低温および高温磁気測定による北大西洋海底のドリフト堆積物（IODP Site U 1314）の磁性鉱物の研究

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Article

Magnetic minerals in sediments from IODP Site U1314 determined by low-temperature and high-temperature magnetism

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Abstract

Magnetic minerals in the sediments from IODP Site U1314 in the North Atlantic have been investigated by low-temperature magnetometry in addition to high-temperature magnetometry. Low-temperature magnetometry is free from thermochemical change of minerals by heating that often complicates the interpretation in high-temperature magnetometry. In addition, we can detect major magnetic minerals effectively using their phase transitions in low temperature. In the results of low-temperature magnetometry, magnetite is considered as the dominant magnetic mineral of the sediments. The results also indicate that the magnetite suffers surface maghemization but that maghemization is not very severe because Verwey transition is observed at ~110 K. In the thermomagnetic curves of sediments in vacuum, the cooling curves were higher than the heating curves. The results are explained by magnetite formation from pyrite by heating.

Keywords: rock magnetism, magnetic mineral, ocean bottom sediments, Integrated Ocean Drilling Program

Introduction

Information of magnetic minerals is essential in interpreting the paleomagnetic and rock magnetic records of sediment cores. In paleomagnetic records of the past geomagnetic field, it is vital to identify the carrier of remanent magnetization to confirm that the remanence faithfully reflect the change in geomagnetic field. On the other hand, in rock magnetic records, the composition of magnetic minerals is utilized to investigate paleoenvironment.

In identifying magnetic minerals, thermomagnetic analysis of magnetic moment or magnetic susceptibility in high temperature is a general method. In such studies, however, thermochemical change of minerals during heating often complicates the interpretation of the results. In contrast, low-temperature techniques are free from such alteration of minerals. In addition, phase transitions of major magnetic minerals（magnetite, hematite, pyrrhotite, etc.）in low temperature are effective in detecting these minerals. The best documented phase transition is the Verwey transition（Verwey 1939）for magnetite. The change in magnetic property associated with the Verwey transition at 110-120 K has often been utilized in detecting magnetite and investigating its state in sediments（e.g., Torii, 1997; Smirnov and Tarduno, 2000; Yamazaki et al., 2003; Housen and Moskowitz, 2006; Inoue and Yamazaki, 2010）.

Taking these advantages in low-temperature mag-

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netometry, we have investigated magnetic minerals in sediments of a core drilled at the Gardar drift in the North Atlantic, from which high-resolution archives of paleomagnetic and paleoenvironmental changes are expected because of high sedimentation rate (e.g. Ohno et al., 2008; Kanamatsu et al., 2009; Hayashi et al., 2010). Since the sediments in the Gardar drift are partly transported by the outflow of Iceland-Scotland Overflow Water (ISOW), the major magnetic fraction consists of titanium-poor magnetite from Icelandic basaltic province (Kissel et al., 2009). Several thermomagnetic curves have been reported from sediments in the Gardar drift. Kissel et al. (2009) reported reversible (in heating and cooling) thermomagnetic curves with the Curie temperature of 580-600℃, typical of titanium-poor magnetite, from Holocene sediments at two sites (MD03-2674Cq and MD03-2676Cq in Fig. 1) in the vicinity of Site U1314. At Site U1314, Ohno et al. (2008) reported thermomagnetic curves with the Curie temperature of about 580℃. However the curves show irreversibility, higher cooling curve than heating curve, which suggests contribution from magnetic components other than magnetite. Similar irreversible thermomagnetic curves were reported at ODP Site 983 located 500 km upstream of the Gardar drift from Site U1314 (Mazaud and Channel, 1999). They attributed the irreversibility to formation of magnetite during heating possibly from pre-existing iron sulfide. For further investigation of the magnetic minerals at Site U1314, here we report and discuss the results of low-temperature magnetic measurements together with high-temperature measurements

Material

Site U1314 was drilled during IODP (Integrated Ocean Drilling Program) Expedition 306 in the southern Gardar Drift (56° 21.9'N, 27° 53.3'W) at 2820 m water depth (Fig. 1). The sediments are rich in nannofossil and clay (Expedition 306 Scientists, 2006). High-temperature and low-temperature magnetic measurements were performed on six bulk (freeze dried) samples between 150 ~ 260 mcd (meter coordinate depth). This interval corresponds to 1.8 ~ 2.7 Ma on the basis of age models in Grützner and Higgins (2010) for the upper part and Hayashi et al. (2010) for the lower part. In addition to these sediment samples, we performed high-temperature measurements on a small (~1cm) rock fragment contained in the sediments. As shown later, X-ray diffraction (XRD) analysis of the rock fragment indicated that it consists mostly of pyrite.

Method

Low-temperature magnetic characteristics were determined on a Quantum Design magnetic property measurement system (MPMS) at Center for Advanced

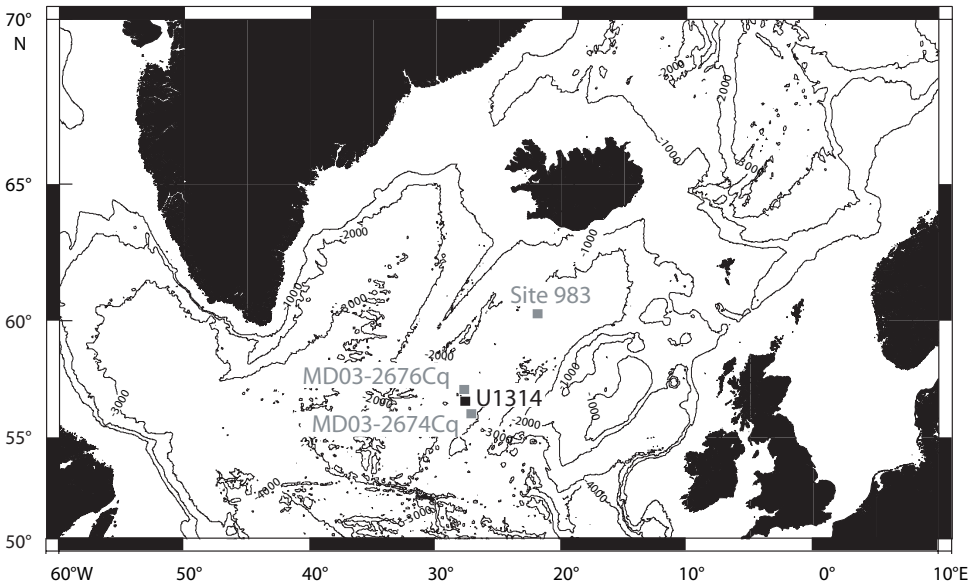

Fig. 1. Location map of Site U1314 together with nearby sites, ODP 983 (Mazaud and Channell, 1999), MD03-2674Cq and MD03-2676Cq (Kissel et al., 2009). Bathymetric contours are given in meters.

Marine Core Research (CMCR), Kochi University. We obtained an isothermal remanent magnetization (IRM) cycling curves, zero-field-cooled (ZFC) warming curves and field-cooled (FC) warming curves. In IRM cycling experiments, IRM was imparted to each sample in a direct-current (DC) field of 2.5 T at room temperature and the sample was cooled from 300 K to 6 K and then warmed back to 300 K. In ZFC warming experiments, each sample was first cooled down to 6 K in zero field and an IRM was imparted in a DC field of 2.5 T. The remanent magnetization was measured in zero field during warming from 6 K to 300 K. In FC warming experiments, the sample was again cooled to 6 K but in this time in an applied field of 2.5 T, and then the remanent magnetization was measured in zero field during warming from 6 K to 300 K. In all low-temperature experiments the rate in cooling or warming was controlled to be 2 K/min, and the magnetization was

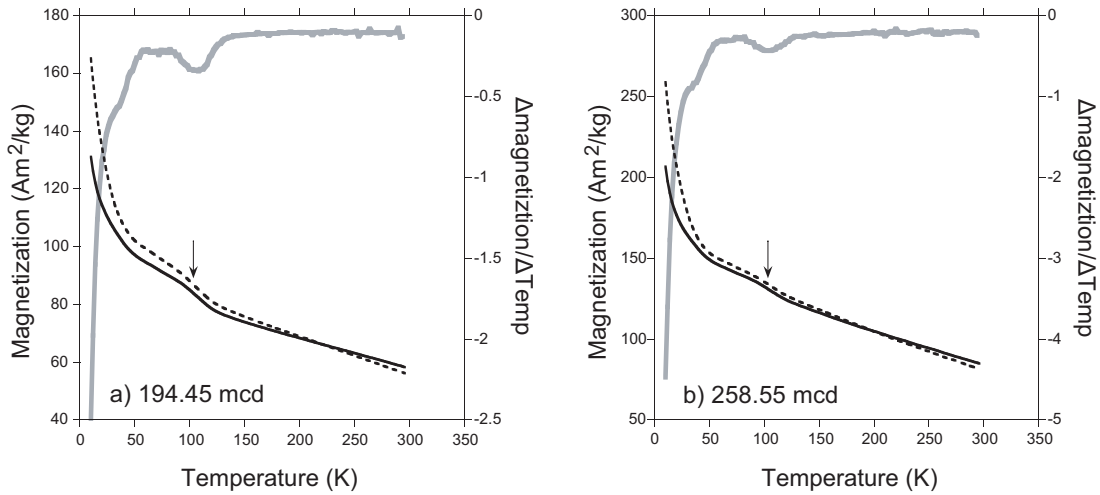

Fig. 2. Typical demagnetization curves of low-temperature isothermal remanent magnetization (IRM) after zero-field-cooling (solid lines) and field-cooling (dotted lines). The differential curves after zero-field-cooling with respect to temperature are shown as grey lines. The arrows indicate Verwey transitions.

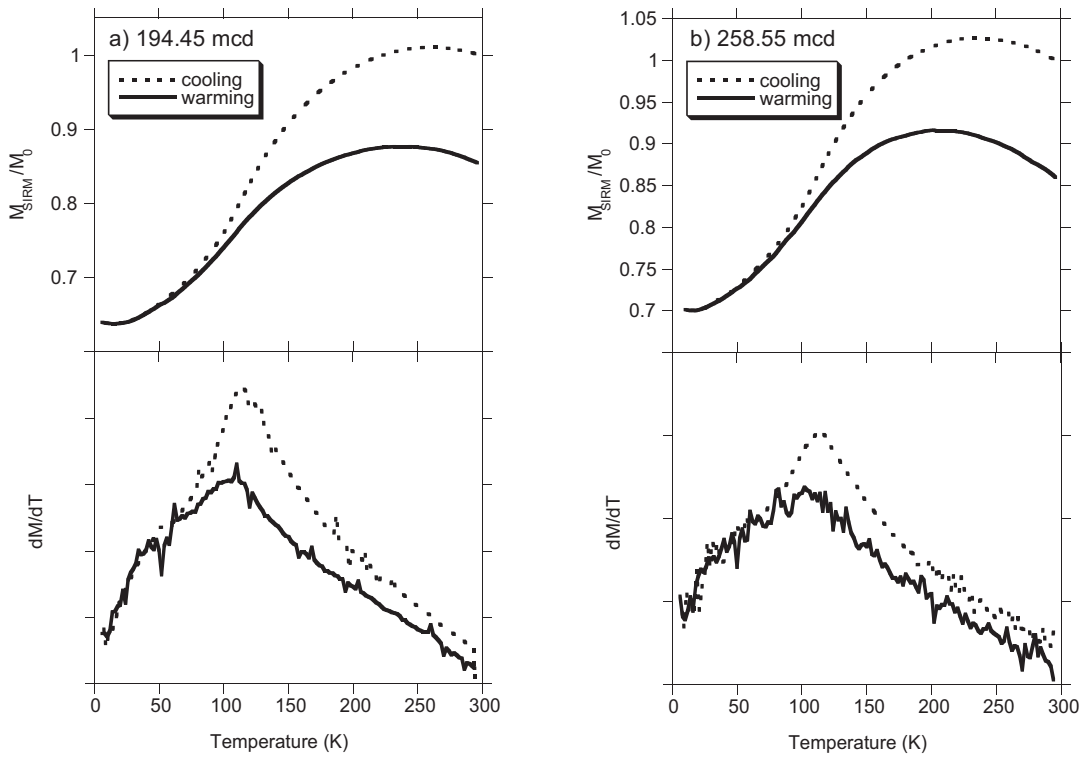

Fig. 3. Typical cooling (dotted lines) and warming (solid lines) curves of IRM imparted at room temperature (upper diagrams) and their differential curves with respect to temperature in arbitrary unit (lower diagrams).

measured twice at each 1 minute interval.

Thermomagnetic curves were obtained with a Natsuhara Giken magnetic balance at CMCR. Heating and cooling (10℃/min) runs between 50℃ and 700℃ were performed both in air and vacuum (< 5 Pa) with a constant DC field (500 mT). Magnetic moment was measured at every 1 second.

The XRD data were collected on a Rigaku X-ray Diffractometer RINT 2100 V, using CuKα radiation monochromatized by a curved graphite crystal in a step of 0.04° with a scan speed of 1 degree/min.

Results

In ZFC and FC warming experiments the IRM imparted at low-temperature is demagnetized in warming as a result of thermal disturbance. In our results (Fig. 2), an increase of the slope at ~110 K indicates the loss of magnetization at Verwey transition of magnetite. No other transitions were observed such as the Morin transition of hematite at ~250-260 K (O.Reilly, 1984) or the transition of pyrrhotite at 34 K (Dekkers et al., 1989). It is noteworthy that FC warming curve is significantly higher than ZFC warming curve below 100 K but the difference between them decreases with warming.

In IRM cycling experiments (Fig. 3), the IRM imparted at 300 K decreases with cooling to 6 K, and then increases as warming to 300K. The difference between the cooling and heating curves at above ~100 K (Fig. 3) is most likely due to loss of remanence as a result of passing Verwey transition (Yamazaki et al., 2003: Inoue and Yamazaki, 2010), which also indicates existence of magnetite. The differential curves with respect to temperature in Fig. 3 clearly indicate inflection points at ~110 K.

In the thermomagnetic curves in heating (Fig. 4) the magnetization decreased with increasing temperature and lost their moment at about 580℃, which indicates the presence of magnetite or titanium-poor titanomagnetite. However, an additional component is suggested from features of these curves: small decrease during heating in magnetization at around 200~300℃, and higher magnetization (J_s/J_0) along the cooling curve than along the heating curve in vacuum. The latter feature indicates formation of magnetite by heating. In contrast, in the thermomagnetic curves in air, magnetization in cooling is lower than heating one, which is interpreted as oxidation of a part of magnetite to hematite.

Fig. 5a shows the XRD data of the rock fragment indicating pyrite as the dominant material. Calcite was also detected. Thermomagnetic curves of the pyrite fragment were obtained in vacuum and air, respectively, after crushing (Fig. 6). In the XRD data of the material after thermomagnetic measurement up to 700℃ in vacuum, magnetite was confirmed to exist (Fig. 5b). In the thermomagnetic curve in vacuum, the high magnetization in the cooling curve with the Curie temperature of ~580℃ is consistent with formation of magnetite, because the magnetization of pyrite, a paramagnetic mineral, is much lower than that of magnetite, a ferromagnetic mineral. In the thermomagnetic curve in air up to 800℃ (Fig. 6b), increase of magne-

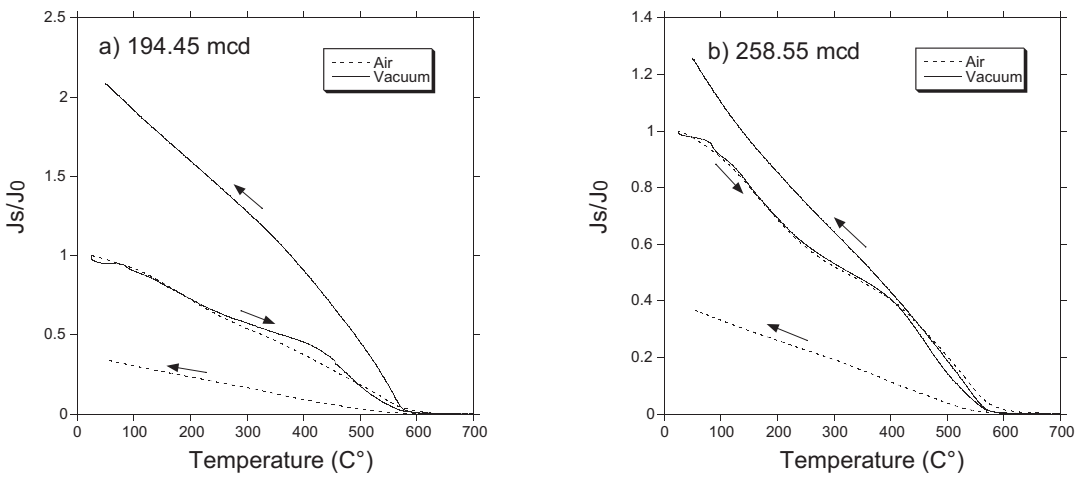

Fig. 4. Typical thermomagnetic curves in vacuum (solid lines) and in air (dotted lines) of sediments. The vertical axis denotes saturation magnetization normalized by the initial value.

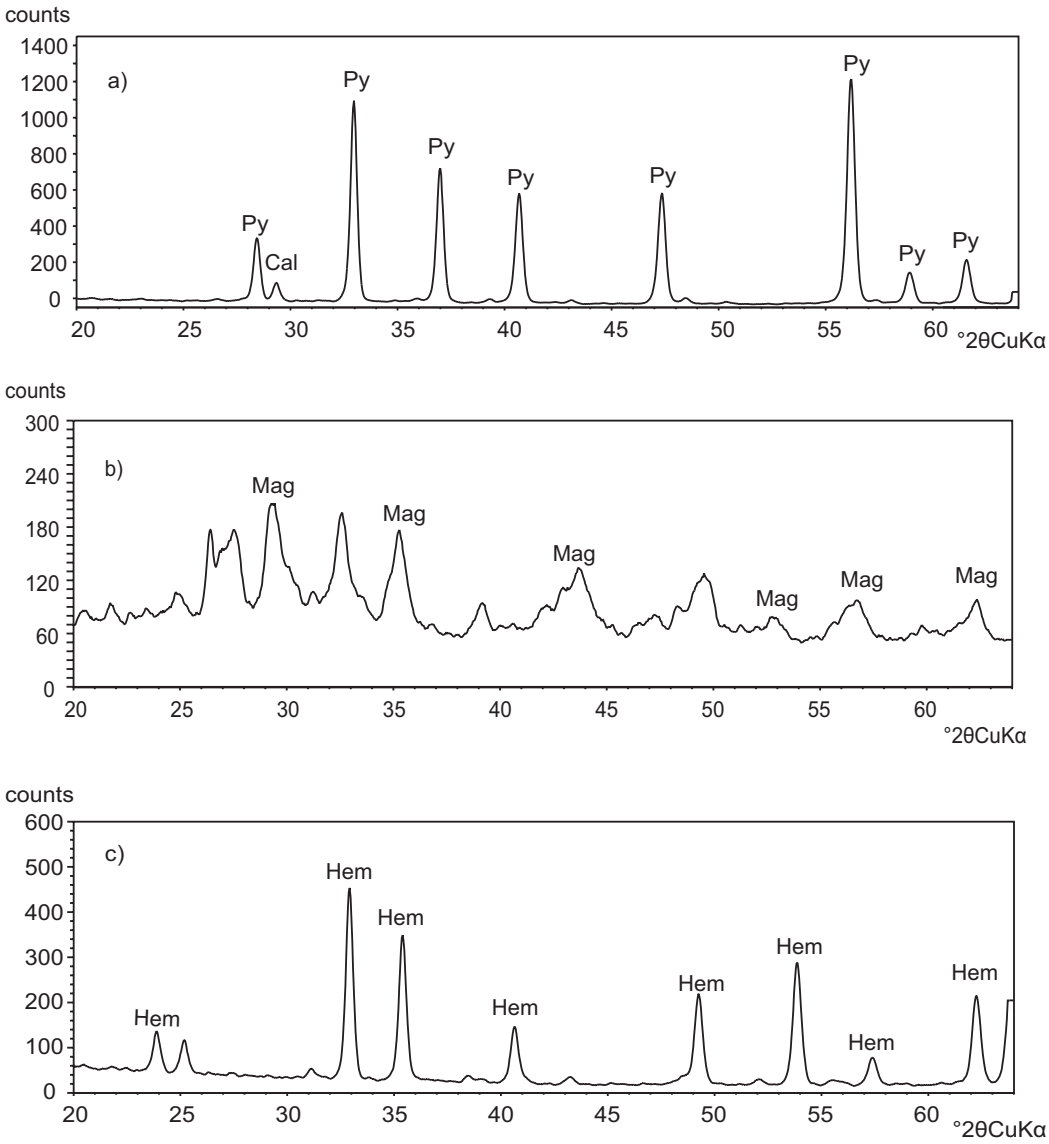

Fig. 5. XRD spectra of pyrite fragment (a) before heating, (b) after heating in vacuum, and (c) after heating in air. Minerals corresponding to identified peaks are denoted as Py (pyrite) , Mag (magnetite) , Hem (hematite) , and cal (calcite) , respectively.

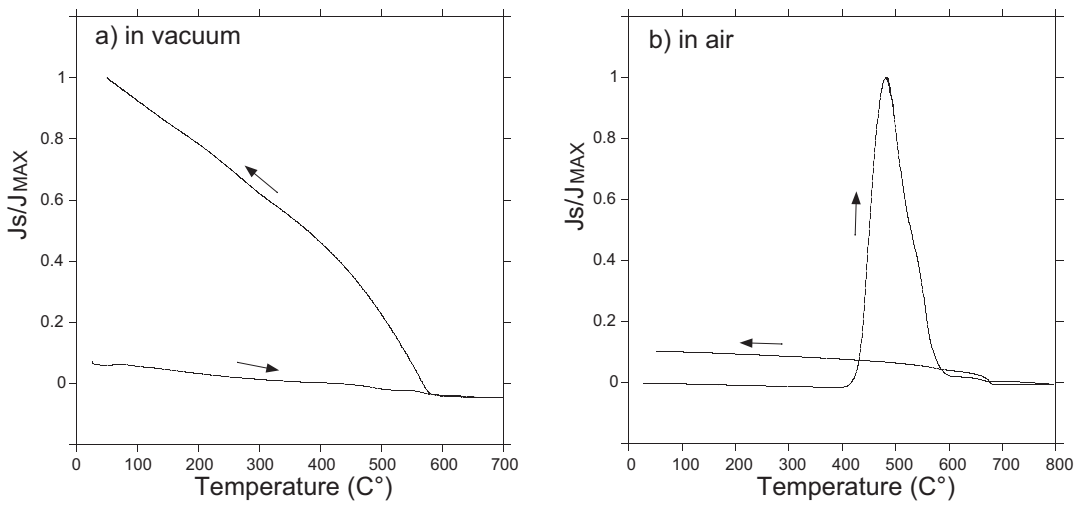

Fig. 6. Thermomagnetic curves of a pyrite fragment (a) in vacuum and (b) in air normalized by the maximum value.

tization at 400–500℃ during heating was observed, which may indicate formation of magnetite. The XRD analysis of the material after this thermomagnetic measurement confirmed that the material is hematite (Fig 5c). Low magnetization during cooling is explained by oxidization of the formed magnetite to hematite.

Discussion

In the low-temperature experiments, the Verwey transition observed at ~110 K in the FC and ZFC warming curves obviously evidences the presence of magnetite. The temperature of the Verwey transition is known to be so sensitive to titanium substitution in magnetite, and the temperature can be lowered below 90 K in low-Ti magnetite (Moskowitz et al., 1998; Muxworthy and McCelland, 2000).

However, compared to the sharp decrease at the Verwey transition of stoichiometric magnetite (e.g. Özdemir et al., 1993), the transitions in our ZFC and FC warming curves are much depressed as is often observed for natural samples (e.g., Torii, 1997; Housen and Moskowitz, 2006). This depression is considered to be the result of oxidation of magnetite grains. If the surface of magnetite grains is coated by maghemite owing to surface oxidation, the transition in ZFC and FC warming is strongly depressed (e.g. Özdemir et al., 1993). Özdemir et al. (1993) also showed that maghemization shifts the temperature of transition to below 100 K. The present results, in which IRM showed transition at ~110 K, indicate that the maghemization is not very severe in our sediments. It is noteworthy that the sharp decrease of IRM below 40 K is also characteristic of surface maghemization (Özdemir et al., 1993).

On the basis of low-temperature magnetometry of sediments as well as of thermomagnetic curves and XRD data of pyrite fragment, we have interpreted the thermomagnetic curves of sediments as follows. Thermomagnetic curves in vacuum have the Curie temperature of ~580℃, indicating magnetite. However, small decrease in magnetization observed at around ~250℃ during heating indicates existence of other components. A possible explanation for this is the inversion of maghemite to weakly magnetic hematite by heating. The temperature (~250℃) of this inflection is around the lower limit of the inversion temperature that has been reported as occurring variously from 250℃ to ≥ 750℃ (Dunlop and Özdemir, 1997).

The higher magnetization during cooling than during heating in vacuum (Fig. 4) is interpreted as formation of magnetite by heating. A possible source of the formation is pyrite in the sediments. It is consistent with that disseminated pyrite staining on millimeter to centimeter scale was observed in most of the sediments at Site U1314 (Expedition 306 Scientists, 2006). In addition, formation of magnetite from pyrite heated in vacuum was confirmed by the thermomagneic curve (Fig. 6) and the XRD data (Fig. 5) of the pyrite fragment. In thermomagnetic curves (Fig. 4), more magnetite was formed in the sample from 194.45 mcd (a) than in the sample from 258.55 mcd (b) although no significant difference was observed between them in low-temperature measurements. This is consistent with the fact that the low-temperature magnetometry is not affected by the amount of paramagnetic pyrite.

As discussed previously, the characteristic of thermomagnetic curves of sediments in vacuum (inflection at ~250℃ during heating and irreversible cooling curve) is consistent with inversion of maghemite to hematite and formation of magnetite from pyrite. On the other hand, part of these characteristics may also be explained by contents of titanomaghemite. If titanomaghemite is present, titanium-poor titanomagnetite is produced as a result of inversion of titanomaghemite by heating. Although magnetite is considered as the dominant magnetic mineral of the sediments at Site U1314 by the low-temperature magnetometry, contribution of a small amount of titanomaghemite may not be excluded.

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低温および高温磁気測定による北大西洋海底のドリフト堆積物（IODP Site U1314）の磁性鉱物の研究

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要　旨

北大西洋深海底堆積物コア試料（IODP EXP. 306 Site U1314）の磁性鉱物の検討を、岩石磁気学的手法と鉱物学的手法を用いて行った。岩石磁気実験は磁気特性測定装置（MPMS）を用いた低温（6K～300 K）実験と磁気天秤を用いた加熱（～700℃）実験を行った。実験の結果にコアの深度による差異は認められず、このコア試料は全体的に均一な磁性鉱物を含むと考えられる。低温実験の結果はマグネタイトの存在を示しており、また熱磁気実験で得られたキュリー温度は580℃で、これらは主な磁性鉱物がマグネタイトであることを示す。低温実験の結果はマグネタイト粒子の表面の酸化によるマグヘマイト化を示唆しているが、110K付近でVerwey転移が見られることから、この表面酸化の進行は軽度であると考えられる。さらに熱磁気実験における非可逆的な加熱冷却曲線は加熱によって他の鉱物からマグネタイトが生成したことを示す。低温実験とX線回折実験の結果から、このマグネタイトの起源はパイライトの熱変質であると考えられる。

キーワード：磁性鉱物、岩石磁気、海底堆積物、統合国際深海掘削計画

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