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Bernard A. Housen
Western Washington University, bernard.housen@wwu.edu

S. K. Banerjee

B. M. Moskowitz

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Low-temperature magnetic properties of siderite and magnetite in marine sediments

B.A. Housen, S.K. Banerjee and B.M. Moskowitz
Department of Geology and Geophysics, and Institute for Rock Magnetism, University of Minnesota, Minneapolis

Abstract. Low temperature magnetic techniques provide useful tools to detect the presence of magnetite and pyrrhotite in sediments through identification of their low temperature transitions, to determine the amount of ultrafine-grained (super-paramagnetic) material in sediments, and can potentially detect the presence of certain types of magnetotactic bacteria. Application of these types of experiments to nannofossil chalks from beneath the Barbados accretionary prism led to some unusual results, which are attributed to the presence of siderite. Thermal demagnetization of low-temperature remanence after cooling in zero field and in a 2.5 T field both displayed large remanence losses from 20 K to 40 K. Below 40 K, the magnetization of the chalks was much higher in the field-cooled experiments than in the zero-field-cooled experiments. Low temperature hysteresis experiments, made after cooling in a 2.5 T field, displayed offsets in magnetization parallel to the direction of the applied field, when measured below 40 K. The offset loops can be due to either an exchange anisotropy between siderite and magnetite phases in the sediments, a defect moment in the siderites, or a canted moment in the siderites. Apparent similarity between the low-temperature thermal demagnetization results from these siderite-bearing sediments, pure siderite, and pure rhodochrosite samples and the well-known 34 K transition in pyrrhotite should lead to caution in identification of pyrrhotite in marine sediments based on low-temperature remanence studies alone.

Introduction

The magnetic properties of marine sediments provide records of many types of global phenomena, ranging from the behavior of the Earth's geomagnetic field [e.g., Valet and Meynadier, 1993], past climate changes [Verosub and Roberts, 1995], to the deformation of active accretionary prisms [Housen et al., 1996]. The fidelity of marine sediments as the recording media of these processes can be adversely affected by post-depositional diagenesis. Thermal demagnetization of low-temperature remanence after cooling in zero field and in a 2.5 T field both displayed large remanence losses from 20 K to 40 K. Below 40 K, the magnetization of the chalks was much higher in the field-cooled experiments than in the zero-field-cooled experiments. Low temperature hysteresis experiments, made after cooling in a 2.5 T field, displayed offsets in magnetization parallel to the direction of the applied field, when measured below 40 K. The offset loops can be due to either an exchange anisotropy between siderite and magnetite phases in the sediments, a defect moment in the siderites, or a canted moment in the siderites. Apparent similarity between the low-temperature thermal demagnetization results from these siderite-bearing sediments, pure siderite, and pure rhodochrosite samples and the well-known 34 K transition in pyrrhotite should lead to caution in identification of pyrrhotite in marine sediments based on low-temperature remanence studies alone.

Sediment Properties and Magnetism at 293 K and Above

The nannofossil chalks occur between 520 and 590 meters below sea floor (mbsf) at ODP Site 948C, are light gray in color,
and are distinctly graded indicating deposition as turbidites [Shipley et al., 1995]. The bedding in these turbidites has shallow (less than 15°) dips. The mineralogy of these chalks, determined by powder X-ray diffraction, consists of calcite, siderite, quartz, and clay minerals (Figure 1). No magnetic minerals (i.e., magnetite, greigite, maghemite, etc.) were detected using X-ray diffraction, likely owing to the low concentration of these trace minerals.

These nannofossil chalks have several distinct magnetic properties at room temperatures and above. Anisotropy of magnetic susceptibility (AMS) fabrics are inverse (with the maximum susceptibility axes perpendicular to bedding, rather than parallel [Rochette, 1988]) [Housen et al., 1996], which is consistent with other studies of siderite-bearing sediments [Ellwood et al., 1986]. Curie temperature experiments were conducted using a Geo-fyzička KLY-2 Kappabridge equipped with a heating furnace, and modified to include a flow of Argon gas into the sample tube to retard oxidation of the sample while heating. Susceptibility was measured every 10 seconds as the sample was heated from room temperature to 700°C, and then cooled from 700°C to 50°C (Figure 2). On heating the susceptibility is very low from room temperature until 370°C. Between 370 and 400°C the susceptibility increases sharply, indicating formation of some new magnetic mineral phase. From 400 to 540°C the susceptibility increases more gradually, with a sharp drop in susceptibility between 540 and 570°C, which likely represents the Curie temperature of magnetite (Figure 2). On cooling from 700°C susceptibility gradually increases from 500°C to 300°C, with magnetic moment measurements taken at 5 to 10 K intervals. The samples were then cooled from 300 K to 5 K in the absence of a magnetic field (referred to as zero-field-cooled (ZFC)); at 5 K a field of 2.5 T was applied to give the sample an IRM. The field was then turned off, and the sample was again heated from 5 K to 300 K, with magnetic moment measurements taken at intervals of 5 to 10 K.

In the ZFC experiments on the nannofossil chalks a sharp drop in remanence between 5 K and 40 K, and a less-pronounced (Figure 3b) or absent (Figure 3a) remanence drop between 110 K and 125 K occurs upon heating from 5 K to 300 K (Figure 3). In the FC experiments on the same samples a marked difference between remanence behavior exists below 40 K. The remanence intensity at 5 K is about one order of magnitude higher after FC treatment; on heating this remanence drops very sharply between 25 K and 40 K (Figure 3). When heating above 40 K the remanence behavior of these samples is identical to that observed during the ZFC experiments (Figure 3). The sharp drop in remanence between 25 K and 40 K which occurred in both sets of experiments is reminiscent of the 34 K magnetic transition in pyrrhotite [Dekkers et al., 1989, Rochette et al., 1990], but the large difference in remanence observed between the FC and ZFC experiments has not been observed in pyrrhotite. The drop in
remanence on heating between 110 K and 125 K (Figure 3b) represents the Verwey transition of magnetite, and is consistent with the Curie temperatures at 540 to 570°C observed during the high-temperature experiments (see Figure 2).

To better understand what is responsible for the large difference in remanence properties between FC and ZFC experiments below 40 K, hysteresis loops were measured at 20 K and at 40 K, after both FC and ZFC treatments. After stabilization at the desired temperature the field was cycled between ±5 T several times before hysteresis measurements to avoid measuring minor loops. To obtain the loops, magnetic moment was measured while the applied field was decreased from 5 T to -5 T, and increased again to 5 T. The initially obtained hysteresis loops were dominated by the paramagnetism of the clay minerals in these samples, which is greatly enhanced at low temperatures. To obtain the ferromagnetic loop, the results were corrected by subtracting the linear susceptibility (multiplied by applied field) obtained from the high-field portion of the loops. Problems with the high-field correction arose from the low-temperature behavior of the paramagnetic clays, whose induced magnetization begins to be saturated by high fields at low temperatures (Figure 4). To overcome this problem, intermediate fields (0.6 to 1.5 T) were used for the high-field slope corrections.

At 20 K, the low temperature hysteresis loops have similar forms; they are very narrow (indicating very low values of coercivity (Hc) and saturation remanence (Jrs)), and all of the loops reach saturation magnetization (Js) at ±0.6 T (Figure 5a,c). At 40 K the low temperature hysteresis loops are more open, with higher values of Hc (70 mT) and Jrs (0.0004 Am²/kg), and reach saturation at about 1.0 T (Figure 5b,d). The ZFC loops at both 20 K and 40 K are symmetrical about the origin, and saturation magnetization at 20 K is about three times greater than saturation magnetization at 40 K (Figure 5a,b). The FC loop obtained at 40 K is identical to the ZFC loop at this temperature (cf., Figure 5b and d), which is consistent with the FC and ZFC remanence experiments (see Figure 3b). The FC loop at 20 K is very different, in that it is completely offset 0.01 Am²/kg along + J from the origin (Figure 5c). The offset in hysteresis at 20 K is repeatable, it only occurs after cooling in the presence of a field, and always disappears when the sample is heated above 40 K.

Attempts were made to further characterize the magnetic properties of these sediments by measuring both high DC field (H = 3 T) and low AC field (H < 0.1 mT) susceptibility as a function of temperature. No conclusive results could be obtained, however, as the susceptibilities of the samples were completely dominated by the clay minerals, exhibiting Curie-Weiss behavior (χ ∝ 1/T-θ).

**Magnetic properties of Siderite (FeCO₃)**

Many of the magnetic properties of the nannofossil chalks can be ascribed to siderite. Siderite bearing sediments often display inverse magnetic fabrics [Ellwood et al., 1986]. Upon heating, magnetite or maghemite is produced by oxidation of siderite [Ellwood et al., 1986]. The primary phase produced by heating these nannofossil chalks is not magnetite, but instead is likely a Mn-ferrite, which would be formed as an oxidation product of siderite with a small amount of rhodochrosite (MnCO₃) substitution. Siderite is an antiferromagnet with a Néel temperature (T_N) of 38 K [Jacobs, 1963]. Rhodochrosite is a canted-antiferromagnet, with a Néel temperature (T_N) of 32 K [Borovik-Romanov, 1959]. Results of low temperature FC and ZFC experiments on a natural siderite powder are very similar to those of the nannofossil chalks (Figure 6). Both FC and ZFC experiments have large drops in remanence between 30 and 40 K, and the FC remanence below 40 K is much larger than the ZFC remanence. The large drop in siderite remanence between 30 and 40 K corresponds to its Néel temperature. The much larger remanence in the FC experiments represents a large TRM as the siderite cools through its T_N. Low temperature hysteresis...
experiments on the pure siderite powders did not, however, reveal any offset in the FC loops below 40 K. High DC field and low AC field susceptibilities of the siderite powders both show a prominent peak in susceptibility at the Néel temperature of 35 K, which is a characteristic of antiferromagnets. The presence of remanence in the siderite does, however, suggest some form of canted or defect moment in these siderite powders.

Offset Hysteresis Loops

Hysteresis loops shifted along +J (parallel to the field applied during cooling) can be produced in mixed magnetic phases by several types of exchange anisotropy in many compounds (i.e., UMn₂, αFe₂O₃, LaFo₃ [see Meiklejohn, 1962]). In this case, cooling through Tₐ of an antiferromagnetic phase (siderite) couples the antiferromagnet’s spins to the ferrimagnetic spins (which are parallel to H) along their interface. The coupling of the ferrimagnetic phase to the strong crystalline anisotropy of the antiferromagnetic phase cannot be overcome with typical laboratory fields. During the hysteresis experiment (below siderite’s Tₐ), the magnetite can be fully magnetized along +H, as this spin configuration will be parallel to the direction in which the ferrimagnetic spins are coupled to the antiferromagnetic spins. For the -H portion of the hysteresis loop, the ferrimagnetic spins are trying to align in a direction which is antiparallel to the exchange-coupled direction. Under laboratory fields (in this case -5T), complete rotation of the magnetite’s magnetization to the -H direction cannot be achieved because the coupling of the siderite’s spins to the ferrimagnetic spins of the magnetite (parallel to +H) cannot be overcome. This incomplete rotation will produce a smaller measured magnetic moment parallel to -H compared to the same field parallel to +H, and reversible loop behavior with zero width.

An alternative explanation is that the offset represents a defect moment, or a canted moment residing in the siderite (or, Fe-Mn carbonate). Cooling through the Néel temperature with a strong field produces a strong alignment of the antiferromagnetic spins. The defect moment would arise from an inequality of spins in the two sublattices, which may be expected in typically impure marine sediments. The offset in remanence in the FC loop at 20 K would indicate that this defect or canted moment cannot be flipped with a 5 T field, which would be expected in either case. Further work will be needed to fully account for the shifted loops measured in the Barbados marine sediments.

Conclusions

Unusual low temperature magnetic properties of nanofossil chalks from beneath the Barbados accretionary prism are due to the presence of siderite. Examination of the low temperature results provides a strong note of caution for future applications of low-temperature magnetic studies to marine sediments. The large decrease in remanence from 20 K to 40 K in these nanofossil chalks and in siderite and rhodochrosite powders is remarkably similar to that observed for pyrrhotite. In Figure 7, ZFC results are plotted for siderite, rhodochrosite, and pyrrhotite. The large drops in ZFC remanence between 30 K and 40 K are extremely similar for all three of these minerals. Both the rhodochrosite and the siderite display much higher remanences below 40 K after FC treatment (see Figure 6 for siderite), thus comparison between FC and ZFC results can help to distinguish between low-temperature magnetic properties of Fe-Mn carbonates and pyrrhotites. Identification of pyrrhotite in marine sediments on the basis of low-temperature remanence studies alone may produce misleading results.

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