Development of scanning SQUID microscope system and its applications on geological samples: A case study on marine ferromanganese crust

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Abstract. We present developments and applications of a high resolution scanning superconducting quantum interference device (SQUID) microscope for imaging magnetic field of geological samples at room temperature. A directly coupled low-temperature SQUID with a 200 μm × 200 μm pickup loop was mounted on a sapphire rod and separated from room temperature by a sapphire window. The environmental noise of the SQUID was successfully reduced by subtracting the signal of an additional reference SQUID placed inside a cryostat. The resulting system noise level was estimated to be about 50 pT. A geological thin section could be placed on a non-magnetic sample holder with an XYZ stage for scanning in an area of 100 mm × 100 mm. The minimum achievable distance from the SQUID to the sample is measured as ~200 μm. An application of the SSM to a marine ferromanganese crust successfully provided beautiful stripe patterns in the magnetic images. The patterns could be correlated to the history of geomagnetic field reversals. The boundaries of the magnetic polarity domains were useful guides for the estimation of the deposition age by correlation with the standard geomagnetic polarity timescale. The established age model gave an average growth rate of ~2.7 mm/Ma, which is consistent with that obtained by radiometric dating using 10Be (~2.6 mm/Ma).

1. Introduction

A scanning SQUID microscope (SSM) is a sensitive magnetic imaging tool and could be used for applications such as detection of magnetic contaminants in food-products and batteries, non-destructive
testing of cracks in metal structure like an airplane frame, and detection of leak currents in electronic circuits. SSM could also be used for various applications on geological materials in order to understand the history of Earth and Planetary bodies. Weiss et al. applied an SSM to a geological sample for the first time [1]. They measured thin sections of meteorites derived from Mars, and suggested a possibility of life on Earth coming from meteorites. Gattacceca et al. conducted magnetic imaging of basalt rocks, which were treated by laser impact, to understand the effect of high pressure on magnetization [2].

Oda et al. applied the SSM used by Gattacceca et al. [2] to a weakly magnetized marine ferromanganese crust and found sub-millimeter to millimeter scale magnetic stripes recording the history of reversals of the Earth’s magnetic field [3]. The detected reversal boundaries were successfully used to provide the deposition ages by correlation with the standard magnetic polarity time scale. Subsequently, an SSM was developed in Japan for geological samples using a low-Tc SQUID, operated above a geological thin section at room temperature and atmospheric pressure [4, 5]. It was used successfully on mapping of magnetic coercivity using isothermal remanent magnetization (IRM) of a marine ferromanganese crust as well as natural remanent magnetization (NRM) recording the polarity of the Earth’s magnetic field in the past [6]. Here, we present the improvements on the SSM system, and applications to a marine ferromanganese crust.

Figure 1. Schematic diagram of main part of a scanning SQUID microscope at AIST [4]. The inset shows an additional reference sensor for reduction of the environmental magnetic noise.

2. System developments and geological applications of scanning SQUID microscope
The developed SSM uses a hollow-structured cryostat [4]. Vertical component of magnetic field is measured with a directly coupled low-temperature SQUID with a 200 μm × 200 μm pickup loop, which
is mounted on a sapphire conical rod. The SQUID sensor is separated from room temperature by a thin sapphire window. Precise and repeatable adjustment of the vacuum gap between the SQUID and the sapphire window could be performed by rotating a micrometer spindle connected to the sapphire rod through the hollow of the cryostat. A field noise of 1.1 pT/√Hz was obtained at 1 Hz when operated in superconducting shield with the low-drift FLL [4]. The output signal was low-pass filtered at 10 Hz [4]. Environmental magnetic noise coming from outside of the two layered magnetic shield made of PC permalloy could be up to 500 pT. A geological thin section is placed on top of a non-magnetic sample holder with an XYZ stage that covers a scanning area of 100 mm × 100 mm. The minimum achievable distance from the SQUID to the sample was measured as ~200 µm.

The new instrument has been successfully applied to various geological thin sections including that of a marine ferromanganese crust [6]. The SSM was also applied to imaging of strongly magnetized parts of a fault rock taken from the Nojima Fault, Japan, where fine magnetic particles were produced due to heating with a rapid and strong fault movement [7]. Further, the SSM was used for imaging of mm-sized magnetic particles in rocks originating from deeper part of the crust in northern Norway. The obtained images were used for modeling the direction and intensity of magnetization of each mineral grain [8]. Recently, dipolar magnetic image of a zircon grain from Jack Hills, western Australia, was obtained using the SSM, which supported the main conclusion that the magnetic moment of zircon grains recorded the Earth’s magnetic field starting from 4.2 billion years ago [9].

In order to reduce environmental noise in the magnetic image of SSM, an additional reference SQUID sensor was placed inside a cryostat. The reference SQUID has the same design as the main SQUID sensor (Fig. 1). Fig. 2 shows benefits of the reference SQUID sensor using a zircon grain. The time series of the measured and the processed data are shown in Fig. 2a. The output of the reference SQUID sensor was subtracted from that of the main SQUID sensor (orange line in Fig. 2a). Most of the disturbances in magnetic field measured by the main SQUID sensor (black line in Fig. 2a) could also be observed in the reference SQUID sensor (purple line in Fig. 2a), which could be eliminated after subtraction (orange line in Fig. 2a). Fig. 2b is the magnetic map of the main SQUID sensor signal (black line in Fig. 2a) based on the measured position, whereas Fig. 2c is the one after subtracting the reference sensor signal using the orange line in Fig. 2a. Although the subtraction of reference SQUID sensor signal was very effective in reducing environmental magnetic noise, there was still a long-term drift. Further, drift correction was applied to the magnetic image, assuming that the averaged magnetic fields corresponding to the upper and lower marginal band areas in Fig. 2c should be zero because these areas are far enough from the sample generating magnetic field. For the correction, 10 data points along the first scan direction were used for each side. Fig. 2e, corresponding to the blue line in Fig. 2a, shows the correction result. In this case, a magnetic image of a magnetic dipole was measured, which was fit by a dipole model using least squares method (Fig. 2e). The residual of the fitting result is shown in Fig. 2f, indicating an average residual field of ~50 pT. Fig. 2g is an optical image of the measured zircon grain.

3. Paleomagnetic measurements of marine ferromanganese crusts using SSM

Marine ferromanganese crusts are promising candidates of ore deposits enriched in useful metallic elements that grow very slowly on rock outcrops in deep sea. They are mainly composed of vernadite that forms hydrologically [10]. They record long-term deep-sea environmental changes for more than tens of millions of years. Yoshima et al. conducted paleomagnetic measurements on thin sliced chips of ferromanganese crust samples with a superconducting rock magnetometer (SRM) and found that the polarity of the Earth’s magnetic field could be recovered [11]. It is known that the Earth’s magnetic field experienced polarity changes in the past [12, 13]. Correlation of the polarity boundaries with the established standard magnetic polarity timescale [14], namely magnetostratigraphy, allows us to provide ages when geological materials were formed. Although reconstructing sequence of polarity of the samples’ magnetization was partially successful using thin sliced chips [15, 16], the minimum achievable thickness of a slice (~1.0 mm) limit the resolution of age estimate.
Figure 2. Demonstration of noise reduction using a reference sensor signal and drift correction during measurement of a weakly magnetic zircon single grain sample. (a) Time series of the measured and processed data. From top to bottom shown in sequence; signal of the reference SQUID sensor (purple), signal of the main SQUID sensor (black), main sensor signal after subtraction of reference sensor signal (orange) and after drift correction (blue). Magnetic images are shown in Figs. 2b through 2f. The fast scan direction was along +Y direction (direction from bottom to top) and the slow scan direction was along +X direction (direction from left to right). (b) Raw magnetic image obtained from the main SQUID sensor (produced from black line in Fig. 2a). (c) Magnetic image of the main signal after subtraction of the reference signal (produced from data shown as orange line in Fig. 2a). (d) Magnetic image of the main signal after correction of drift (produced from data shown as blue line in Fig. 2a). (e) Fit result of a dipole model onto magnetic image of the signal after drift correction (Fig. 2d) using least squares minimization method. The dipole magnetic moment direction is downward making an angle of about 54 degrees from the horizontal plane. (f) Residual magnetic field image of the least squares fitting conducted in Fig. 2e. (g) Optical image of the measured zircon grain. The orientation is the same as the magnetic images.
Magnetic field mapping was conducted with an SSM on thin sections of ferromanganese crust from Shotoku [3] (Site A in Fig. 3; collected during R/V Moana Wave Cruise MW9506) and Takuyo-Daigo Seamounts [6] (Site B in Fig. 3; collected during R/V Natsushima Cruise NT09-02), respectively. They recovered beautiful stripes in the magnetic field images, which provided growth rates based on age estimates (i.e. $5.1 \pm 0.2$ mm/Ma for Shotoku Seamount; $3.4 \pm 0.1$ mm/Ma for Takuyo-Daigo Seamount; Ma: million years) using magnetostratigraphy. The result was consistent with the radiometric dating using a cosmogenic nuclide $^{10}$Be (i.e. $6.0 \pm 0.2$ mm/Ma for Shotoku Seamount; $2.9 \pm 0.2$ mm/Ma for Takuyo-Daigo Seamount).

In addition to the previously studied two sites, we newly conducted magnetic field mapping with an SSM at National Institute of Advanced Industritl Science and Technology (AIST) on a ferromanganese crust sample collected from Hanzawa Seamount, northwester Pacific (Site C in Fig. 3; Lat=25°42.58’ N, Lon=146°44.90’ E, Water Depth= 4362 m; collected during R/V KAIYO Cruise KY12-16). The sample was retrieved from an outcrop with the surface layer preserved using a remotely operated vehicle while observing with a camera. A thin section with a thickness of 54 µm was made for magnetic imaging with the SSM. Measurement of NRM with the SSM was conducted on the thin section followed by measurements after alternating field demagnetizations (AFD) at five steps (5, 10, 15, 20 and 30 mT) in order to obtain clearer magnetic images. Furthermore, an optical microscope image was obtained.

**Figure 3.** Sampling sites of marine ferromanganese crusts shown on bathymetric map. (A) Shotoku Seamount [3], (B) Takuyo-Daigo Seamount [6], and (C) Hanzawa Seamount (this study).

**4. Results of Measurements on the Hanzawa Seamount ferromanganese crust**

Among the magnetic images obtained for the thin section of the ferromanganese crust sample, measurements after AFD at 20 mT provided the clearest magnetic stripes that can be used for the interpretation of ultra-fine scale magnetostratigraphy (Fig. 4b). The magnetic image after AFD at 20 mT showed relatively weak magnetic fields ranging from -5 nT to +5 nT. In order to extract polarity reversal boundaries precisely, the magnetic-field profile was obtained from averaging the values parallel to the growth layers within the region of relatively straight magnetic stripes (regions between two vertical broken lines in Fig. 4b). Then, the obtained profile (bottom diagram in Fig. 4d) was correlated with a standard geomagnetic polarity timescale (middle diagram in Fig. 4d). Based on the correlation, we obtained a series of data points for a relation between age and depth, allowing to estimate an average growth rate of $\sim 2.67 \pm 0.04$ mm/Ma (red circles in Fig. 4e), which is consistent with that obtained by
radiometric dating using $^{10}$Be ($\sim 2.56 \pm 0.04$ mm/Ma [15]; black diamonds in Fig. 4e). For comparison, the results of magnetic polarity stratigraphy based on SRM measurements of thin sliced chips taken from the same ferromanganese sample [15] is also shown on the upper diagram in Fig. 4d and Fig. 4e (green triangles). It is noteworthy that the data points obtained from thin sliced chips are similar, but the resolution is limited compared with the data points obtained with the SSM. The ultra-fine scale magnetostratigraphy is successful in estimating formation age of a ferromanganese crust with a lot of precisely controlled data points without laborious works (accelerator mass spectrometry following chemical treatments) needed for radiometric dating.

Figure 4. Results of natural remanent magnetization measurements with SSM on a thin section sample from Hanzawa Seamount. (a) Optical microscope image, (b) magnetic image (after AFD at 20 mT), and (c) overlay of magnetic image on microscope image. (d) Correlation of magnetic reversal patterns with the standard geomagnetic polarity timescale. Top: Magnetic polarity interpretation based on thin sliced chips [15], Middle: Standard geomagnetic polarity timescale (GTS2012 [14]), Bottom: averaged magnetic profile along the depth, obtained from the magnetic image taken by the SSM between two vertical broken lines in Fig.4a. (e) Depth versus age estimated for a thin section using the SSM (red circles) plotted together with that for $^{10}$Be [15] (black diamonds) and that for thin sliced chips [15] (green triangles).
5. Discussions
Including this study, ultra-fine scale magnetostratigraphy using an SSM has been conducted successfully on three ferromanganese crust samples from the northwestern Pacific; i.e. Shotoku Seamount [3], Takuyo-Daigo Seamount [6] and Hanzawa Seamount (this study). Table 1 shows the summary for the estimated growth rates based on magnetostratigraphy using the SSM comparing with those estimated using $^{10}\text{Be}$. It could be said that the values based on two methods agree with each other with only a maximum of 20% discrepancies. This means that the SSM is applicable to ultra-fine scale magnetostratigraphy for constructing age model and estimation of the average growth rate. However, there still exists slight discrepancies. Therefore, further investigation is necessary to understand the mechanism of magnetization lock-in and reliability of the two methods, based on more examples.

The growth rates were almost constant at each site for the measured age range, however, those were different from site to site ranging from ~2.7 to ~5.1 mm/Ma. Noguchi et al. reported smaller growth rate of ~1.5 mm/Ma at Ryusei Seamount based on magnetic polarity identification using thin sliced chips [15]. On the other hand, Usui et al. reported that growth rates for ferromanganese crust samples taken from Takuyo-Daigo Seamount varies slightly between 2.3 and 3.5 mm/Myr using $^{10}\text{Be}$ [10]. It is expected that systematic magnetic polarity measurements using scanning SQUID microscopes on large number of marine ferromanganese crust samples would enable to unveil growth rate distributions both on local and global scales.

Calculation of a map of relative abundance of magnetically hard minerals based on sequential acquisitions of artificial magnetization images obtained at 0.3T and 1.4T was also successful for a ferromanganese crust sample from Takuyo-Daigo Seamount [6]. They showed that ratio of hard magnetic component increased for the part of the thin section younger than 3 Ma. In fact, eolian dust particles rich in magnetically hard minerals (magnetic coercivities higher than 300 mT; i.e. hematite and goethite) had increased since 2.6 Ma at a drilling site in northern Pacific (ODP Site 885) [17]. We will conduct imaging of magnetic coercivity on a thin section of Hanzawa Seamount, and compare the result with that of Takuyo-Daigo Seamount in the future.

Table 1. Comparison of growth rates (mm per million years) based on SSM and $^{10}\text{Be}$ methods.

| mm/Ma | Shotoku Seamount [3] | Takuyo-Daigo Seamount [6] | Hanzawa Seamount (this study) |
|-------|----------------------|---------------------------|-------------------------------|
| Scanning SQUID Microscope | $5.1 \pm 0.2$ | $3.37 \pm 0.06$ | $2.67 \pm 0.04$ |
| $^{10}\text{Be}/^{9}\text{Be}$ | $6.0 \pm 0.2$ | $2.93 \pm 0.15$ | $2.56 \pm 0.04$ |

6. Conclusions
Following developments of the SSM at AIST, Japan [4, 5], we installed a reference SQUID sensor exactly same as the main SQUID sensor attached to the tip of a sapphire rod. The demonstration using a zircon single crystal has shown successfully that the reference sensor effectively reduced environmental magnetic noise leading to minimization of residuals (averaging ~50 pT) for modelling with a magnetic dipole. We applied the SSM to a thin section of a marine ferromanganese sample obtained from Hanzawa Seamount, northwestern Pacific. The result showed the fine magnetic stripes corresponding to the polarity reversals. From correlation with the standard geomagnetic polarity timescale, the average growth rate was estimated at 2.67±0.04 mm/Ma. It is consistent with the estimate using $^{10}\text{Be}$ (2.56±0.04 mm/Ma).

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