Ultrafine-scale magnetostratigraphy of marine ferromanganese crust

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ABSTRACT

Hydrogenetic ferromanganese crusts are iron-manganese oxide chemical precipitates on the seafloor that grow over periods of tens of millions of years. Their secular records of chemical, mineralogical, and textural variations are archives of deep-sea environmental changes. However, environmental reconstruction requires reliable high-resolution age dating. Earlier chronological methods using radiochemical and stable isotopes provided age models for ferromanganese crusts, but have limitations on the millimeter scale. For example, the reliability of 

\[ \frac{^{10}\text{Be}}{^{9}\text{Be}} \] chronometry, commonly considered the most reliable technique, depends on the assumption that the production and preservation of 

\[ ^{10}\text{Be} \] are constant, and requires accurate knowledge of the 

\[ ^{10}\text{Be} \] half-life. To overcome these limitations, we applied an alternative chromometric technique, magnetostratigraphy, to a 50-mm-thick hydrogenetic ferromanganese crust (D96-m4) from the northwest Pacific. Submillimeter-scale magnetic stripes originating from approximately oppositely magnetized regions oriented parallel to bedding were clearly recognized on thin sections of the crust using a high-resolution magnetostratigraphy technique called scanning SQUID (superconducting quantum interference device) microscopy. By correlating the boundaries of the magnetic stripes with known geomagnetic reversals, we determined an average growth rate of 5.1 ± 0.2 mm/m.y., which is within 16% of that deduced from the

\[ \frac{^{10}\text{Be}}{^{9}\text{Be}} \] method (6.0 ± 0.2 mm/m.y.). This is the finest-scale magnetostratigraphic study of a geologic sample to date. Ultrafine-scale magnetostratigraphy using SQUID microscopy is a powerful new chronological tool for estimating ages and growth rates for hydrogenetic ferromanganese crusts. It provides chronological constraints with the accuracy promised by the astronomically calibrated magnetostratigraphic time scale (1–40 k.y.).

INTRODUCTION

Hydrogenetic ferromanganese crusts are typically formed through accumulation of colloidal precipitates of iron-manganese oxide on seamounts away from terrigenous sources, where sedimentation is scarce. Due to their continuous slow growth rate (1–10 mm/m.y.), hydrogenetic ferromanganese crusts record long-term environmental variations, including bottom-water circulation patterns (van de Flierdt et al., 2004) and supply of dust and sediments from continents (Banakar et al., 2003). The crusts also record extraterrestrial events such as meteoroid impacts (Prasad, 1994).

In order to reconstruct geological and oceanographic signatures from ferromanganese crusts, it is crucial to provide a reliable fine-scale age model for each crust. A first-order age model was established by dividing the thickness of the crust by the age of the substrate assuming constant growth (e.g., Barnes and Dymond, 1967). Subsequently, absolute dating techniques were attempted using radioactive tracers, such as U-Th series (younger than 750 ka; Ku, 1976) and 

\[ \frac{^{10}\text{Be}}{^{9}\text{Be}} \] (younger than 10 Ma; Graham et al., 2004) dating.

For ferromanganese crusts older than 10 Ma, chronologies were established based on empirical formulae on the Co flux into the ferromanganese crusts (e.g., Puteanus and Halbach, 1988). However, these empirical formulae have not been well documented theoretically, and Frank et al. (1999) found disagreement between the Co chronometer and 

\[ \frac{^{10}\text{Be}}{^{9}\text{Be}} \] dating. Alternatively, 

\[ ^{187}\text{Os}/^{188}\text{Os} \] chronology was successfully applied on a ferromanganese crust by comparing its 

\[ ^{187}\text{Os}/^{188}\text{Os} \] isotopic curve with the evolution of 

\[ ^{187}\text{Os}/^{188}\text{Os} \] in seawater established from sediments (Klemm et al., 2005). Although this method has an advantage of covering long-term ranges back to 80 Ma, its low resolution leads to considerable errors, to several million years.

Magnetostatigraphy could provide an alternative, independent dating technique for ferromanganese crusts. Given the rate of geomagnetic reversals in the Cenozoic, a successful magnetostatigraphy should provide more than one chronological control point per million years. Once a magnetostatigraphic correlation is established, the accuracy of the age model is secured by the astronomically calibrated magnetostratigraphic time scale (1–40 k.y.; Lourens et al., 2004), which is not possible with the other geochemical methods alone. Crevelius et al. (1973) pioneered the investigation of natural remanent magnetization (NRM) in ferromanganese nodules and found evidence of geomagnetic reversals. Paleomagnetic studies of thin (1–4 mm thick) slices of ferromanganese crusts were performed by Chan et al. (1985) and Linkova and Ivanov (1993), but magnetostatigraphic correlations were not successful due to poor resolution of the paleomagnetic chronos.

The first apparently successful identification of paleomagnetic chronos in ferromanganese crusts was reported by Joshima and Usui (1998). They reported magnetostatigraphic correlations at 2.5 mm intervals from three ferromanganese crusts consistent with Co-based growth rates and radiochemical ages of substrate rocks. However, they found that the magnetostatigraphy-based growth rate for crust sample D96-m4 (16–17 mm/m.y.) was approximately three times higher than that based on 

\[ \frac{^{10}\text{Be}}{^{9}\text{Be}} \] ages (6 mm/m.y.; Usui et al., 2007), indicating that paleomagnetic chronos and/or subchrons were mismatched due to poor spatial resolution.

A spatial resolution finer than 1 mm is crucial to enable successful magnetostatigraphic correlations for slowly growing (1–10 mm/m.y.) ferromanganese crusts. However, preparation of specimens thinner than 1 mm from fragile crusts is not realistic. Thus, we developed an alternative method to construct age models for the crusts using a new high-resolution paleomagnetic method known as room-temperature scanning superconducting quantum interference device (SQUID) microscopy. Here we describe the results on thin sections of ferromanganese crusts.

SAMPLE AND PREPARATION

Ferromanganese crust D96-m4 was selected from one of the three crust samples used by Joshima and Usui (1998). It was collected as an unoriented sample by dredging the Shotoku seamount (30°48.7′N, 138°19.14′E, water depth 1940 m) in the northwest Pacific Ocean during the R/V Moana Wave cruise MW9507 in June 1996. The seamount is part of a currently inactive volcanic arc of Nishi-Shichito Ridge (Tamaki, 1985). A basalt sample from close to
the location of D96-m4 has an $^{40}$Ar/$^{39}$Ar plateau age of 9.0 ± 0.4 Ma (Ishizuuka et al., 2003). The crust is 50 mm thick, is brownish-black, and in cross section shows densely packed, weakly laminated growth patterns. The matrix mainly consists of an iron-manganese mineral, vermiculite, and contains minor detrital quartz, plagioclase, smectite, and, rarely, apatite. The Mn/Fe ratio ranges from 0.78 to 1.01, and it contains <0.2% Cu, Ni, and Co (Joshima and Usui, 1998).

A block of ferromanganese crust (Fig. 1A; left) was taken next to that studied by Joshima and Usui (1998). Two slabs (length 35 mm, width 5 mm) were cut perpendicular to the growth layers and perpendicular to each other, and polished thin sections of 0.2 mm thickness were made for scanning SQUID microscopy (MA1 and MB1 in Fig. 1A). Next to these slabs, a columnar block was cut (15 mm × 20 mm; MC in Fig. 1A) and sliced parallel to the growth laminations at intervals of 1.5 mm intervals using a 0.3-mm-thick diamond wire saw. The NRM and anhysteretic remanent magnetization (ARM) of the slices were measured with a SQUID moment magnetometer.

**SQUID AND ELECTRON MICROSCOPY**

Scanning SQUID microscopy is a new tool for high-resolution mapping of remanent magnetization in samples (Weiss et al., 2007). The instrument uses a monolithic directly coupled niobium-based planar SQUID with a field sensitivity of ~0.01 nT at a frequency of ~0.01 Hz (Baudenbacher et al., 2003; Fong et al., 2005; Weiss et al., 2007). It measures the vertical component of the magnetic field above thin sections. Measurements of the two thin sections MA1 and MB1 with the SQUID microscope were taken inside a magnetic shield in planar grids with 85 μm spacing at a sensor-to-sample distance (and approximate horizontal spatial resolution) of ~170 μm. Measurements were conducted for NRM before and after alternating field (AF) demagnetization at steps of 10, 20, 30, and 40 mT, and after giving the sample an ARM (direct current field = 100 μT, alternating current field = 100 mT).

After SQUID microscopy, backscattered electron images (BEI) were obtained with an electron probe microanalyzer (EPMA, JEOL JXA-8900) at electron acceleration, probe current, and pixel sizes of 15 kV, 12 nA, and 2 μm, respectively. Compositional images (Si, Al, Ti, Mn, Fe, K, Mg, Ca, and P) were obtained by using the EPMA with a pixel size of 20 μm. On selected spots, major elements were examined with an electron probe diameter of 4 μm.

**RESULTS**

The NRMs of the slices (MC in Fig. 1A) are stable both for normal (Fig. 1B) and reversed (Fig. 1C) polarity intervals. An overprinting magnetization (probably viscous in origin) was removed after AF demagnetization at 10 mT.

Declination and inclination (Figs. 1D and 1E; solid circles) are similar to those measured previously on the same crust (Joshima and Usui, 1998; gray circles in Figs. 1D and 1E). Although the polarity boundary observed at 5 mm depth can be recognized as the last geomagnetic reversal polarity boundary observed at 5 mm depth can be recognized as the last geomagnetic reversal (Baudenbacher et al., 2003; Fong et al., 2005; Weiss et al., 2007). The instrument uses a monolithic directly coupled niobium-based planar SQUID with a field sensitivity of ~0.01 nT at a frequency of ~0.01 Hz (Baudenbacher et al., 2003; Fong et al., 2005; Weiss et al., 2007). It measures the vertical component of the magnetic field above thin sections. Measurements of the two thin sections MA1 and MB1 were taken with parallel growth layers. Markers on scale of ±5 nT. Thin black lines in B–G indicate outer rim of crust. Arrows indicate spots where titanomagnetite grains were observed with electron probe microanalyzer.

**Figure 1.** A: Backscattered electron images of thin sections (MA1 and MB1) and photo of columnar block (MC) used for bulk measurements from block of crust D96-m4 (left). MA1 and MB1 were taken with parallel growth pictures on their surface and perpendicular to each other; MA1 (MB1) with surface facing +X (+Y) axis. Marks on scale of columnar block (MC) are specimen boundaries. B,C: Typical vector end-point diagrams of bulk paleomagnetic measurements on thin-sliced specimens are plotted for normal polarity intervals (depth = 1.5 mm) and reversed polarity intervals (depth = 8.3 mm), respectively. Solid circles (open circles) denote magnetization vector at each demagnetization step projected onto horizontal (vertical) plane. Numbers denote demagnetization steps (in mT). NRM—natural remanent magnetization; Div—division. D: Declination after alternating field (AF) demagnetization at 20 mT. E: Inclination after AF demagnetization at 20 mT. F: Intensity of NRM before demagnetization. G: Intensity of anhysteretic remanent magnetization (ARM) plotted versus corrected depth (solid circles). Thin sliced specimens were cut parallel to growth layer. Corrected depth is depth corrected for dip angle (32°) of MC. Declination and inclination (in D, E; measured by Joshima and Usui, 1998) after 10 mT alternating field demagnetization are also plotted as gray circles and lines.

**Figure 2.** Analysis of thin-section MB1. A: Backscattered electron image (BEI). B: Natural remanent magnetization (NRM) before demagnetization with scale of ±5 nT. C: With scale of ±100 nT. D: NRM after 20 mT alternating field demagnetization with scale of ±5 nT. E: With scale of ±100 nT. F: Anhysteretic remanent magnetization (ARM) with scale of ±100 nT. G: With scale of ±5 nT. Thin black lines in B–G indicate outer rim of crust. Arrows indicate spots where titanomagnetite grains were observed with electron probe microanalyzer.


MAGNETIC MINERALS

Magnetization intensity contrasts. By the unidirectionally magnetized layers with confi rms that the magnetic stripes are produced (Fig. 2C) and after (Fig. 2E) demagnetization. However, these regions surrounding the region is producing the downward magnetic fi eld. However, these regions might represent the regions where magnetization is occurring. From the 24 thin slices used for magnetization measurements, 4 normal and 10 reversed-polarity stable magnetization directions were determined. Using these 14 directions, a mean direction was determined as declination 233.7° and inclination 46.7° (with a 95% confidence circle of radius 6.5°) after inverting the reversed polarity directions. The positive inclination indicates that the ferromanganese crust was growing upward on the upper surface of the rock forming the seamount, although the crust was not oriented due to the sampling by a dredger.

After AF demagnetization, ARM was imparted upward perpendicularly to the surface of each thin section. Figure 2F shows that the magnetic field produced by ARM is dominantly upward with some intensity variation. The pattern does not directly correspond to the pattern of magnetic stripes observed for NRM. In Figure 2G (stretched intensity scale), there are tiny regions where a negative field (blue to light blue) is observed, indicating weakly ferromagnetic material. Strong negative fields (blue) in Figures 2E and 2F can be interpreted as magnetic dipoles originating from multidomain magnetic minerals not aligned to the DC bias fi eld direction. Support for this interpretation is provided by the observation that the orientations of many of these dipoles change by tens of degrees or more between the NRM image and the AF 20 mT image. This instability indicates a low-coercivity source, which will be susceptible to ARM noise, as expected for multidomain grains.

The other weakly negative field (light blue) might represent the regions where magnetization is weak and the positive magnetization surrounding the region is producing the downward magnetic field. However, these regions are very small and most of the rest of the thin section is associated with a positive field. This confirms that the magnetic stripes are produced by upward and downward magnetization, and rules out the possibility that these are produced by the unidirectionally magnetized layers with magnetization intensity contrasts.

MAGNETIC MINERALS

Observations with the EPMA revealed that the sources of strong NRM dipole fields before (Fig. 2C) and after (Fig. 2E) demagnetization consist of Fe oxides with sizes of a few tens of microns containing ~7% Ti with minor amounts of Al, Mn, and Mg (arrows in Fig. 2). Preliminary analysis of electron backscatter diffraction data indicates the presence of titano-magnetite of several microns, implying the presence of single domain (SD) and pseudo-single domain (PSD) grains. A thermomagnetic analysis on a magnetic extract revealed that Curie temperature is ~550 °C, which is consistent with titano-magnetite (Fe_{3-z}Ti_zO_4) with z = 7% (Dunlop and Özdemir, 1997), expected from EMPA analyses. These data collectively indicate that the major ferromagnetic mineral in our ferromanganese crust sample is titano-magnetite. The EPMA analyses indicate that the abundance of titano-magnetite is <<1%. In fact, magnetite and titano-magnetite are known accessory minerals in hydrogenetic ferromanganese crusts (Bogdanova et al., 2008). The chemical composition of the titano-magnetite indicates a volcanic origin, implying that the NRM is predominantly a detrital remanent magnetization, although the possibility of a chemical origin cannot be ruled out.

ABSOLUTE AGE AND GROWTH RATE ESTIMATED BY MAGNETOSTRATIGRAPHY

We have chosen the magnetic image of NRM before demagnetization to identify the magnetic polarity boundaries because of the NRM’s generally single component nature (as indicated by measurements of slices; Figs. 1B and 1C), and because further demagnetization did not enhance the magnetic stripes due to contamination of magnetic dipoles (Figs. 2C and 2F). We attempted to enhance the visibility of normal and reversed stripes with further data processing. First, we applied upward continuation (Blakely, 1996) of 200 μm (370 μm from surface of thin sections) on the original magnetic image to reduce the effect of magnetic dipoles, which have lower spatial resolution than the magnetic stripes.

Second, the following data processing was conducted to recognize the polarity boundaries for magnetostatigraphic correlation. Several tens of characteristic growth layer boundaries with significant contrast on BEIs were traced and registered as reference lines for the datum planes of simultaneous precipitation to be straightened. Mapping was conducted on the magnetic image parallel to the long axis with the previously registered reference lines (Figs. 3A and 3E). The lower boundary lines of the thin sections were used as baselines. From the straightened magnetic images, magnetic field values of ~10 to +10 nT were extracted and summed perpendicularly to the growth axis within the ferromanganese crust. Magnetic field values >10 nT were neglected because these are considered as noise mostly originating from randomly oriented dipole sources. Finally, the zero crossings were extracted as magnetostatigraphic boundaries and correlated with the standard magnetostatigraphic time scale of Lourens et al. (2004). The angle of the growth layers and the lines perpendicular to the baseline changes from 0° to 38°, implying a maximum distortion of the time scale by no more than 27%.

Figure 3 illustrates the results of data processing on MA1 and MB1 and their magnetostatigraphic correlations. Both MA1 (Fig. 3A) and MB1 (Fig. 3E) show magnetic stripes parallel to the surface of the ferromanganese crust after the above corrections. Most of the zero crossings (Figs. 3B and 3D) were correlated with the standard magnetostatigraphic time scale (Lourens et al. 2004; Fig. 3C). Correlations were primarily made based on the long polarity chron, including Brunhes normal and Matuyama reversed chron. The extracted polarity boundary depths were plotted versus ages (Fig. 3F). Growth rates are estimated to be 4.99 ± 0.43 and 4.90 ± 0.32 mm/m.y. (errors are in 2σ) for the upper
for the 10Be half-life of 1.387 ± 0.012 m.y. Laboratory experiments led to the best estimate
recently, a sequence of carefully designed experiments which were used to test the accuracy of experimentally derived half-lives of radioactive isotopes such as 10Be in ferromanganese crusts.

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