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# Formation age of the dual structure and environmental change recorded in hydrogenetic ferromanganese crusts from Northwest and Central Pacific seamounts

Keisuke Nishi <sup>a,\*</sup>, Akira Usui <sup>b</sup>, Yoshio Nakasato <sup>c</sup>, Hisato Yasuda <sup>d</sup>

<sup>a</sup> Department of Geology, Graduate School of Integrated Arts and Sciences, Kochi University, Japan

<sup>b</sup> Department of Geology, Kochi University, Japan

<sup>c</sup> Sumiko Resources Exploration and Development, Co., Japan

<sup>d</sup> Center for Advanced Marine Core Research, Kochi University, Japan

### A R T I C L E I N F O

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#### ABSTRACT

Thick hydrogenetic ferromanganese (Fe—Mn) crusts from the northwest and central Pacific seamounts often show a distinct dual structure composed of a typical hydrogenetic porous, friable upper part of Fe—Mn oxides (Layer 1) and the underlying dense, hard phosphatized growth generation of Fe—Mn oxides (Layer 2 in this study). Layer 2 always appears above the substrate rock and composes the lower part of the crust; it is never found as the upper crust layer in contact with seawater. The chemical composition of Layer 2 clearly differs from the younger Layer 1 hydrogenetic Fe—Mn oxides, and is depleted in Fe, Al, Ti, and Co, and enriched in Ni, Cu, and Zn relative to Layer 1. The Be isotope age models of the crusts were refined with paleomagnetic and paleontological information, and applied to selected crust samples. The age model indicates fairly continuous growth from the substrate to the surface and fairly constant growth rates during the past 17 Ma. The growth rate from the Miocene to the present has varied by a factor of two, about 2–4 mm/Myr in Layer 1, while Layer 2 has similar but more variable growth rates than Layer 1.

The calculated age for the base of Layer 1, and possibly the age of termination of phosphatization, is never younger than the late Miocene. The age seems to vary with water depth, shallower-water crusts (between 991 and 1575 m) showing a younger age of about 10 Ma whereas the deeper-water (2262 m) crusts have extrapolated ages for the base of Layer 1 of be  $17.1 \pm 2.5$  Ma. This trend indicates that phosphatization took place in a less-oxidizing environment during growth of Layer 2, followed by a weakened oxygen-minimum zone or intensified AABW during growth of Layer 1.

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#### 1. Introduction

Hydrogenetic ferromanganese crusts (hereafter, Fe—Mn crusts) grow by accumulation of Fe and Mn oxides from ambient seawater onto outcrops of volcanic or sedimentary rocks, which serve as a substrate. Fe—Mn crusts extensively occur on the sea floor of the northwest and central Pacific (e.g., Halbach et al., 1989; Usui et al., 1994, Hein et al., 2000) and generally contain 20–30% Mn, 15–20% Fe, 0.5–1.1% Co; 0.3–0.7% Ni in the central Pacific (Hein et al., 1986). Cobalt, Ni, Pt and rare earth elements (REEs) are expected to be economic marine resources in the future. Fe—Mn crusts are potential archives for paleoceanographic and geological environmental changes, such as redox, alkalinity, and tectonic conditions (e.g., Amakawa et al., 1991; Hein et al., 1992; Ling et al., 1997; Ren et al., 2007). Fe—Mn crusts

\* Corresponding author. E-mail address: b14d6a01@s.kochi-u.ac.jp (K. Nishi). have been growing at extremely slow rates of several mm/Myr (e.g., Segl et al., 1984; Puteanus and Halbach, 1988; Usui et al., 2007). The dominant mineral phase is vernadite, a poorly crystalline Fe—Mn oxyhydroxide that may have been influenced by changes in physico-chemical properties in seawater and ocean circulation.

Most hydrogenetic Fe—Mn crusts in the northwest and central Pacific consist of two growth generations: a phosphatized older growth generation and a non-phosphatized younger generation (e.g., Halbach et al., 1989; Koschinsky et al., 1997). We describe this dual structure in detail, using structural, mineralogical, and chemical properties accompanied with chronological data. We refer to this dual structure as Layer 1 (non-phosphatized younger generation) and Layer 2 (phosphatized older generation).

Two or three major episodes of phosphogenesis were determined using Sr isotopes of the phosphate (carbonate fluorapatite (CFA)) as late Eocene through to middle Miocene for equatorial Pacific seamounts (Hein et al., 1993). Those phosphogenesis events are inferred to have







phosphatized the older generations of hydrogenetic Fe—Mn crusts (Hein et al., 2000).

We attempt to determine the boundary age between Layers 1 and 2 by determining the age of the base of Layer 1 and assuming no hiatus between Layers 1 and 2. Age of base of Layer 1 is important to characterize the change of past ocean environment. We confirmed the presence of this dual structure from more than sixty samples from the area between the Kyushu–Palau Ridge to the west and the Mid-Pacific seamounts to the east. Our objectives are to characterize growth structures and mineral and chemical compositions in Layers 1 and 2, and determine the age of the base of Layer 1 using <sup>10</sup>Be/<sup>9</sup>Be isotopes. These data are required to determine the environmental changes that occurred at that time.

#### 2. Samples and geological setting

We selected eight representative samples from more than sixty samples that contain both Layers 1 and 2 (Fig. 1; Table 1). Many of the samples were collected by dredge, and hence accurate water depths were unknown and the upper surface of the crusts might not have been well-preserved. For other sites, we were able to collect in-situ and intact samples without destruction or contamination, using remotely operated vehicle (ROV) manipulators or monitored drill. Six of the eight samples selected were collected with an ROV or a camera-monitored drill (hereafter, BMS: benthic multi-coring system). The ROV enabled us to determine physicochemical data of seawater, such as salinity, temperature, dissolved oxygen and water depth for the time of sample collection. The BMS can collect the crusts together with substrate rocks. Two samples were dated by means of microfossil biostratigraphy as well as <sup>10</sup>Be/<sup>9</sup>Be isotope dating. Therefore, the age data for these samples are accurate enough to discuss the temporal and spatial changes of Fe-Mn oxides with oceanographic profiles and water depth, and to reconstruct the paleoenvironment.

The estimated age of the oceanic crust in the study area is Jurassic to Cretaceous (180.0–139.6 Ma) based on ocean-floor magnetic isochrons (Müller et al., 1997). The estimated ages of the Magellan Seamounts, the Marcus-Wake Seamounts, and the Mid-Pacific Seamounts are 121.0–74.0 Ma, 105.9–81.5 Ma, and 127.6–74.8 Ma, respectively (Clouard and Bonneville, 2005). The samples of this study are located in the Magellan seamounts (Takuyo-Daigo Seamount and JA06 Seamount), near the Marcus-Wake seamounts (JA02 Seamount), and the Mid-Pacific seamounts (JB09 Seamount). MC10CB07 is located in the

Caroline seamounts near the Marshall Islands of which the substrate rock is 82–72 Ma (Okamoto and Usui, 2014).

#### 3. Methods of analysis

The polished thin sections of the crusts were prepared using a new, dry-polishing technique described by Owada et al. (2013). The separated columns through the crusts were sliced at 3 mm intervals perpendicular to the growth structure and ground in an agate mortar after airdrying at 35 °C for 2 h. We analyzed structure and compositional features using an ore microscope, X-ray diffraction (XRD: Rigaku Geigerflex 2038), micro-focus X-ray fluorescence analytical microscope (XGT-7200 V, HORIBA Co.), and Schottky field emission scanning electron microscope/energy dispersive X-ray spectroscopy (JEOL JSM-7001F) at Kochi University. The bulk chemical analyses (ICP-OES/MS) were conducted at the Ontario Geological Survey, Canada (OGS). Mineralogical and chemical analyses were conducted for all powdered samples at 3 mm intervals.

Chemical separation and acceleration mass spectroscope (AMS) analysis were undertaken at the Institute of Geological and Nuclear Science (GNS), New Zealand by I. Graham, A. Zondervan, and R. Ditchburn. <sup>10</sup>Be/<sup>9</sup>Be ratios were measured at approximately 1 cm intervals from the top surface to the bottom of the crusts except for sample #959R08. Details of methods were described by Graham et al. (2004a). In summary, powdered sub-samples < 0.5 g were leached for 30 min in hot 6 M HCl, then measured for natural <sup>9</sup>Be by ICP-OES. The ICP-OES is a custom-built instrument that can resolve spectral interference from vanadium and titanium in the sample matrix, and yields 2% relative precision ( $1\sigma$ ). 1 mg of <sup>9</sup>Be carrier ( $^{10}\text{Be}/^{9}\text{Be} \approx 10^{-14}$  atom atom<sup>-1</sup>) was then added to the remaining leachate for <sup>10</sup>Be analysis that was extracted by hydroxide precipitation and cation exchange chromatography. We used a  $^{10}$ Be/ $^{9}$ Be ratio of 1.29  $\pm$  0.05  $\times$  10<sup>-7</sup> for initial value and half-life of  $^{10}\text{Be}$  of 1.387  $\pm$  0.012 Ma after Oda et al. (2011), Korschinek et al. (2010), and Chmeleff et al. (2010) for calculation. Graham et al. (2004a, 2004b) measured precise <sup>10</sup>Be/<sup>9</sup>Be ratios of deep-sea clay sediments and associated buried manganese nodules whose rim ages are consistent with diatom biostratigraphy, and then validates the utility of <sup>10</sup>Be/<sup>9</sup>Be dating back to 12 Ma and extended the extrapolated ages back to 17 Ma for deep-sea sediments. We discarded all calculated ages older than 17 Ma and verified the Be age by paleomagnetic dating (Oda et al., 2011) and foraminifera paleontology (Yasuda, this study). Furthermore, we estimated the ages towards the bottom by extrapolating the average growth rate beyond the measured ages up to the base of



Fig. 1. Locations of analyzed Fe--Mn crust samples (A-F). Reference samples with dual structure shown as thick crosses.

### Table 1

Sample location and thickness of Layers 1 and 2 of Fe--Mn crusts.

| Location   | Sample no. | Sampling device <sup>a</sup> | Latitude  | Longitude  | Water depth (m) | Layer 1 <sup>b</sup> (mm) | Layer 2 <sup>b</sup> (mm) | Substrate                |  |
|--|------------|------------------------------|-----------|------------|-----------------|---------------------------|---------------------------|--------------------------|--|
| R/V Hakurei-maru No. 2 cruise (Metal Mining Agency of Japan)                                     |            |                              |           |            |                 |                           |                           |                          |  |
| MC10 Smt. (A)  | MC10CB07   | Dredge                       | 9°57.9′N  | 148°16.2′E | 2262            | 60                        | 50                        | Altered volcanic rock    |  |
| JA10 Smt. (Rykachev Guyot) (B)   | JA10AD38   | Dredge                       | 17°03.7′N | 162°39.7′E | 1575            | 45                        | 30                        | Altered volcanic breccia |  |
| JA02 Smt. (Lamont Guyot) (C)   | JA02BMS03A | BMS                          | 21°36.2′N | 159°28.0′E | 1361            | 35                        | 40                        | Altered basalt           |  |
| JA06 Smt. (Penglai Smt.) (D)   | JA06BMS02A | BMS                          | 19°32.3′N | 158°30.5′E | 1284            | 55                        | 65                        | Basalt                   |  |
| JB09 Smt. (E)  | JB09BMS02A | BMS                          | 17°59.7′N | 171°56.4′E | 1260            | 40                        | 35                        | None                     |  |
| NT09-02 Leg2 of the R/V Natsushima cruise (Japan Agency for Marine-earth Science and Technology) |            |                              |           |            |                 |                           |                           |                          |  |
| Takuyo-Daigo Smt. (F)  | HPD#959R08 | ROV                          | 22°50.5′N | 153°12.6′E | 991             | 30                        | 10                        | Limestone?               |  |
| Takuyo-Daigo Smt. (F)  | HPD#958R12 | ROV                          | 22°50.4′N | 153°12.9′E | 1572            | 30                        | 30                        | None                     |  |
| R/V Hakurei cruise (Japan Oil, Gas and Metals National Corporation)                              |            |                              |           |            |                 |                           |                           |                          |  |
| Takuyo-Daigo Smt. (F)  | FPG03      | PG                           | 23°18.4′N | 153°06.1′E | 1142            | 35                        | 40                        | Red ironstone            |  |

<sup>a</sup> BMS: Benthic Multi-coring System, ROV: Remotly Oparated Vehicle, PG: Power Grab.

<sup>b</sup> Layer 1: thickness of non-phosphatized layer, Layer 2: thickness of phosphatized layer.

Layer 1. Thus we use these estimated ages as well as direct isotope ages as valid data back to the early Miocene around 17 Ma.

#### 4. Results

#### 4.1. Growth structures of Fe-Mn crusts

We confirm the well-defined boundary ages of the crusts from more than sixty crust samples from the northwest and central Pacific. We defined the boundary of Layers 1 and 2 that meets all of the following requirements: (1) Fe—Mn oxide layers are impregnated with apatite under the microscope, (2) the abrupt increase in the intensity of apatite is clearly identified by XRD, (3) the phosphorus concentration is 1.0% or more in Layer 2. Fe—Mn crusts examined in this study consist of 2 to 4 distinct sublayers of Layers 1 and 2: Layers 1-a, 1-b, 2-a, and 2-b (Fig. 2).

Layer 1-a, which is mainly the uppermost few millimeters of the crusts, is black to brownish black with a relatively dense structure. Layer 1-b, underlies Layer 1-a, is reddish to brownish black with lots of pores and includes detrital or biogenic sediment. Layer 2 is dense, hard, metallic black and includes sparse detritus. The voids and structures in this layer are characteristically filled or impregnated with apatite. Layer 2-a is black, dense, but also includes microfossils (mainly foraminifera) between growth cusps. Layer 2-b shows a laminated structure, occurs just above the substrate rock, and is black, and extremely dense, with sparse detritus. Layer 2-b is seen only in four of the eight crusts selected for study: FPG03, #959R08, JA06BMS02A, and JA02BMS03A.

Under the microscope, these samples typically display columnar, laminar, mottled, and layered structures (Fig. 3). Layer 1-a contains comparatively short columnar and laminar structures. Layer 1-b shows a long columnar structure and detritus-rich between columns



Fig. 2. Photographs of representative Fe--Mn crust samples. Dashed lines indicate the boundaries of Layers 1 and 2. Scale bars represent 2 cm.



Fig. 3. Photomicrographs of representative structures in analyzed Fe—Mn crust samples under the microscope; (a) Columnar structure common in all samples. (b) Laminar structure with pores and detritus. (c) Dense columnar structure in Layer 2. Pore space is impregnated with apatite. (d) Layered structure generally more dense and less porous.

and mottled structures. Fe—Mn crusts include detritus such as quartz, plagioclase, clay minerals, and other material. Fine-grained detritus occurs in voids associated with columnar structure and coarse-grained detritus is usually in Layer 1-b. Crusts sampled near the equatorial region contain abundant biogenic sediment particles such as foraminifera. Layer 2-a displays dense and mature columnar and mottled structures. Layer 2-b exhibits a layered structure of parallel and partly wavy lamination. The dominant mineral component is vernadite in Layer 2, but the growth structure is partly similar to that of buserite. The amount of detrital minerals in Layer 2 is clearly lower than that in Layer 1. Especially in Layer 2-b, detrital minerals and open voids are rare. No clear evidence of truncation of growth structures, or erosion discontinuities

were seen under the microscope, but these would be hard to detect in laminated, mottled, or massive sections.

#### 4.2. Composition of Fe-Mn crusts

The major Fe—Mn mineral component is vernadite, a hydrous poorly crystalline oxide, which commonly forms by hydrogenetic precipitation from seawater (Usui et al., 1986). Generally, minor and trace elements are mainly associated with five mineral components in the crusts; vernadite, amorphous Fe oxyhydroxide, detrital aluminosilicates, apatite, and biogenic skeletons. For example, Mn, Co, and Ni are



Fig. 4. Depth profile of composition of selected elements in the two Fe--Mn crusts.

associated with the vernadite and Si, Al, and K always comprise part of the detrital phase (Koschinsky and Halbach, 1995; Hein et al., 2000).

Layer 1 is composed of mainly vernadite, quartz, and plagioclase, lesser smectite and calcite, and rarely phillipsite or buserite as determined by XRD. Layer 2 always includes vernadite and apatite, and rarely quartz and plagioclase. The X-ray intensities of quartz and plagioclase vary with water depth and time. The detritus in the crusts is low at a depth of approximately 1000 m, and are more abundant in samples from deeper waters.

The amounts of Fe and Mn vary from the base to surface of crusts in Layers 1 and 2 (Figs. 4, 5). In Layer 1, except for crust MC10CB07 taken from the equatorial area, Mn and Ti usually decrease but Fe content increases from the boundary of the two layers to the surface. Aluminum contents of crusts JA10AD38, JA06BMS02A, and MC10CB07 are highest in Layer 2-b, and for the others, Al increases from the substrate to the surface of the crusts. The concentrations of Fe, Al, Ti and Co are low in Layer 2 compared to Layer 1; Layer 2 shows slightly higher concentrations of Ni, Cu, and Zn; specifically, the average Fe, Al, and Ti concentrations in Layer 1 are approximately 13%, 0.9%, and 1.0% compared to 6.1%, 0.3%, and 0.4%, respectively in Layer 2.

### 4.3. Growth rate of crusts and age of the base of Layer 1

We firstly compared the  ${}^{10}\text{Be}/{}^9\text{Be}$  ratio of modern seawater with the extrapolated ratio at the top surface for each sample to check whether the crust was actively growing (Table 2). Thus the extrapolated  ${}^{10}\text{Be}/{}^9\text{Be}$  ratio using top two data sets of the crusts falls between  $0.95 \times 10^{-7}$  and  $1.30 \times 10^{-7}$  (average  $1.14 \times 10^{-7}$ ) within analytical error. This range is similar to the measured  ${}^{10}\text{Be}/{}^9\text{Be}$  ratio of modern seawater in the north Pacific ( $1.19 \times 10^{-7}$ ; von Blanckenburg and Bouchez, 2014). This result indicates that the surface age is approximately zero within analytical error. The Be isotope age model (Fig. 6) suggests that the crusts have grown continuously and constantly at approximately 2–4 mm/Myr within Layer 1 without any significant break, except for a faster rate in part for MC10CB07 and JA10AD38. The growth rate can change for example due to detrital supply (see increase of Al >3 wt.% at 20–30 mm depths in JA10AD38).

The well-preserved planktonic foraminifera found in sections of the crusts MC10CB07 and JA10AD38 indicates typical Miocene age, for example, *Orbulina bilobata*, *O. suturalis*, *O. universa*, *Globigerinoides triloba*, *G. immaturus*, *G. dehiscens*, *G. baroemoenensis*, and *Praeorbulina glomerosa*. The genus *Orbulina* was clearly identified on the basis of its

characteristic shape of a single globular structure of two chambers. We did not observe species of the *Morozovella* group, characteristic of the Paleogene, or the typical Cretaceous planktonic foraminiferal genus *Globotruncana*. Among the species, *Praeorbulina glomerosa* identified at 85 mm depth (measured Be age is around 17 Ma) of MC10CB07 crust specifically denotes the Zone N8–N9 (around 17–14 Ma). All other identified ages of the Neogene foraminifera and <sup>10</sup>Be/<sup>9</sup>Be ages are generally consistent and cover Layer 1, indicating the period of growth of crusts from the early-middle Miocene to the present.

We also calculated the age of the base of Layer 1 by linear extrapolation of growth rates in the younger parts, assuming a constant and continuous growth pattern throughout Layer 1. This has been applied to thick ferromanganese crusts in earlier literatures as old as 26 Ma (Ling et al., 1997). Most of the calculated ages of the base of Layer 1 are Miocene and Layer 2 is never younger than Miocene. These ages change broadly with water depth, and the shallowest depth sample shows about 10 Ma, and the deepest-water sample shows 17.1  $\pm$  2.5 Ma. There is no evidence of a temporal hiatus at the boundary of Layers 1 and 2, if we assume that all measured Be isotope ages are reliable.

#### 5. Discussion

#### 5.1. Reliability of <sup>10</sup>Be/<sup>9</sup>Be dating and growth patterns

The Be isotope technique has been first thought questionable due to possible post-depositional remobilization (Ku et al., 1982). However, recalculation of the diffusivity of Be ( $<10^{-9}$  cm<sup>2</sup>/year) showed the highly immobile nature of Be in the crusts (Henderson and Burton, 1999). Oda et al. (2011) supported the reliability of <sup>10</sup>Be/<sup>9</sup>Be dating by comparison with another independent method of ultrafine-scale magnetostratigraphy using SQUID (superconducting quantum interference device) microscopy. The <sup>10</sup>Be/<sup>9</sup>Be ratio is the most widely used and now the most reliable technique for dating ferromanganese crusts and nodules back to about 12-10 Ma (Hein et al., 2000), although paleontological, radiochemical (U-series isotopes), stable isotopes (Os isotopic ratios compared to sea water values), and paleomagnetic techniques (Joshima and Usui, 1998; Oda et al., 2011) have been successfully used (O'nion et al., 1998; Reynolds et al., 1999; Nielsen et al., 2009; Horner et al., 2015). Graham et al. (2004a) measured the <sup>10</sup>Be/<sup>9</sup>Be ratios of deep-sea clay sediments with associated buried ferromanganese nodules, and the sediment ages were determined up to 18.4 Ma, but this age was calculated using the old half-life of <sup>10</sup>Be (1.5 Myr), corrected as 16.7 Ma using recent data (Korschinek et al., 2010). In this paper,



Fig. 5. Histograms in comparison of major and minor element concentrations of Layers 1 and 2.

| Table | 2 |
|-------|---|
|       |   |

40.0-45.0

55.0-60.0

<sup>10</sup>Be/<sup>9</sup>Be ratios and ages of Fe--Mn crusts.

| mm $(\pm 2\sigma)$ $hgc (hu)$ mm $(\pm 2\sigma)$ $hgc (hu)$ MC10CB07JB09BMS02ASurface $1.24 \times 10^{-7}$ $Surface$ $1.08 \times 10^{-7}$ $0-3.0$ $1.08 \pm 0.04 \times 10^{-7}$ $0.4$ $0-3.0$ $9.54 \pm 0.59 \times 10^{-8}$ $0.6$ $9.0-12.0$ $1.11 \pm 0.05 \times 10^{-8}$ $4.9$ $6.0-9.0$ $4.35 \pm 0.26 \times 10^{-8}$ $2.2$ $15.0-18.0$ $2.49 \pm 0.11 \times 10^{-9}$ $7.9$ $12.0-15.0$ $1.19 \pm 0.07 \times 10^{-8}$ $4.8$ $44.5-47.5$ $3.61 \pm 0.41 \times 10^{-11}$ $16.4$ $18.0-21.0$ $4.49 \pm 0.27 \times 10^{-9}$ $6.7$ $68.5-75.5$ $2.74 \pm 0.41 \times 10^{-11}$ $16.9$ $25.0-29.0$ $2.06 \pm 0.13 \times 10^{-9}$ $8.3$ $34.0-39.0$ $9.30 \pm 0.77 \times 10^{-10}$ $9.9$ $34.0-39.0$ $9.30 \pm 0.77 \times 10^{-10}$ $9.9$ <b>JA10AD38</b> 4.06 \times 10^{-7}4.00 $25.0-28.5$ $3.12 \pm 0.24 \times 10^{-9}$ $7.4$ $9.5-12$ $6.26 \pm 0.38 \times 10^{-8}$ $4.0$ $28.5-32.0$ $2.68 \pm 0.21 \times 10^{-9}$ $7.8$ $17-19.5$ $2.62 \pm 0.18 \times 10^{-9}$ $7.8$ $17.19.5 \times 10.2^{-9}$ $8.3$ $17-19.5$ $2.62 \pm 0.18 \times 10^{-9}$ $7.8$ $12.2 \times 10.24 \times 10^{-9}$ $7.8$   | Depth      | <sup>10</sup> Be/ <sup>9</sup> Be                       | Age (Ma)  | Depth      | <sup>10</sup> Be/ <sup>9</sup> Be | Age (Ma)   |
|--|------------|---|-----------|------------|-----------------------------------|------------|
| $\begin{array}{c c c c c c c c } \mbox{MC10CB07} & JB09BMS02A & JD^{-7} & Surface & 1.08 \times 10^{-7} & Surface & 1.08 \times 10^{-7} & 0.4 & 0^{-3.0} & 9.54 \pm 0.59 \times 10^{-8} & 0.6 & 0.9 & 0.54 \pm 0.59 \times 10^{-8} & 0.6 & 0.9 & 0.54 \pm 0.59 \times 10^{-8} & 0.6 & 0.9 & 0.55 \pm 0.26 \times 10^{-8} & 2.2 & 0.55 & 0.5$ | mm         | $(\pm 2\sigma)$   | nge (wid) | mm         | $(\pm 2\sigma)$                   | Age (Ivia) |
| Surface $1.24 \times 10^{-7}$ Surface $1.08 \times 10^{-7}$ 0-3.0 $1.08 \pm 0.04 \times 10^{-7}$ 0.4 $0-3.0$ $9.54 \pm 0.59 \times 10^{-8}$ 0.69.0-12.0 $1.11 \pm 0.05 \times 10^{-8}$ 4.9 $6.0-9.0$ $4.35 \pm 0.26 \times 10^{-8}$ 2.215.0-18.0 $2.49 \pm 0.11 \times 10^{-9}$ 7.9 $12.0-15.0$ $1.19 \pm 0.07 \times 10^{-8}$ 4.844.5-47.5 $3.61 \pm 0.41 \times 10^{-11}$ 16.4 $18.0-21.0$ $4.49 \pm 0.27 \times 10^{-9}$ 6.7 $68.5-75.5$ $2.74 \pm 0.41 \times 10^{-11}$ 16.9 $25.0-29.0$ $2.06 \pm 0.13 \times 10^{-9}$ 8.3JAIOAD38 $34.0-39.0$ $9.30 \pm 0.77 \times 10^{-10}$ 9.9JAIOAD38 $4.0 - 49.0$ $1.56 \pm 0.30 \times 10^{-10}$ 13.4Surface $1.06 \times 10^{-7}$ $4.0$ $25.0-28.5$ $3.12 \pm 0.24 \times 10^{-9}$ 7.4 $4.5-7$ $1.78 \pm 0.10 \times 10^{-8}$ $4.0$ $28.5-32.0$ $2.68 \pm 0.21 \times 10^{-9}$ 7.4 $9.5-12$ $6.26 \pm 0.38 \times 10^{-9}$ $6.1$ $28.5-32.0$ $2.68 \pm 0.21 \times 10^{-9}$ 7.8 $17-19.5$ $2.62 \pm 0.18 \times 10^{-9}$ $7.8$ $120 \pm 0.05 \times 10^{-9}$ $7.8$  | MC10CB07   |   |           | JB09BMS02A |                                   |            |
|  | Surface    | $1.24 \times 10^{-7}$                                   |           | Surface    | $1.08 \times 10^{-7}$             |            |
| 9.0-12.0 $1.11 \pm 0.05 \times 10^{-8}$ 4.9 $6.0-9.0$ $4.35 \pm 0.26 \times 10^{-8}$ 2.2         15.0-18.0 $2.49 \pm 0.11 \times 10^{-9}$ 7.9 $12.0-15.0$ $1.19 \pm 0.07 \times 10^{-8}$ 4.8         44.5-47.5 $3.61 \pm 0.41 \times 10^{-11}$ 16.4 $18.0-21.0$ $4.49 \pm 0.27 \times 10^{-9}$ 6.7 $68.5-75.5$ $2.74 \pm 0.41 \times 10^{-11}$ 16.9 $25.0-29.0$ $2.06 \pm 0.13 \times 10^{-9}$ 8.3 $34.0-39.0$ $9.30 \pm 0.77 \times 10^{-10}$ 9.9 $4.35 \pm 0.00 \times 10^{-10}$ 9.9       13.4         Surface $1.06 \times 10^{-7}$ $4.0 - 49.0$ $1.56 \pm 0.30 \times 10^{-10}$ 13.4         Surface $1.06 \times 10^{-7}$ $4.0$ $25.0-28.5$ $3.12 \pm 0.24 \times 10^{-9}$ 7.4 $4.5-7$ $1.78 \pm 0.10 \times 10^{-8}$ $4.0$ $25.0-28.5$ $3.12 \pm 0.24 \times 10^{-9}$ 7.4 $9.5-12$ $6.26 \pm 0.38 \times 10^{-9}$ $6.1$ $28.5-32.0$ $2.68 \pm 0.21 \times 10^{-9}$ $7.8$ $17-19.5$ $2.62 \pm 0.18 \times 10^{-9}$ $7.8$ $7.8$ $7.9$ $7.8$ $7.8$ $7.8$ $7.9$ $7.8$ $7.9$ $7.8$ $7.8$ $7.9$ $7.8$ $7.9$ $7$   | 0-3.0      | $1.08 \pm 0.04 	imes 10^{-7}$                           | 0.4       | 0-3.0      | $9.54 \pm 0.59 \times 10^{-8}$    | 0.6        |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$  | 9.0-12.0   | $1.11 \pm 0.05 \times 10^{-8}$                          | 4.9       | 6.0-9.0    | $4.35 \pm 0.26 \times 10^{-8}$    | 2.2        |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$  | 15.0-18.0  | $2.49 \pm 0.11 \times 10^{-9}$                          | 7.9       | 12.0-15.0  | $1.19 \pm 0.07 \times 10^{-8}$    | 4.8        |
| $68.5-75.5$ $2.74 \pm 0.41 \times 10^{-11}$ $16.9$ $25.0-29.0$ $2.06 \pm 0.13 \times 10^{-9}$ $8.3$ $34.0-39.0$ $9.30 \pm 0.77 \times 10^{-10}$ $9.9$ <b>JA10AD38</b> $44.0-49.0$ $1.56 \pm 0.30 \times 10^{-10}$ $13.4$ Surface $1.06 \times 10^{-7}$ $44.0-49.0$ $1.56 \pm 0.30 \times 10^{-10}$ $13.4$ $0-2.0$ $9.09 \pm 0.58 \times 10^{-8}$ $0.7$ <b>HPD#959R08</b> $7.4$ $4.5-7$ $1.78 \pm 0.10 \times 10^{-8}$ $4.0$ $25.0-28.5$ $3.12 \pm 0.24 \times 10^{-9}$ $7.4$ $9.5-12$ $6.26 \pm 0.38 \times 10^{-9}$ $6.1$ $28.5-32.0$ $2.68 \pm 0.21 \times 10^{-9}$ $7.8$ $17-19.5$ $2.62 \pm 0.18 \times 10^{-9}$ $7.8$ $7.4$ $7.4$ $7.4$ $12.245$ $2.09 \pm 0.15 \times 10^{-9}$ $8.2$ <b>HDT#055P12</b> $7.4$ $7.4$   | 44.5-47.5  | $3.61 \pm 0.41 \times 10^{-11}$                         | 16.4      | 18.0-21.0  | $4.49 \pm 0.27 \times 10^{-9}$    | 6.7        |
| JA10AD38 $34.0-39.0$ $9.30 \pm 0.77 \times 10^{-10}$ $9.9$ JA10AD38 $44.0-49.0$ $1.56 \pm 0.30 \times 10^{-10}$ $13.4$ Surface $1.06 \times 10^{-7}$ HPD#959R08       74 $0-2.0$ $9.09 \pm 0.58 \times 10^{-8}$ $0.7$ HPD#959R08 $3.12 \pm 0.24 \times 10^{-9}$ $7.4$ $4.5-7$ $1.78 \pm 0.10 \times 10^{-8}$ $4.0$ $25.0-28.5$ $3.12 \pm 0.24 \times 10^{-9}$ $7.4$ $9.5-12$ $6.26 \pm 0.38 \times 10^{-9}$ $6.1$ $28.5-32.0$ $2.68 \pm 0.21 \times 10^{-9}$ $7.8$ $17-19.5$ $2.62 \pm 0.18 \times 10^{-9}$ $7.8$ $7.4$ $7.4$ $7.4$ $12.245$ $2.09 \pm 0.15 \times 10^{-9}$ $8.2$ HPD#0558P12 $7.4$  | 68.5-75.5  | $2.74 \pm 0.41 \times 10^{-11}$                         | 16.9      | 25.0-29.0  | $2.06 \pm 0.13 \times 10^{-9}$    | 8.3        |
| JA10AD38 $44.0-49.0$ $1.56 \pm 0.30 \times 10^{-10}$ $13.4$ Surface $1.06 \times 10^{-7}$ $1.56 \pm 0.30 \times 10^{-10}$ $13.4$ $0-2.0$ $9.09 \pm 0.58 \times 10^{-8}$ $0.7$ HPD#959R08 $4.5-7$ $1.78 \pm 0.10 \times 10^{-8}$ $4.0$ $25.0-28.5$ $3.12 \pm 0.24 \times 10^{-9}$ $7.4$ $9.5-12$ $6.26 \pm 0.38 \times 10^{-9}$ $6.1$ $28.5-32.0$ $2.68 \pm 0.21 \times 10^{-9}$ $7.8$ $17-19.5$ $2.62 \pm 0.18 \times 10^{-9}$ $7.8$ $22.245$ $20.9 \pm 0.15 \times 10^{-9}$ $8.2$ HPD#058P12  |            |   |           | 34.0-39.0  | $9.30 \pm 0.77 \times 10^{-10}$   | 9.9        |
| Surface $1.06 \times 10^{-7}$ 0-2.0 $9.09 \pm 0.58 \times 10^{-8}$ $0.7$ HPD#959R084.5-7 $1.78 \pm 0.10 \times 10^{-8}$ $4.0$ $25.0-28.5$ $3.12 \pm 0.24 \times 10^{-9}$ $7.4$ 9.5-12 $6.26 \pm 0.38 \times 10^{-9}$ $6.1$ $28.5-32.0$ $2.68 \pm 0.21 \times 10^{-9}$ $7.8$ 17-19.5 $2.62 \pm 0.18 \times 10^{-9}$ $7.8$ 17-20.5 $2.09 \pm 0.15 \times 10^{-9}$ $8.2$ HPD#058P12   | JA10AD38   |   |           | 44.0-49.0  | $1.56 \pm 0.30 \times 10^{-10}$   | 13.4       |
| $0-2.0$ $9.09 \pm 0.58 \times 10^{-8}$ $0.7$ HPD#959R08 $4.5-7$ $1.78 \pm 0.10 \times 10^{-8}$ $4.0$ $25.0-28.5$ $3.12 \pm 0.24 \times 10^{-9}$ $7.4$ $9.5-12$ $6.26 \pm 0.38 \times 10^{-9}$ $6.1$ $28.5-32.0$ $2.68 \pm 0.21 \times 10^{-9}$ $7.8$ $17-19.5$ $2.62 \pm 0.18 \times 10^{-9}$ $7.8$ $7.4$ $7.4$ $7.4$  | Surface    | $1.06 \times 10^{-7}$                                   |           |            |                                   |            |
| 4.5-7 $1.78 \pm 0.10 \times 10^{-8}$ 4.0 $25.0-28.5$ $3.12 \pm 0.24 \times 10^{-9}$ 7.4         9.5-12 $6.26 \pm 0.38 \times 10^{-9}$ $6.1$ $28.5-32.0$ $2.68 \pm 0.21 \times 10^{-9}$ 7.8         17-19.5 $2.62 \pm 0.18 \times 10^{-9}$ 7.8       7.8       7.8         22.245 $2.09 \pm 0.15 \times 10^{-9}$ 8.2       HDD #055P12  | 0-2.0      | $9.09 \pm 0.58 \times 10^{-8}$                          | 0.7       | HPD#959R08 |                                   |            |
| 9.5-12 $6.26 \pm 0.38 \times 10^{-9}$ $6.1$ $28.5-32.0$ $2.68 \pm 0.21 \times 10^{-9}$ $7.8$ 17-19.5 $2.62 \pm 0.18 \times 10^{-9}$ $7.8$ 22.245 $2.09 \pm 0.15 \times 10^{-9}$ $8.2$  | 4.5-7      | $1.78 \pm 0.10 	imes 10^{-8}$                           | 4.0       | 25.0-28.5  | $3.12 \pm 0.24 	imes 10^{-9}$     | 7.4        |
| 17-19.5 $2.62 \pm 0.18 \times 10^{-9}$ 7.8<br>22.245 $2.09 \pm 0.15 \times 10^{-9}$ 8.2 HDD#058P12   | 9.5-12     | $6.26 \pm 0.38 \times 10^{-9}$                          | 6.1       | 28.5-32.0  | $2.68 \pm 0.21 \times 10^{-9}$    | 7.8        |
| $22.245$ $2.08 \pm 0.15 \times 10^{-9}$ $8.2$ <b>UDD#058D13</b>  | 17-19.5    | $2.62 \pm 0.18 \times 10^{-9}$                          | 7.8       |            |                                   |            |
| 22-24.J 2.00 ± 0.13 × 10 0.3 <b>ΠΓυ#330Κ12</b>   | 22-24.5    | $2.08 \pm 0.15 \times 10^{-9}$                          | 8.3       | HPD#958R12 |                                   |            |
| 27-29.5 $1.74 \pm 0.12 \times 10^{-9}$ 8.6 Surface $9.48 \times 10^{-8}$   | 27-29.5    | $1.74 \pm 0.12 \times 10^{-9}$                          | 8.6       | Surface    | $9.48 \times 10^{-8}$             |            |
| $41-43.5 		 2.34 \pm 0.32 \times 10^{-10} 		 12.6 		 0-3.0 		 8.66 \pm 0.40 \times 10^{-8} 		 0.8$   | 41-43.5    | $2.34 \pm 0.32 \times 10^{-10}$                         | 12.6      | 0-3.0      | $8.66 \pm 0.40 	imes 10^{-8}$     | 0.8        |
| 53.5-56 $2.38 \pm 1.18 \times 10^{-11}$ 17.2 15.0-18.0 $4.70 \pm 0.23 \times 10^{-9}$ 6.6  | 53.5-56    | $2.38 \pm 1.18 \times 10^{-11}$                         | 17.2      | 15.0-18.0  | $4.70 \pm 0.23 \times 10^{-9}$    | 6.6        |
| $30.0-33.0 \qquad \qquad 6.86 \pm 0.43 \times 10^{-10} \qquad \qquad 10.5$   |            |   |           | 30.0-33.0  | $6.86 \pm 0.43 \times 10^{-10}$   | 10.5       |
| JA02BMS03A   | JA02BMS03A |   |           |            |                                   |            |
| Surface $1.08 \times 10^{-7}$ <b>FPC03</b>   | Surface    | $1.08 \times 10^{-7}$                                   |           | FPG03      |                                   |            |
| 0-4.0 $8.01 \pm 0.46 \times 10^{-8}$ 1.0 Surface $1.26 \times 10^{-7}$   | 0-4.0      | $8.01 \pm 0.46 \times 10^{-8}$                          | 1.0       | Surface    | $1.26 \times 10^{-7}$             |            |
| 4.0-6.0 $3.85 \pm 0.25 \times 10^{-8}$ 2.4 0-3.0 $1.12 \pm 0.07 \times 10^{-7}$ 0.3  | 4.0-6.0    | $3.85 \pm 0.25 	imes 10^{-8}$                           | 2.4       | 0-3.0      | $1.12 \pm 0.07 	imes 10^{-7}$     | 0.3        |
| 6.0-9.0 $2.48 \pm 0.16 \times 10^{-8}$ $3.3$ $9.0-12.0$ $3.26 \pm 0.21 \times 10^{-8}$ $2.8$   | 6.0-9.0    | $2.48 \pm 0.16 \times 10^{-8}$                          | 3.3       | 9.0-12.0   | $3.26 \pm 0.21 \times 10^{-8}$    | 2.8        |
| 12.0-15.0 $6.95 \pm 0.50 \times 10^{-9}$ 5.818.0-21.0 $9.47 \pm 0.61 \times 10^{-9}$ 5.2   | 12.0-15.0  | $6.95 \pm 0.50 \times 10^{-9}$                          | 5.8       | 18.0-21.0  | $9.47 \pm 0.61 	imes 10^{-9}$     | 5.2        |
| $18.0-21.0 		 2.77 \pm 0.20 \times 10^{-9} 		 7.7 		 27.0-30.0 		 1.91 \pm 0.13 \times 10^{-9} 		 8.4$   | 18.0-21.0  | $2.77 \pm 0.20 \times 10^{-9}$                          | 7.7       | 27.0-30.0  | $1.91 \pm 0.13 \times 10^{-9}$    | 8.4        |
| $28.0-31.0 		 6.75 \pm 0.67 \times 10^{-10} 		 10.5 		 39.0-42.0 		 4.09 \pm 0.55 \times 10^{-10} 		 11.5$   | 28.0-31.0  | $6.75 \pm 0.67 \times 10^{-10}$                         | 10.5      | 39.0-42.0  | $4.09 \pm 0.55 \times 10^{-10}$   | 11.5       |
| 34.0-37.0 $2.28 \pm 1.14 \times 10^{-10}$ 12.7 $42.0-46.25$ $2.52 \pm 0.39 \times 10^{-10}$ 12.5   | 34.0-37.0  | $2.28 \pm 1.14 \times 10^{-10}$                         | 12.7      | 42.0-46.25 | $2.52 \pm 0.39 \times 10^{-10}$   | 12.5       |
| 40.0-43.0 $4.72 \pm 2.59 \times 10^{-11}$ 15.8   | 40.0-43.0  | $4.72 \pm 2.59 \times 10^{-11}$                         | 15.8      |            |                                   |            |
| IAA6RMS02A   | IA06BMS02A |   |           |            |                                   |            |
| Surface $130 \times 10^{-7}$   | Surface    | $1.30 \times 10^{-7}$                                   |           |            |                                   |            |
| $D_{-2}^{-2} = 0.07 \times 10^{-7} = 0.2$  | 0-2.5      | $1.30 \times 10^{-7}$<br>$1.14 \pm 0.07 \times 10^{-7}$ | 0.2       |            |                                   |            |
| $25-50$ $813+046\times10^{-8}$ 09  | 25-50      | $813 \pm 0.46 \times 10^{-8}$                           | 0.9       |            |                                   |            |
| $75-100$ $42+02\times 10^{-8}$ 22  | 75-100     | $424 + 0.22 \times 10^{-8}$                             | 2.2       |            |                                   |            |
| $130-160$ $188 \pm 0.11 \times 10^{-8}$ $39$   | 130-160    | $1.21 \pm 0.22 \times 10^{-8}$                          | 3.9       |            |                                   |            |
| $190-220$ $768+045\times10^{-9}$ 56  | 19.0-22.0  | $7.68 \pm 0.45 \times 10^{-9}$                          | 5.6       |            |                                   |            |
| $300-35.0$ $1.65+0.11\times10^{-9}$ 8.7  | 30.0-35.0  | $1.65 \pm 0.11 \times 10^{-9}$                          | 8.7       |            |                                   |            |

Note: The surface value was extrapolated from the top two reliable data.

 $1.06 \pm 0.07 \times 10^{-9}$ 

 $2.58 \pm 0.58 \times 10^{-10}$ 



9.6

12.4

Fig. 6. Growth patterns of Fe-Mn crusts from northwest and central Pacific. Solid horizontal lines indicate the age of base of Layer 1. Solid and dashed lines in growth curves show reliable and less reliable datum, respectively.

we assumed the practical maximum reliable extrapolated Be age is around 17–15 Ma, while the measured secured age is 12 Ma. This limitation of validation of  ${}^{10}\text{Be}/{}^{9}\text{Be}$  dating corresponds the limit of reliable  ${}^{10}\text{Be}/{}^{9}\text{Be}$  measurement in the order of  $10^{-11}$ , measured ages older than 18 Ma were discarded if any.

The microscopic structures of our samples indicate that there was no significant hiatus (break of growth), but rather continuous from the substrate to modern surface. The growth rates from the Pliocene to the present are relatively uniform, about 2–4 mm/Myr. The crust surface Be isotopes are similar to the modern seawater value. These results indicate that Fe—Mn crusts have been growing from the middle Miocene to the present.

#### 5.2. Formation of dual structure with Fe-Mn crusts

The ternary diagram of  $(Ni + Cu + Co) \times 10$ /Fe/Mn for Layers 1 and 2 can be used to discriminate the genetic types of Fe-Mn deposits (Fig. 8). The major mineral component of our Fe-Mn crusts is vernadite. Vernadite in marine manganese deposits is poorly crystalline, with only two broad 1.4 Å and 2.4 Å XRD reflections that never form significant crystals but form aggregates of randomly stacked, nanoscale particles. The bulk XRD mineralogy indicates the presence of typical vernadite in both Layers 1 and 2, but the bulk composition of Layer 2 is more similar to buserite composition. Buserite may have formed partly by early diagenetic processes on the Fe—Mn crust surface at the time of phosphatization, where dissolution and reprecipitation of Mn took place under suboxic conditions after effective separation of Mn from Fe. Buserite is highly reactive to inter-sphere cation adsorption. The order of preference of buserite for adsorption of trace metals is Ni » Cu > Zn » Ca > Mg > Na (Usui and Mita, 1995). Thus, it is reasonable to assume that Layer 2 formed under less-oxidizing conditions than Layer 1 because of the abundant Ni, Cu, and Zn, significantly high Mn/ Fe ratio (maximum 6.3), and lower Co concentrations. Layer 2-b shows the dense layer structure and high Mn/Fe ratio often observed only in shallower water-depth crusts. This may indicate that the past environment under which Layer 2 formed was at times more reducing. This is consistent with suboxic conditions accompanying phosphogenesis (Koschinsky et al., 1997). Such a gradual physicochemical condition from reducing to oxidizing, and associated with different patterns of precipitation of manganese is also assumed in the ancient shallow-water environments during the process of regression and transgression (Frakes and Bolton, 1992).

Halbach et al. (1989) and Koschinsky et al. (1997) linked the phosphogenesis of crusts with an expansion of the oxygen-minimum zone (OMZ) and suboxic conditions. According to Zachos et al. (2001), the global ice volume remained low and bottom-water temperatures tended to be slightly higher from the latter part of the Oligocene (27–26 Ma) until the middle Miocene (~15 Ma). This warm phase peaked in the early middle Miocene climatic optimum (17–15 Ma), and was followed by a gradual cooling and reestablishment of a major ice-sheet on Antarctica by 10 Ma.

Fig. 9 shows a model for the formation of the dual structure of Fe—Mn crusts, modified from the model of Koschinsky et al. (1997). The ages of the base of Layer 1 are centered on the middle Miocene, and indicate no significant growth hiatus but rather continuous growth over the boundary of Layers 1 and 2 based on thin section observations. This could be verified using Os isotope stratigraphy. The summary of ages for the base of Layer 1 of the dual structure shows a broad tendency of a younger age at shallower water depths (Fig. 7).

We assume that intensified global circulation of oxygenated bottom water since early to middle Miocene, caused a more oxidizing deep-sea environment and reduction of the OMZ. Subsequently, when the extent of Antarctic ice increased the Antarctic Bottom Water (AABW), the OMZ was then reduced and weakened by oxygen-rich water supplied from deeper water masses. We also suggest that the end of phosphatization of Fe—Mn crusts may not have been contemporary but ended earlier



**Fig. 7.** Ages of base of Layer 1 versus water depth. Solid circles and open diamonds indicate this study and reference samples (Ling et al., 1997), respectively. The bars are analytical error and the range of water depth.

with the deeper-water crusts; there may have been a progression in the cessation of phosphatization from deeper-water to shallower depths, but that relationship needs verification with additional data. This change can be explained by a simple model assuming change from an expanded to a less intense OMZ and/or by intensified AABW.

#### 6. Conclusions

The characteristics of growth structures, chemical composition, and growth rates and ages of the Fe—Mn crusts were described using microscopy, XRD, XRF, and <sup>10</sup>Be/<sup>9</sup>Be dating on a millimeter scale. We focused on the distinctions between Layers 1 and 2, which show different chemical and mineralogical compositions and possibly different environments of formation in time and water depth.

(1). Layer 2 is the lowermost, oldest layer and shows high Mn/Fe ratio, Ni, Cu, and Zn compared with the overlying Layer 1, although the dominant mineral in both layers is vernadite. The Mn mineralogy of Layer 2 also shows characteristics similar to buserite, which is thought to form under less-oxidizing



**Fig. 8.** Ternary diagram of Fe:Mn:(Co + Ni + Cu) \* 10 for Layers 1 and 2; field A is diagenetic, field B hydrogenetic. Field C hydrothermal (field modified from Bonatti et al., 1972; Hein et al., 2008). Open circles and solid circles denote Layer 1 and Layer 2, respectively.

#### Early to Middle Miocene Late Miocene Sea level Sea level Phosphate-rich (which would be related to increased surface-water bioproductivity) 4 Narrowed oxygen minimum zone Intensified and expanded Formation of phosphatized oxygen minimum zone Formation of phosphatized ferromanganese crusts Oxygen-poor ferromanganese crusts Oxygen-rich Formation of non-phosphatized ferromanganese crusts Oxygen-poor Formation of non-phosphatized Oxygen-rich ferromanganese crusts Moderate supply of Antarctic Increasing current activity

Seamount



of the AABW

conditions. These mineralogical and chemical characteristics of Layer 2 suggest an oxygen depleted environment compared to the modern ocean.

Bottom Water (AABW)

(2). The <sup>10</sup>Be/<sup>9</sup>Be ages suggest that the Fe—Mn crusts have been growing since the middle Miocene, or earlier. The calculated ages for the base of Layer 1 demonstrate a broad tendency of variation with modern water depth. The shallowest-water Layer 1 base age is approximately 10 Ma, while the boundary for a deeper-water crust is extrapolated to be  $17.1 \pm 2.5$  Ma. We suggest that termination of the phosphate mineralization may not have been contemporaneous through all water depths, but ended earlier at deeper depths. This relationship is consistent with a simple model of an expanded and reduced OMZ in relation to the general cooling of the Neogene surface seawater and intensified AABW.

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