	0.09	1.57	0.91	0.36	0.14	0.81

Column 1: A of large nodule, Station 252, Fig. 3.
2: B of large nodule, Station 252, Fig. 3.
3: C of large nodule, Station 252, Fig. 3.
4: Small area in core of large nodule, Station 252.
5: A of small nodule, Station 281, Fig. 4.
6: B of small nodule, Station 281, Fig. 4.
7: C of small nodule, Station 281, Fig. 4.
8: Small rounded area in small nodule, Station 281.

across the layer radially toward the narrow high-nickel laminations to be described.

Narrow, hard, highly reflective laminations 1.0 to 4.0 microns wide occur; these are the crenulated laminations (C of Fig. 4). Equally reflective and hard material also occurs in discontinuous lozenges, ringed by necklaces of clastic silicate grains (B of Figs. 3 and 4). That the

matter in this similar-appearing material is all similar in composition is demonstrated by the analyses in Columns 2, 6 and 7 of Table 3. It will be noted that these are all high in nickel and low in iron.

Somewhat similar-looking material, but in segregations significantly different in shape, rounded to sub-rounded, and ringed by larger and more continuous silicate layers, was found in a nodule from Station 281. This material was found to be very high in iron and abnormally low in nickel (Column 8, Table 3).

Isolated lozenge-shaped areas, of medium hardness and medium grey in colour, also ringed by necklaces of clastic silicate, were found in the outer zone of the large nodule from Station 252 (C in Fig. 3). The material in these segregations is very high in nickel and very low in iron (Column 3, Table 3).

Electron beam scanning

One of these high-nickel segregations from C in Fig. 3 was selected for electron-beam scanning over a 300-micron-square area. A sample-current photomicrograph was taken of this material (Fig. 5). The intensity and distribution of the characteristic x-radiation of the elements analyzed for were recorded on the oscilloscope. In this way, a two-dimensional distribution of the elements could be obtained (Figs. 6, 7, 8, 9, 10).

Electron microprobe results

Studies of the analyses in Table 3 and of the correlation diagrams show that variations in chemical compositions correlate with the areas selected for analyses, and that there exist striking sympathetic and antithetic variations between certain elements. The correlations are shown diagramatically in Figs. 11, 12, 13. Nickel and copper show a strong sympathetic variation, whereas nickel and iron show a very strong antithetic variation. Iron and manganese also show a strong antithetic variation. Copper and nickel vary sympathetically with manganese. These results are in accord with those found by most other workers (Burns & Fuerstenau 1966; Aumento, Lawrence & Plant 1968; Cronan & Tooms 1968), but not all (Gager 1968).

Cobalt did not show consistent variation from sample to sample in the Redpath material. Similarly, Cronan & Tooms (1968) did not find any significant relationship between iron and cobalt in their studies, although Burns & Fuerstenau (1966) appeared to find a positive correlation. It would seem that the relationship of cobalt to the other elements is less clear cut and more variable than that of iron, manganese, copper and nickel.
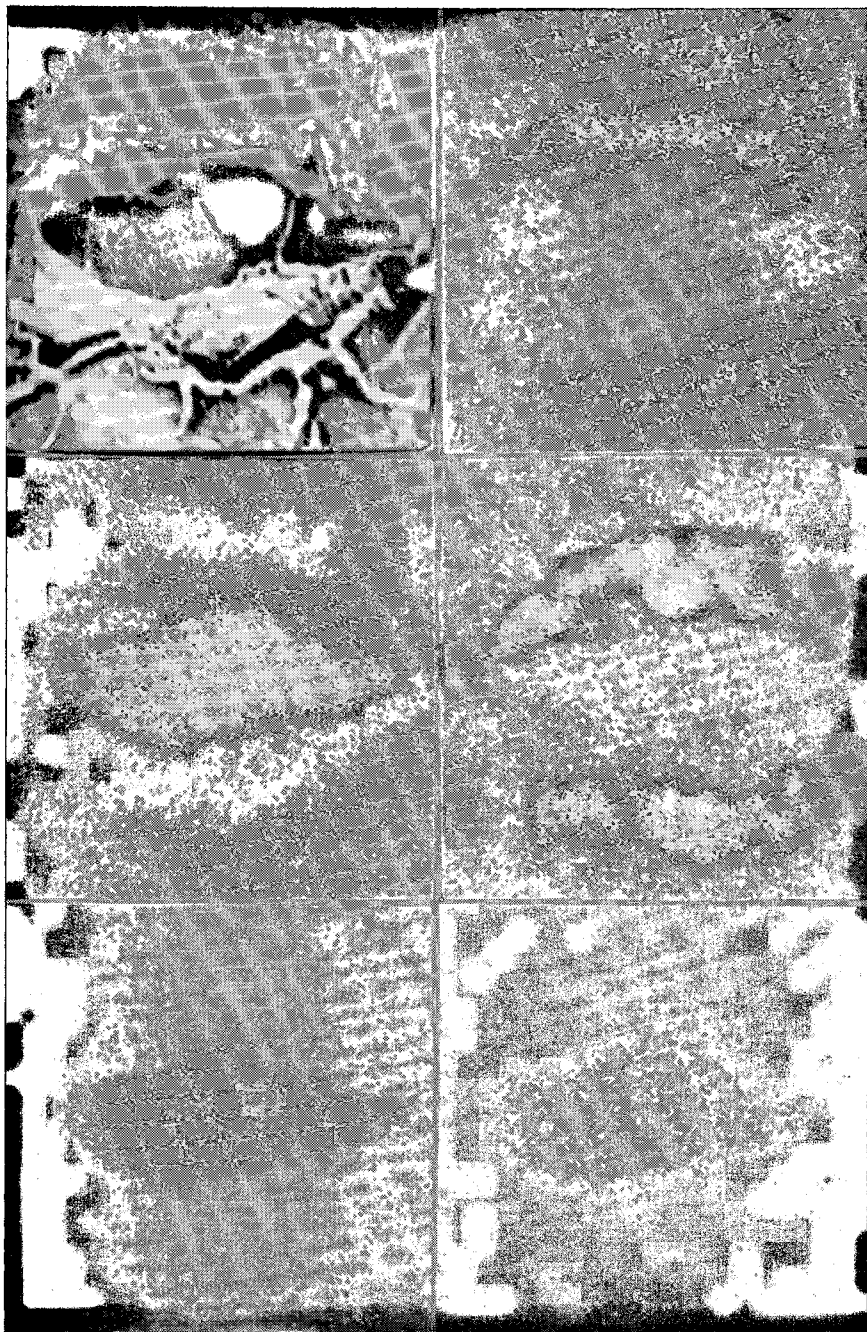
SUMMARY AND CONCLUSIONS

The manganese nodules from Challenger Stations 252 and 281 found in the Redpath Museum collections are seen to be quite typical specimens of two areas in the Central Pacific Ocean, except for dehydration and other changes that have taken place during storage.

Through electron probe studies we have been able to correlate findings from chemical, optical, and x-ray crystallographic studies with the detailed picture of the occurrence and quantities of the different elements within the nodules.

The small nodules from Station 281 appear to have formed from aggregates of several colloidally-precipitated manganese-iron micro-nodules, sometimes, but not always, around a nucleus of altered volcanic material. Since in these nodules the manganese-rich areas are much more crystalline than the iron-rich areas, it may well be, as Cronan & Tooms (1968) have suggested, that the crystallization of the manganese phases provided a mechanism for the formation of rich segregations by the migration of manganese and associated elements such as nickel and copper to centres of crystallization, and the depletion of these elements in the areas between. Once centres of concentration were formed, these areas might continue to be enriched through chemical scavenger action as long as sea-water conditions permitted.

The larger nodules from Station 252 suggest a slightly more complex history. Since no definite nucleus could be observed in the sectioned nodule, the core appears to have been formed from an agglomeration of colloidal particles. The manganese phase is relatively well crystallized to 10 Å manganite and shows nickel and copper enrichment. The clay found filling cracks, in the core only, suggests that some time may have elapsed before the crustal layers were added, perhaps under changed ocean floor conditions. The small but very nickel-rich areas seen in the outer zone of the large nodule may record selective enrichment under particularly

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FIG. 5. (top left) Sample-current photomicrograph of a 300-micron-square area of large nodule from Station 252.

FIG. 6. X-ray photomicrograph showing characteristic x-radiations of Fe from area of Fig. 5.

FIG. 7. (middle left) X-ray photomicrograph showing characteristic x-radiations of Mn from area of Fig. 5.

FIG. 8. X-ray photomicrograph showing characteristic x-radiations of Si from area of Fig. 5.

FIG. 9. (lower-left) X-ray photomicrograph showing characteristic x-radiations of Ni from area of Fig. 5.

FIG. 10. X-ray photomicrograph showing characteristic x-radiations of Cu from area of Fig. 5.
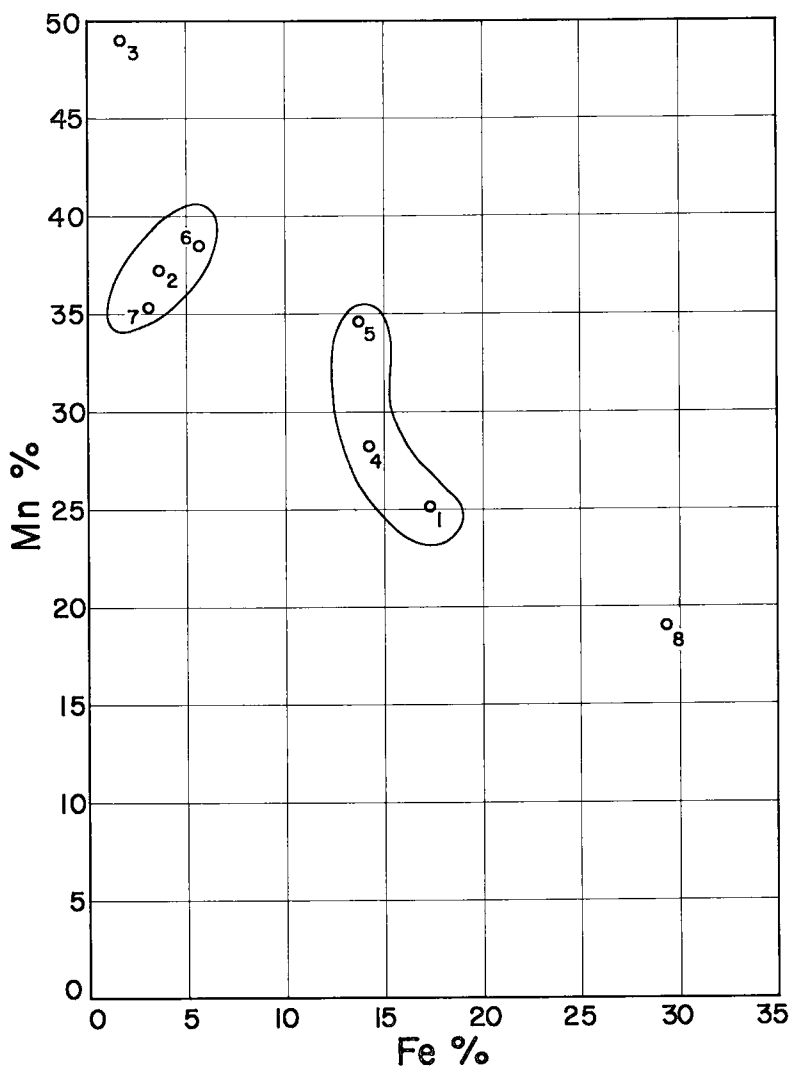
FIG. 11. Correlation diagram for Fe and Mn, Redpath Museum nodules studied with electron microprobe. Numbers refer to columns in Table 3.

favourable conditions for concentration of these elements from enriched sea water through the rather porous crust.

The slight accumulation of birnessite as black material on the outer surface only of the nodule from Station 252 suggests a final period of formation under conditions different from those which preceded it.
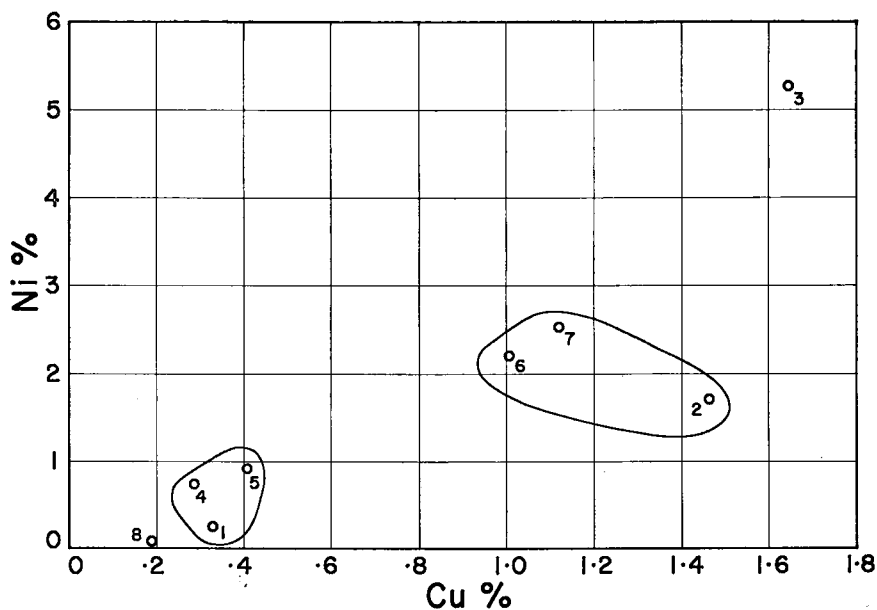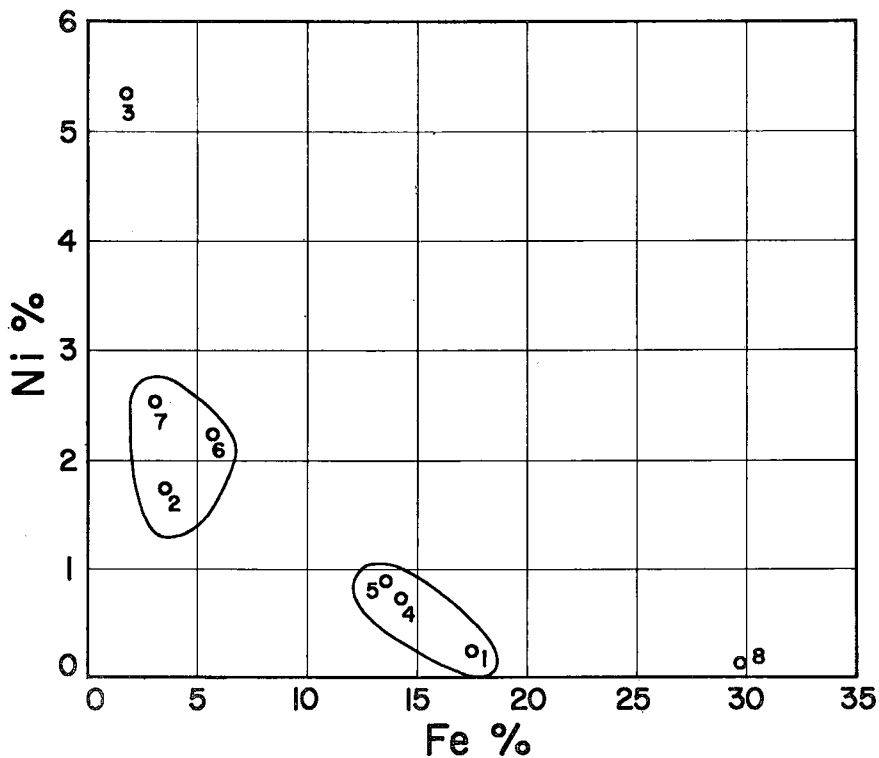
FIG. 12. Correlation diagram for Ni and Cu, Redpath Museum nodules studied with electron microprobe. Numbers refer to columns in Table 3.

FIG. 13. Correlation diagram for Ni and Fe, Redpath Museum nodules studied with electron microprobe. Numbers refer to columns in Table 3.

Jones & Milne (1956) in their study of birnessite from Birness, Scotland, concluded that it was formed by air-oxidation of manganous oxides, and believed that the process was analogous to the oxidation in the laboratory of an alkaline manganous solution which, if prolonged, leads to the formation of "manganous manganite". Frondel, Marvin & Ito (1960) described birnessite resulting from the oxidation of ore on a mine dump at Cummington, Massachusetts, and as a weathering product from old surface workings at Sterling Hill, New Jersey. Since birnessite is found only on the surface of the Redpath nodule, and nowhere inside the nodule itself, it would appear that it is here, also, an oxidation product, developed over the years of storage in the Redpath Museum.

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