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# Mineralogy and Internal Structures of a Ferromanganese Crust from a Seamount, Central Pacific

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# 중앙태평양 해저산지역 망간각의 광물 및 내부구조

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*Abstract*

**A study on the mineralogy and internal features have been carried out on a sample of ferromanganese crust from a Central Pacific seamout. The distribution of manganese mineral vernadite ($\delta$-$MnO_2$) in the different layers indicates typical hydrogenous origin under a continuous change of growth conditions during crustal formation. Various internal structures are discerned within the crust which may be attributed to different growth conditions. The growth structure changes and the distinct break in the formation of the crust at about 2 cm depth are assumed to be the results of Miocene to mid-Pleistocene global palaeoceanographic events.**

요약 : 태평양지역의 200마일 배타적 경제수역에 주로 분포하는 망간각은 평균 1%이상의 코발트를 함유하고 있어 해저광물자원으로 높은 개발가치를 가지고 있다.

중앙태평양 한 해저산에서 채취된 망간각의 내부구조와 광물조성에 대한 연구를 통해 망간각 형성 환경에 따른 성장구조 및 광물성분을 검토하였다. 해양의 높은 산화환경하에서 자생한 수성기원의 버나다이트는 망간각 여러 층내에서 유일한 망간산화물로 존재하며, 망간각 상·하부에서 버나다이트의 다른 산출 상태는 형성기간 동안 지속적으로 변화한 해양 환경을 암시한다. 망간각의 표층으로부터 약 2cm 깊이에 존재하는 성장결층과 내부구조의 변화는 마이오세 이후 현세에 이르기까지 고해양환경에 있었던 일련의 해양변화에서 기인된 것이다.

## INTRODUCTION

Ferromanganese deposits have been described from a number of seamounts and seamount chains by Cronan and Tooms (1969), Heezen et al. (1973), Halbach et al. (1982), Craig et al. (1982), Hein et al. (1985, 1987), Aplin and Cronan (1985), among others. Special studies on crusts have been carried out recently by Glasby and Andrews (1977), Nesteroff (1982), Friedrich and Schmitz-Wiechowski (1980), von Stackelberg et al. (1984), Segl et al. (1984). Because the cobalt content of ferromanganese crusts is often 4-5 times that of deep-sea nodules and some of these deposits lie within the 200-mile "economic zone", they are of particular interest as a marine resource.

In general, the crusts display a range of complex structural features which reflect their complex depositional history. However, no satisfactory explanation of the origin of these structural changes within the crusts has previously been made. This paper presents the results of studies of a ferromanganese crust recovered from a seamount of the Central Pacific. Internal features and mineralogy in the

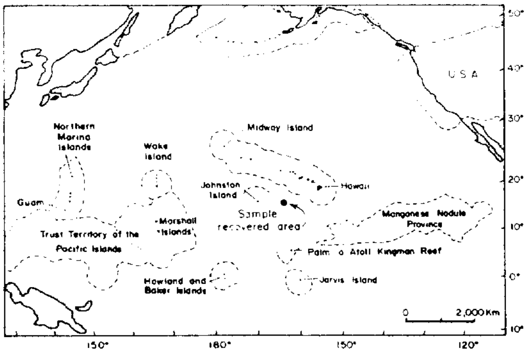

Fig. 1. Location of sampling area (●) and exclusive economic zone (○).

different growth zones through the crust were studied in an attempt to discern environmental controls that may affect ferromanganese oxide concretion in a geological setting. It should be noted that only the mineralogy and the structures over small areas of a single seamount crust has been investigated in this study.

## SAMPLE LOCATION AND DESCRIPTION

A sample of ferromanganese crust was recovered by dredging near the summit of a seamount at a depth of 2,100 m (13° 09'N and 165° 29'W) in the Central Pacific, during the R/V Sonne Cruise in 1985 (Fig. 1).

Fig. 2. The studied ferromanganese crust of 5 cm thickness accreting on substrate.

The sample is slightly rounded in shape and shows two growth stages. The surface at the top is smooth and gently rounded, and the flanks are slightly mammilated as the typical botryoidal growth of ferromanganese materials. The crust has a maximum thickness of about 5 cm, thinning out toward the flank where a thickness of only 1 cm is observed. Layers of different thicknesses are weakly visible and may reflect changes in environmental conditions during deposition and also internal features. Two growth generations can be distinguished by the presence of a growth hiatus existing at the depth of 17 to 24 mm from the surface (Fig. 2).

### *Regional Geology*

The origin of the Mid-Pacific Mountains in the Central Pacific Ocean is genetically related to late Cretaceous basaltic volcanism. According to Clague (1981), the first geologic event of a basaltic eruption was 100 to 106 My. Jackson and Schlanger (1976) proposed that the entire region underwent epeirogenic uplift 80 to 85 My and a covering of shallow water carbonate sediments developed by 70 to 80 My. During the following time, 50 to 60 My, this region began to submerge with intermittent volcanism and continued to subside through the Tertiary period accompanied by the deposition of pelagic calcareous ooze. From Middle Miocene to Late Pliocene, around 12 My, no deposition and/or erosion has taken place because of increased bottom current activity (Nishimura, 1981). This hiatus can be related to the erosional event associated with the development of a large ice cap on Antarctic and the resulting AABW (Antarctic Bottom Water) flow (van Andel et al., 1975). From Late Pliocene, clay sediments with siliceous planktonic tests were again deposited and seamount regions, above the CCD (Carbonate Compensation Depth), thin calcareous ooze layers of Quaternary age have been reported by Halbach et al. (1982).

Table 1. Subsample assemblage of the ferromanganese crust studied

| Subsample | | Main Components | Color | Remarks |
|---|---|---|---|---|
| No. | depth(mm) | | | |
| B-1 | 0-4 | Fe-Mn material with small amount of sediment | dark reddish brown to black from upper part to lower part | younger generation sequence with weak lamination |
| B-2 | 5-10 | | | |
| B-3 | 11-16 | | | |
| B-4 | 17-24 | | | hiatus of growth |
| B-5 | 25-31 | | | older generation sequence with compact and dense material |
| B-6 | 32-35 | | | |
| B-7 | 36-39 | | | |

## METHOD

The crustal sample was prepared by two different methods with the aim of accentuating internal structures as surface expressions and elucidating the mineralogy at each layer.

X-ray diffraction analysis with a Phillips PW 1730 diffractometer (Ni-filtered Cu-K$\alpha$ radiation) was performed on seven subsamples taken at different depths (Table 1). This analysis was carried out in order to determine mineralogical variations from surface (younger layers) to bottom (older layers) within the crust and, if any, between microstructural components. Polished sections were prepared using standard electron probe mounting techniques. Whole crust with a part of the substrate was first embedded within epoxy resin in order to minimize fragmentation and to conserve the original outer growth surface. During this process a vaccum pump was used in order to cause the epoxy to penetrate into the interior of the crust, which tended to solidify and fill the very-small pore spaces. Petrographic features on the well prepared polished section were examined by using a ore microscopy of Leitz orthoplan-pol.

## RESULTS

### *Mineralogy*

It is extremely difficult to determine the mineralogy of ferromanganese oxide deposits by using X-ray techniques because the heterogeneities and complex internal structure of manganese crust make it hard to determine the nature of the mineral crystallites (Burns and Burns, 1977). As mentioned above, all X-ray diffraction patterns studied show high backgrounds with weak, partly diffuse single peaks (Fig. 3).

The main manganese oxide phase in the crust is the vernadite ($\delta$-$MnO_2$) which has been identified by diffraction the lines at 2.4 and 1.4 Å (Burns and Burns, 1977). Todorokite and birnessite are not detected. The second hydrous oxide phase is X-ray amorphous oxyhydroxide. Burns and Burns (1977) have reported that $\delta$-$MnO_2$(vernadite) and $FeOOH \cdot xH_2O$ are highly susceptible to epitaxial intergrowth which leads to an extremely fine-grained mineral association.

The older part of the crust, directly adjacent to substrate, consists almost entirely of X-ray amorphous ferromanganese oxyhydroxide phases and vernadite. The younger part of the crust also consists of amorphous ferromanganese oxyhydroxide phases together with vernadite and small amounts of silicate minerals, mostly quartz and plagioclase. Vernadite was detected in relatively minor amounts in the layers of the younger part when compared to those of the older part. Goethite was not found through nearly all layers but was detected in trace amounts in certain layers of

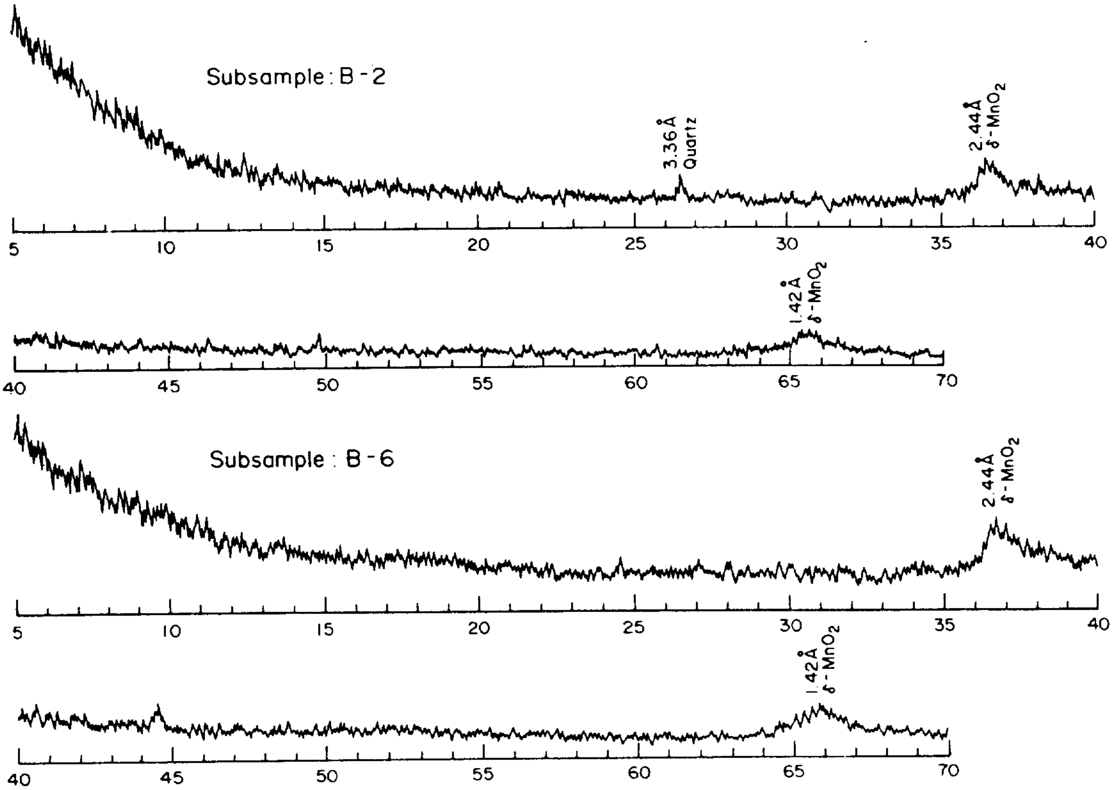

Fig. 3. X-ray diffraction patterns of upper (B-2) and lower part (B-6) of the crust showing dominant vernadite with trace of quartz.

Table 2. Mineral assemblage of the ferromanganese crust as revealed by X-ray diffraction analysis

| Subsample | | Main components | Common components | Traces | Remarks |
|---|---|---|---|---|---|
| No. | depth(mm) | | | | |
| B-1 | 0-4 | amorphous | $\delta$ -MnO$_2$ | quartz | |
| B-2 | 5-10 | amorphous | $\delta$ -MnO$_2$ | quartz | Fig. 3 |
| B-3 | 11-16 | amorphous | $\delta$ -MnO$_2$ | quartz | |
| B-4 | 17-24 | amorphous | $\delta$ -MnO$_2$ | — | |
| B-5 | 25-31 | amorphous | $\delta$ -MnO$_2$ | — | |
| B-6 | 32-35 | amorphous | $\delta$ -MnO$_2$ | — | Fig. 3 |
| B-7 | 36-39 | amorphous | $\delta$ -MnO$_2$ | — | |

the older part. No phosphorite was identified in the crust (Table 2).

Consequently, the manganese oxide phases are slightly different in composition between the two parts. After the first part was formed there was a significant time delay before formation of the second part began. The observed difference in phases seems to be due either to an increasing degree of crystallinity with age caused by consolidation and dehydration, or to changes in environmental conditions during growth of the crust (Friedrich and Schmitz-Wiechowski, 1980).

### Internal Features

The crust shows two different growth gen-

Fig. 4. Textural features of botryoidal growth in gray to white colored laminations. Black specks, seams, and irregular masses are silicates and pore spaces.

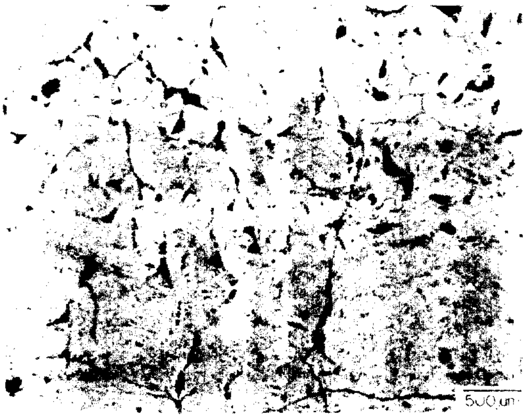

Fig. 5. Typical columnar structure in the upper part of the crust with various sized botryoids and pore spaces.

erations. The older part has a thickenss of 12 to 22 mm and the younger one, 16 to 24 mm. The two growth generations are bounded by a very thin discontinuous phosphorite layer occuring at the depth of 17 to 24 mm from surface, which indirectly implies a change in environmental conditions during the growth of the crust.

The internal structure varies macroscopically with major rhythmic concentric layers, one or more centimeters thick containing sublayers of millimetric range. Ore microscopic studies based on the structural sequence along a traverse crossing the crust from surface to bottom have confirmed differences in the internal structure. Similar to manganese nodules (Sorem and Foster, 1972; Sorem and Fewkes, 1977), ferromanganese crust have various types of lamellae and colloform structures (Friedrich and Schmitz-Wiechowski, 1980).

Columnar structure: the columnar structure consists of radially oriented columns (Fig. 4,5). The columns display a typical botryoidal-colloform texture and each column characteristically shows a delicate branching pattern. This structure occurs predominantly in the upper layers of the younger part.

Compact structure: the compact structure consists of dense layers of isotropic ferromanganese material, which is composed of convex growth laminae of about 1 μm thickness. However, the laminae pinch out contineously, so that individual lamina can not be traced (Fig. 6). The reflectivity in the compact zone is relatively lower than that of the other structure zone, because of the dense and homogeneouse material.

Mottled structure: the mottled structure is characterised by a chaotic layer, discontinuous pattern, and high porosity (Fig. 6). Globules with micro-scale concentric laminations occur within and adjacent to the interstices. Microfossils and approximately 15% clay are contained in the mottled zone.

Contact zone between crust and substrate: The boundary between the crust and the substrate is not uniform. In general, however, there was sharp contact between both (Fig. 7). At the contact between highly altered sediment material and the crust, there is a yellow to white layer mainly composed of nontronite. Nontronite often shows a chemical reaction rim of 50 μm thickness and also is partially penetrated by ferromanganese oxides.

The mixed types of columnar and compact structures are recognized in the interstices and pods at the boundary. Almost all interstices are filled with laminae of ferromanganese ox-

Fig. 6. Ferromanganese-oxide concretions showing two different growth features, compact structure (upper) and mottled structure (lower).

Fig. 7. Ferromanganese-oxide concretions of columnar structure accreting with a relatively sharp contact boundary on substrate.

ides forming well laminated compact structures. Pods and/or cavities are characterized by the presence of globules of ferromanganese oxides composed of concentric layers, similar to micronodules.

## DISCUSSION

It is observed that ferromanganese deposits on seamounts occur as crusts on exposed volcanic or sedimentary rocks, whereas abyssal ferromanganese deposits occur as nodules overlying or embedded within unconsolidated basin sediments. There are two genetic differences between seamount and abyssal ferromanganese deposits. First, the seamount encrustations grow by slow precipitation of inorganic colloidal particles consisting of hydrated metal oxides from near-bottom seawater. Abyssal nodules in deep-sea basin regions are also supplied with metals from the interstitial water by an upward diffusion process of disolved hydrated metal ions (Halbach et al., 1982) in the surface layer of the sediments. This growth occurs in both the top (seawater) and bottom (sediment) facing sides (Raab, 1972). Secondly, there is no apparent influence of the substrate type on crust formation in contrast to abyssal nodules which are sensitive to sediment type (Craig et al., 1982). Ferromanganese crusts are formed by the deposition of Fe and Mn hydroxide flocs from seawater and trace metals are adsorbed on these flocs during their transport through the water column (Toth, 1980). The ferromanganese crusts on exposed hard substrate in the flank of seamount, being unhindered by sediment deposition, are thick and more homogeneous. In contrast, ferromanganese pavements in shelf areas are intermittent its accretion due to isolation of the pavement from the water column by sediment (Craig et al., 1982). In view of these considerations, sediment influx and bottom water circulation are two processes which control the exposure of the substrate surface and the transport of ferromanganese flocs to such a surface for the formation of a ferromanganese oxide deposit.

The environmental complexity such as sediment influx and bottom current velocity is reflected by both the physical and chemical characteristics of marine ferromanganese oxides deposits. The sample of crust examined in this study has visible layers that suggest internal variations in mineralogical composition and in structure. As Glasby and Andrews (1977) have noted in manganese crust from the Hawaiian Ridges, microlaminations of

5-10 $\mu$m wide are recognized and these laminae usually cannot be traced over large areas of the crust, suggesting that the crust accrate in multiple episodes.

X-ray diffraction analysis of seven samples at different positions within the crust (Table 2) show that vernadite is dominant and todorokite is absent. Goethite is concentrated in trace amounts only in the lower part of the crust. The upper layers with brownish yellow lenses consist mainly of quartz and feldspar. There is an upward increase of amorphous ferromanganese oxides and a decrease of vernadite which was presumably caused by a continuous change of growth conditions during formation (Friedrich and Schmitz-Wiechowski, 1980). The mineralogy of the crust dominated by vernadite and with an absence of todorokite is similar to ferromanganese deposits in other seamount and oceanic plateau settings (Cronan, 1977). According to Toth (1980), the mineralogy of a hydrothermal crust is characterized by well crystallized birnessite and/or todorokite. The occurence of vernadite, however, is found in hydrogenetically grown crust (Halbach et al., 1982). The absence of iron-rich layers, confirmed by petrographic study along the substrate/crust contact area, at the base of the crust indicates that ferromanganese accretion is not dependent on catalyzing reactions (Burns and Burns, 1977) or by release of elements due to submarine weathering (Bonatti et al., 1972).

The relatively broad boundary between layers suggests that, although primary accretion processes produce an internal layered structure, the distribution and proportion of iron and manganese minerals were affected by the results of remobilization of elements.

Diagenetic growth by the upward movement of metal ions within the near-surface sediment as predicted for most of the manganese nodules by Calvert and Price (1977) can be excluded for a crust growing on a volcanic substrate. From investigation of the underlying basalt the flux of metals from its weathered surface is insufficient to explain the thickness of the crust. The evidence of diagenesis with increasing crust thickness was found, however, that internal remobilization of elements in the boundary between layers has occured.

Of particular interest is the contact between the substrate material and the overlaying ferromanganese crust. According to Craig et al. (1982), a thin layer of volcanic glass typically defines the contact between fresh volcanic substrates and ferromanganese crust from the Hawaii Islands. With increasing basement age along the Hawaiian Archipelago, substrate materials are progressively more altered and interpenetration of ferromanganese dendrites into the substrate is more common. The substrate/crust contact in the crust is generally sharp but ferromanganese dendrites penetrate into the substrate as deep as nearly 10 $\mu$m in the limited areas of contact with sedimentary material, especially nontronite.

Friedrich and Schmitz-Wiechowski (1980) recently described in detail internal structures of a ferromanganese crust 20-40 cm thick. They distinguished mottled (high porosity and chaotic layers), compact (dense and diffuse convex laminations), columnar (convex growth laminae and cusp-like features) and pillar-like structures (individual cuspate growth laminae). Mottled structures are mainly found in the lower parts of the crust, compact structures occur predominantly in the middle zone, whereas columnar and pillar structures are found alternatively in the upper zone of the crust. However the pillar-like structures were not found in this crust and mottled structures exist only within compact structures at the middle zone of younger part (Fig. 8).

Following the assumptions of Heye (1978) based on the relationship of growth rates and growth structures, compact and mottled structures were regarded as indicators of fast growth by an enhanced supply of iron and sil-

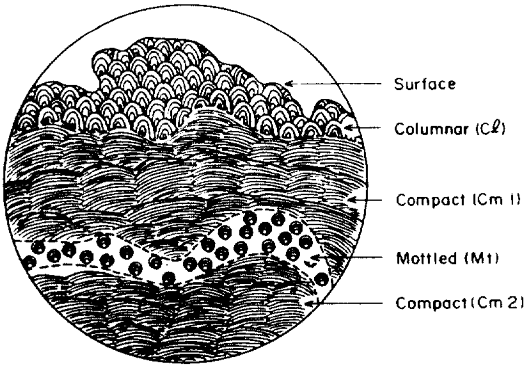

Fig. 8. Sketch of a polished section showing the structural change from columnar through compact (Cm 1) and mottled to compact (Cm 2) in the upper part (0-16 mm depth) of the crust.

icate-derived by weathering of basalt. Columnar and pillar structures were assumed to indicate slow growth rates, mainly due to precipitation from seawater (Friedrich and Schmitz-Wiechowski, 1980). It is accepted that the relative growth rates of ferromanganeses deposit is correlated with the growth structures. Nesteroff (1982) found that the tops of the domes of individual botryoids grow faster than the depressions in between the domes. A lower rate of transformation of sediments in the depressions leads to an accentuation of the topographic irregularities and ulimately results in the formation of botryoidal surface, which is the typical characteristic of colummar structure. Kang (1984), and Kang and Kosakevitch (1984) proposed physical models of botryoidal growth in ferromanganese oxide deposits. On the basis of the physical and chemical models of the formation of ferromanganese oxides, the principal and stable growth feature under normal seawater conditions is the columnar structure rather than the other ones (Kang and Kosakevitch, 1984). Compact and mottled structures might be formed during abnormal sea water conditions, e.g, relatively high current velocity, sediment content, and saturation of mineralizing elements, etc. However, the relative growth rate differences may not be concerned with growth direction, which was interrupted by a period of phosphorite deposition and the younger accretionary layer continuing to the present time. According to Halbach et al. (1982), the younger crust generation of the seamount pavement never exceeds a thickness of about 4 cm and the younger crust with an average thickness of about 2 cm should not be older than 10 My (growth rate assumed by 2 mm/m.y. after Heye and Marchig, 1977). An episode of high phosphorite accumulation occured during Miocene (Arthur and Jenkyns, 1981). From the study of sediment cores near the site at which the present crust was recovered (von Stackelberg, 1979), a hiatus began some 15 My and post-hiatus sedimentation started about 3 My continuing to present time. These two features are above all caused by the increased flow of Antarctic Bottom Water during late Miocene (van Andel et al., 1975; Ciesielski et al., 1982).

The accretion rate of our crust was estimated by two basic assumptions: first, long-term continuous growth conditions (Craig et al., 1982), and secondly, changes of the internal structures of the crust may reflect global palaeoceanographic events (Segl et al., 1984). From this simple consideration, the estimated accretion rates are from 1.7 mm/m.y. to 2.4 mm/m.y. on the basis of occurence of a phosphorite layer at the depth of 17 to 24 mm from surface and the fact that the phosphorite formation occured around 10 My during Miocene (Arthur and Jenkyns, 1981). The estimated accretion rates for the crust studied are comparable to those reported for ferromanganese crust deposits (Craig et al., 1982; Halbach et al., 1983; Segl et al., 1984; von Stackelberg et al., 1984). Craig et al. (1982) calculated the accretion rates as 2.2 to 2.5 mm/m.y. on the basis of maximum thickness of crust and the basement age of rocks at the sample site. Halbach et al. (1983) determined the growth rate values between 0.2 and 2.7 mm/m.y. from the Central Pacific seamount

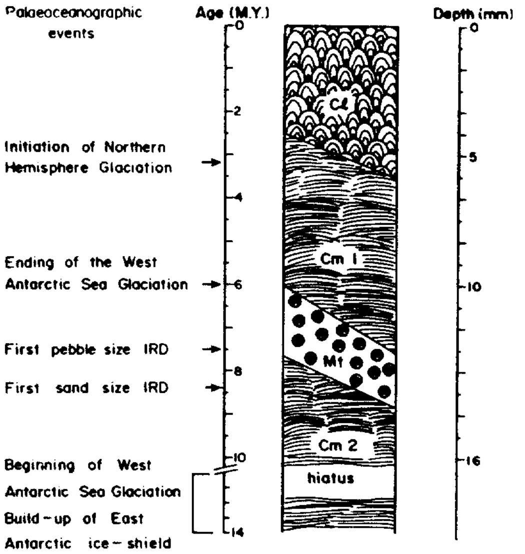

Fig. 9. Assumed ages for the different structures of the upper part and correlation with the palaeoceanographic time markers during late Tertiary to early Quaternary.

assumed by Heye (1978).

The crust is characterized by two different growth phases; the older growth sequence inarea. Mangini et al. (1983) found, using $^{10}$Be-dating, growth rates of 2.7 mm/m.y. for the upper 16 mm and 4.8 mm/m.y. between 16 mm and 38 mm section within a ferromanganese crust.

According to Segl et al. (1984), a frame reference for deriving the age of our sample may be taken from the comprehensive compilation of major Miocene to Mid-Pleistocene events and episodes of Ciesielski et al. (1982). In Fig. 9, the change from columnar structure (Cl) to compact structure (Cm 1) is assumed to correlate with the Northern Hemisphere glaciation dated around 3 My. From compact structure (Cm 1) to mottled structure (Mt), the change correlates with the ending of the West Antarctic Sea glaciation and the beginning of the modern bottom wate circulation dated around 7.4-6.2 My. Evidence for a change in growth pattern at around 6 My is recorded in several other crusts from the North, Central and South Pacific (Segl et al., 1984). Mottled structures intercalated between compact structures Cm 1 and Cm 2 probably coincide with the occurrence of first pebble and sand-size ice-rifted detritus, which is considered to be an indicator for increased Antartic Circumpolar Circulation (Ciesielski et al., 1982). Compact structure Cm 2 corresponds with the ferromanganese deposits after phosphate formation around 10 My. Finally, the growth of the older part began with build-up of the East Antarctic ice shield of 13-16 My (Segl et al., 1984).

The preponderance in interpretation of growth history of ferromanganese oxide accumlation lie, however, on the age determination with the most promising technique, which would certainly help to better understand the growth history of our sample and to justify the conclusions of this study.

## CONCLUSIONS

According to the results presented in this paper:

The crust studied consists of two macroscopically distinguishable main parts which are built up of individual macro and micro layers. The mineralogy is dominated by vernadite and amorphous oxyhydroxides. These facts suggest that the crust was formed by deposition of ferromanganese flocs from seawater.

Internal structures show discrete growth layers and suggest that these deposits accreted intermittently, under the influence of global environmental conditions. The estimated growth rates (approximately 2 mm/m.y.), are comparable to hydrogenous ferromanganese oxide accretion in other deep-sea deposit settings and the accretion process is similar to other ferromanganese deposits.

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