Low-Temperature Oxidation and Subsequent Downcore Dissolution of Magnetite in Deep-Sea Sediments, ODP Leg 161 (Western Mediterranean)

M. TORII

Division of Earth and Planetary Sciences, Graduate School of Science, Kyoto University, Kyoto 606-01, Japan

(Received April 23, 1997; Revised August 25, 1997; Accepted August 25, 1997)

Low-temperature experiments document changes in magnetic mineralogy in Pleistocene hemipelagic sediments at ODP Holes 976D and 977A. The Verwey transition was observed only for samples below ~1.3 mbsf, which suggests depth-limited appearance of stoichiometric magnetite in the sediment column. Primary magnetite is interpreted to be covered with a maghemite skin as a result of in situ low-temperature oxidation on the sea floor. The oxidized maghemite skin gradually dissolves with depth, and the Verwey transition is observed below ~1.3 mbsf. This depth matches the iron redox boundary inferred on the basis of a sediment color change from tan to green.

1. Introduction

Deep-sea sediment is a continuous recorder of Earth history. Fluctuations of the geomagnetic field recorded in sediments gives insight into the deep interior of the Earth. The magnetic record in the sediment is carried by magnetic minerals of diverse origin: aeolian, detrital, biogenic, authigenic, cosmogenic, etc. Changes in the magnetic mineralogy, grain size and abundance are themselves indicators of environmental changes in and around the sedimentary basin (Thompson and Oldfield, 1986; Verosub and Roberts, 1995). As the magnetic minerals can be sensitive to chemical conditions in the sediment, diagenetic change and authigenic formation of magnetic minerals are also important factors in the sedimentary environment (Karlin, 1990; Leslie et al., 1990; Tarduno and Wilkinson, 1996).

During the ODP Leg 161 cruise, we found downcore decreasing trends in rock magnetic parameters such as low-field susceptibility and saturation isothermal remanence at most sites (Shipboard Scientific Party, 1996a, b). Unfortunately paleomagnetic results were largely degraded by high-coercivity radial remagnetization which make a horizontal component of remanence perpendicular to a half-cut surface of cores. Although the radial remagnetization was interpreted as a result of inward radial overprint residing in the outer part of core sample (Shipboard Scientific Party, 1996c), the mechanism to induce such remanence has been not fully understood so far. Beside the radial remagnetization problems, the downcore decrease in the intensities of several magnetic parameters could be additional reasons for an unsatisfactory onboard magnetostratigraphy. After the cruise, we therefore continued rock magnetic studies to appraise the effect of the downcore changes in magnetic properties.

2. Samples and Shipboard Measurements

ODP Leg 161 covered the western half of the Mediterranean and drilled six locations in 1995, at Site 974 to Site 979 (Fig. 1). Pleistocene sediments were recovered by using an advanced piston corer (APC). The recovered sediments are dominantly hemipelagic, nanofossil-rich or nanofossil clay (Comas, Zahn, Klaus et al., 1996). For shore-based rock magnetic study, we focused on sediments from two sites in the Alboran Sea, Site 976 and Site 977. These two sites were selected because of limited time available on shipboard. Samples from Hole 974B (Tyrhenian Sea) were also used for comparison.
Discrete cubic samples were collected on board with a polycarbonate cubic box (7 cm³ in volume). Samples were sealed in a plastic bag and kept in a refrigerator as much as possible to prevent drying and oxidation. Low-field susceptibility ($\chi_0$), anhysteretic remanent magnetization (ARM), saturation isothermal remanent magnetization (SIRM) and back-field IRM to calculate $S_{-0.3T}$ (Bloemendal et al., 1992).

Fig. 1. Drilling sites of ODP Leg 161 in the western Mediterranean.

Fig. 2. Downcore rock magnetic properties at Hole 976B measured on board. Simplified after Shipboard Scientific Party (1996a).
were measured on board along with other routine paleomagnetic measurements (Shipboard Scientific Party, 1996c).

Onboard rock magnetic data showed exponential downcore decay to about 100 meters below sea floor (mbsf). ARM, SIRM and $\chi_0$ for the upper part of Hole 976B decreased rapidly and stabilized below 100 mbsf, except for samples from Section 976B-6H (Fig. 2). The exponential decay was interpreted as a selective dissolution of fine magnetic grains due to sediment diagenesis (Shipboard Scientific Party, 1996a). Although downcore dissolution is the most likely cause of downcore intensity decrease, we had little information about the magnetic mineralogy. For this reason, our shore-based study was mainly focussed on the magnetic mineralogy of those samples from Sites 976 and 977 for which we had most shipboard information.

3. Laboratory Procedures

We generally applied low-temperature methods to investigate the magnetic mineralogy of the sediments. Although high-temperature methods such as Curie point measurement are well established, such measurements can encounter difficulties when samples are heated above $\sim$300°C because of the artificial authigenic production of magnetic minerals (Holm and Verosub, 1988; Torii, 1995). Thermochemical changes of the magnetic minerals also hinders straightforward interpretation of the results (van Velzen and Zijderveld, 1992; Torii et al., 1996). Unlike the high-temperature methods, low-temperature experiments are free from thermochemical change and/or artificial production of minerals (Mauritsch and Turner, 1975). We also made experiments only on bulk samples, in order to be free from bias caused by magnetic separation of minerals (Bloemendal et al., 1993; Hounslow and Maher, 1996).

Low-temperature magnetic characteristics were determined on a Quantum Design magnetic property measurement system (MPMS-2) at the Low-Temperature Laboratory of Kyoto University. Wet sediment (~50 mg) was taken from each discrete sample and wrapped with thin plastic film. The wrapped sediment was then tightly packed in a plastic straw which is a standard sample holder for the MPMS. Each sample was first cooled down to 5 K without an applied DC field ("zero field cooling") and then an IRM was imparted by applying a DC field of 1.0 T at 5 K. For most bulk sediment samples, it was generally difficult to attain saturation IRM at 5 K by applying a large field, even as high as 5 T. The DC field was applied for 10 seconds and the superconducting magnet was immediately quenched to reduce the residual field to the order of the ambient field intensity (~50 $\mu$T) in the laboratory. Then IRM was measured while changing the temperature up to room temperature. We measured IRM at 5 K, 6 K, 8 K, 10 K, 12 K, 15 K, and at five degree intervals from 15 K to 300 K. The thermal demagnetization of IRM from 5 to 300 K required about eight hours to make a complete measurement sequence for one sample.

We calculated the IRM difference for each temperature step ($\Delta$IRM/$\Delta$T) to better show stepwise changes in IRM intensity occurring during the sample warming (Torii et al., 1996). Figure 3 shows typical examples of thermal demagnetization curves of IRM. Decay of IRM from 5 K to 300 K is plotted along with the $\Delta$IRM/$\Delta$T curve. Possible magnetic phase transitions are shown by stepwise decreases in IRM curves. However such transitions are more unambiguously indicated by abrupt changes in the $\Delta$IRM/$\Delta$T curves. The Verwey transition (Verwey, 1939), which appears for stoichiometric magnetite (Özdemir et al., 1993) at 110–120 K, becomes evident only for the samples below 1.7 mbsf (Fig. 3). Although the Verwey transition is clearly visible only for the deeper samples, small but unambiguous “notches” on the $\Delta$IRM/$\Delta$T curve at about 120 K are seen even in the uppermost samples (Fig. 3). These notches are readily detectable only with the aid of the $\Delta$IRM/$\Delta$T curves.

A stepwise drop of IRM at about 270 K is seen in some samples (Fig. 3). This temperature is nearly the same as the Morin transition of hematite, although slightly higher. We believe this drop is caused by the melting of ice in the wet sediment samples. The fabric of the sample could be slightly altered when the volume of the sample decreases by the melting of ice and could introduce noise in the measurements. This was confirmed by comparing the measurements after drying the samples where no obvious drops at about 270 K occurred.
4. Results

Thermal demagnetization of low-temperature IRM was performed for sediment samples from Holes 976D, 977A and 974B using an MPMS (Figs. 4–6). The results are next described separately for each hole.
4.1 Hole 976D

Twenty-four samples from 0.04 to 28.2 mbsf were given the low-temperature treatment. Normalized thermal demagnetization curves for each sample are plotted with sample depth in Fig. 4. Samples from 0.04 mbsf (Sample 976D-1H-1, 4–6 cm) to 1.2 mbsf (Sample 976D-1H-1, 120–122 cm) show smooth thermal decay of IRM acquired at 5 K. A slight stepwise change at about 120 K is visible but not as obviously as in lower samples. These small changes are unambiguously shown by the ΔIRM/ΔT curve (Fig. 3).

All samples below 1.7 mbsf (Sample 976D-2H-1, 20–22 cm) show a distinct drop of remanent magnetization between 100 K and 120 K which is characteristic of the Verwey transition for stoichiomet-
Fig. 5. Downcore change in normalized demagnetization curves of IRM for Hole 977A. (a) 0 to 21.15 mbsf and (b) to 97.22 mbsf. The Verwey transition appears only below 1.7 mbsf and disappears below 70 mbsf. Much lower transitions, about 30 K, are sometimes observed below 40 mbsf.
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Fig. 5. (continued).
Fig. 6. Downcore change in normalized demagnetization curves of IRM for Hole 974B. The Verwey transition is generally difficult to observe at this hole.

Birch magnetite with grains larger than the superparamagnetic (SP) to single-domain (SD) threshold (Özdemir et al., 1993). One sample (Sample 976D-4H-1, 20-22 cm) does not show any stepwise change in magnetization at the Verwey transition temperature. No remarkable change in lithology was reported on board for this sample interval except for abundant pyrite grains.

It is also noteworthy that IRM intensity both at 5 K and 300 K systematically decreases with depth,
as shown in Fig. 3. The topmost sample (Sample 976D-1H-1, 4–6 cm) has an IRM of $-8 \times 10^{-7}$ Am$^2$ at 5 K, whereas the lowermost sample (Sample 976D-4H-5, 20–22 cm) shows $-1 \times 10^{-7}$ Am$^2$. As well as the general decay trend observed at Hole 976B (Fig. 2), these observations are evidence of a systematic downcore decrease in magnetic content of the sediments at this site.

4.2 Hole 977A

This Hole was the most intensively studied by the low-temperature method. With a total of 74 samples measured from 0.04 to 97.22 mbsf, corresponding to about half of the length of the APC cored interval. The age of the deepest sample is about 0.6 Ma based on the basis of biostratigraphy (Shipboard Scientific Party, 1996b). Normalized thermal demagnetization curves are shown in Figs. 5(a) and (b). Just as in Hole 976D, the uppermost samples, from 0.04 mbsf (Sample 977A-1H-1, 4–6 cm) to 1.38 mbsf (Sample 977A-1H-1, 1.38–1.40 cm), failed to clearly show the Verwey transition. Below 1.7 mbsf, we could see the Verwey transition is seen unambiguously till 55.8 mbsf (Sample 977A-7H-3, 130–132 cm).

Although the Verwey transition is the predominant magnetic feature in this depth interval, in some parts such as 8.73 to 11.39 mbsf, we could not see any stepwise decrease in magnetization. Below 58 mbsf, the Verwey transition is rarely seen. Most samples show a rapid decrease in IRM intensity during warming up to 30 K. Some of these samples suggest a magnetic transition at about 35 K, e.g., Sample 977A-6H-2, 21–23 cm, Sample 977A-7H-5, 130–132 cm, Sample 977A-9H-2, 21–23 cm, and so on. The transition at 35 K is presumably due to the presence of pyrrhotite (Dekkers, 1989; Rochette et al., 1990) or siderite (Housen et al., 1996).

4.3 Hole 974B

We measured 26 samples from 0.5 mbsf to 85.44 mbsf at Hole 974B from the Tyrrhenian Sea (Fig. 6). The results are discordant with the other two sites from the Alboran Sea. The Verwey transition is obviously seen for only one or two samples (e.g., Sample 974B-1H-1, 81–83 cm). Two curves (Sample 974B-6H-6, 82–83 cm and Sample 974B-7H-1, 120–121 cm) show abrupt decreases when warmed a little above 5 K, followed by almost no change in intensity up to room temperature. These samples were collected from organic-rich layers. We also see a transition at about 20 K for Sample 974B-9H-3, 129–131 cm.

5. Discussion

The low-temperature measurements strongly suggest a systematic downcore change in magnetic mineralogy at Holes 976D and 977A. In general, isothermal remanences imparted at 5 K decayed monotonically when warmed up to room temperature. The temperature dependence of IRM is an exponentially decreasing curve for samples particularly from the uppermost sediment, i.e., 0–1.2 mbsf for Hole 976D (Fig. 3) and 0–1.4 mbsf for Hole 977A (Fig. 4). For most samples obtained below these depths, the Verwey transition at about 120 K was distinctly observed along with the exponential decay. The appearance of the Verwey transition marks a change in mineralogy controlled by the depth below sea floor.

The Verwey transition emerges at 110–120 K when stoichiometric magnetite is dominant in the sample. There is no apparent size dependence of the transition temperature above SP/SD threshold size as elucidated by Özdemir et al. (1993). They documented the sharp Verwey transition for stoichiometric magnetite grains in the size range from 37 nm to 1.5 mm. We therefore infer the occurrence of stoichiometric magnetite grains of SD or larger in the sediment below ~1.3 mbsf. The sediments from the upper part have strong remanences compared to the lower part. Natural remanent magnetization (NRM) intensities are of the order of $10^{-1}$ to $10^{-2}$ A/m in the top 1 mbsf for both holes 976D and 977A (Shipboard Scientific Party, 1996a, b). SIRM, ARM and $\chi_0$ are all high in the upper part (Figs. 2 and 3). These facts suggest the relative abundance of magnetic minerals larger than SP/SD threshold size in the upper part. The absence of the Verwey transition in the upper part can not be attributed either to the depletion of magnetic minerals or dominance of SP grains.
Two questions arise about the depth-limited change in magnetic mineralogy. (1) What is the magnetic mineral or minerals in the sediments above \(-1.3\) mbsf? (2) What is the mechanism for the emergence of pure magnetite below \(-1.3\) mbsf? Whatever magnetic minerals are involved, the sediments of the upper part show larger intensities of SIRM and ARM as shown in Fig. 2.

Although there may be other alternatives, our preferred hypothesis is that the observed magnetic properties are due to low-temperature oxidation (maghemitization) of the original magnetite and its subsequent dissolution below the iron redox boundary in the sediment column. The primary, dominant magnetic mineral in the deep-sea sediments is presumably magnetite of either terrigenous or biogenic origin (Petersen et al., 1986; Vali and Kirschvink, 1989; Yamazaki et al., 1991). We believe that the magnetite is rapidly oxidized at about the water/sediment interface and covered with a thin film of maghemite. Although partly oxidized magnetite is commonly found in deep-sea sediments (Kent and Lowrie, 1974; Johnson et al., 1975; Henshaw and Merrill, 1980; Vali and Kirschvink, 1989; Karlin, 1990), oxidation at sediment/water interface may be less commonly observed. König et al. (1997) reported that ferric/ferrous ratio is surprisingly constant in the upper oxic sediment (tan color zone). This is one of the evidence to suggest early oxidation of iron-bearing minerals in deep-sea sediments. If the magnetite is covered with an oxidized skin, the loss of remanence at the Verwey transition could be suppressed as much as 90\% and the transition smeared to lower temperatures (Özdemir et al., 1993). The effect of oxidation is dramatic in that the maghemite skin suppresses the transition even though pure magnetite still remains in the central part of the grain (Özdemir et al., 1993). The thermal decay curves of IRM show a small but stepwise decrease at about 120 K for the samples above \(-1.3\) mbsf (Figs. 3, 4, and 5). Those small discontinuities could be the subdued Verwey transition caused by oxidized magnetite with an unoxidized core.

Another possibility is that the dominant magnetic mineral in the upper part is titanomagnetite or titanomaghemite of terrigenous origin (Channell and Hawthorne, 1990). Titanium impurities in magnetite tend to suppress the Verwey transition (Senanayake and McElhinny, 1981; Schmidbauer and Readman, 1982). If the dominant magnetic mineral is titanomagnetite in the upper part, the temperature dependence curve of IRM would not show any obvious Verwey transition. This model implies that the dominant magnetic mineral changes abruptly at \(-1.3\) mbsf; the upper part is dominated by titanomagnetite and the lower part by pure magnetite. Such a sudden change in such mineralogy, occurring without any remarkable change in lithology, seems unlikely.

The formation of authigenic magnetite throughout the sediment column is another one of the possible ideas to explain the appearance of the Verwey transition below \(-1.3\) mbsf (Karlin et al., 1987). In the upper part, newly formed SP or nearly SP size SD magnetite grains could dominate the core (Shipboard Scientific Party, 1996b). The grains may grow with depth and begin to show the Verwey transition below a certain depth. The difficulties with this idea are as follows: First, a considerable amount of IRM remains after warming up to 300 K for the samples from the upper part (Fig. 3). If the SP grains dominate the samples, we cannot expect a large IRM at room temperature; and second, the total amount of magnetic mineral abundances seem decrease downcore on the basis of decreasing trends in such parameters as \(\chi_0\) and SIRM (Fig. 2). IRM's at 5 K and 300 K also demonstrate downcore decreases as shown in Fig. 3. An overall decreasing trend is suggested by the rock magnetic parameters for the whole Pleistocene sections. A downcore increasing trend is, however, more likely for authigenesis to have occurred in the sediment column.

If extracellular precipitated magnetite dominate in the upper part, it may subdue the Verwey transition. GS-15, well-known anaerobic bacterium, produces extracellular SP magnetite grains which does not show the Verwey transition (Moskowitz et al., 1993). The downcore dissolution of those SP grains may prompt to reveal the Verwey transition in the lower part of the core. However this scenario is not also preferable judging from the higher SIRM intensity in the upper section (Fig. 2) as discussed above.

The dissolution of magnetic minerals below \(-1.3\) mbsf plays an important role in the appearance of the Verwey transition. The maghemite skin which covers stoichiometric magnetite grains is first dissolved as the chemical environment of the sediment turns into a reducing one. The disappearance of the oxidized
skin reveals the Verwey transition for the samples below ~1.3 mbsf. As the chemical etching progresses, the remaining magnetite grains are dissolved and iron ions possibly recrystallize as pyrite (Canfield and Berner, 1987; Channell and Hawthorne, 1990).

A change in color from tan to green generally pinpoints the iron redox boundary in the sediment column (Lyle, 1983; König et al., 1997). At holes 976D and 977A, a greyish yellow brown color (typically 10YR 4/2) is observed for the uppermost sediment (0–1.2 mbsf). Then the color changes sharply with depth to grayish olive (5YR 5/2) or to olive gray (5GY 5/2), as described by Shipboard Scientific Party (1996a, b). The change in color exactly corresponds to the appearance of the Verwey transition. The Verwey transition becomes distinct in the olive colored sediment. Below the iron redox boundary, the dissolution of the maghemite skin takes place and finally whole grains are dissolved (Karlin, 1990).

The results from Hole 974B are substantially different from those of the other two holes. The Verwey transition is not visible as either a sharp or a smeared out transition even in the deeper part of the sediment column. This site lies about 50 km east of Site 652 (ODP Leg 107, in 1986) in the Tyrrenian Sea (Shipboard Scientific Party, 1996d). Channell and Hawthorne (1990) studied dissolution of titanomagnetite and subsequent pyritization at this site, which could be main reason for an unsuccessful magnetostratigraphy (Channell et al., 1990). The dominant magnetic mineral at Site 652 was titanomagnetite (Channell and Hawthorne, 1990) which might have been provided by nearby submarine or island arc volcanos. As mentioned above, titanomagnetite would not reveal the Verwey transition and thus would show any obvious drop of IRM at 120 K (Fig. 6). Marked low-temperature transitions at about 30–40 K possibly indicate the presence of pyrrhotite, as an accessory mineral of pyrite (Linssen, 1988), or siderite (Coleman et al., 1993). These low-temperature transitions are all associated with the occurrence of sapropel layers and their details are reported elsewhere (Aubourg et al., 1998).

6. Conclusions

1) IRM (1 T) imparted at 5 K was progressively demagnetized up to 300 K by using an MPMS. Depth dependent appearance of the Verwey transition was observed for Holes 976D and 977A. The Verwey transition was invisible or subdued for the samples from the upper part (0–1.3 mbsf).

2) We interpret the depth-dependent appearance of the Verwey transition as follows: The primary magnetic mineralogy of the sediments is dominated by stoichiometric magnetite, which is quickly oxidized to maghemite at about the sediment/water interface. An oxidized maghemite skin covering the magnetite core suppresses the Verwey transition. The maghemite skin is gradually dissolved with depth and the core magnetite is disclosed below ~1.3 mbsf. Although the Verwey transition does clearly appear, magnetite is continuously dissolved downcore. This should be one of the reasons to degrade paleomagnetic records of the studied cores.

3) The sediment changes from tannish to greenish in color at ~1.2 mbsf both at holes 976D and 977A. This change marks the iron redox boundary in the sediment column and also matches the depth where the Verwey transition appears. Reducing conditions act to dissolve the oxidized skin of magnetic minerals in the green colored sediment. The phase transition at 35 K indicates the presence of pyrrhotite or siderite in the sediments and thus also implies reducing conditions.

This paper is published as a part of the Scientific Results of Leg 161 of Ocean Drilling Program. The author thanks H. Fukusawa and R. Wilkens for their help in obtaining sediment color data, A. Otsuka for his help in using the MPMS at the Low-Temperature Laboratory of Kyoto University, and C. Aubourg for discussions during the cruise. He is also grateful to M. Comas, R. Zahn, A. Klaus, and all the shipboard scientific party and crew of Leg 161. He is much indebted to D. J. Dunlop and Ö. Özdemir for their constructive comments and improvements on the original manuscript. Thanks are also due to S. K. Banerjee, R. E. Karlin and H. Shibuya for their thoughtful reviews and helpful comments. Discussions at the third Santa Fe Conference on Rock Magnetism in 1996 were beneficial to the author. The study was partly supported by the Ocean Research Institute, University of Tokyo.
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