GEOPHYSICAL RESEARCH LETTERS, VOL. 22, NO. 23, PAGES 3167-3170, DECEMBER 1, 1995

"Wasp-waisted" hysteresis loops from a pyrrhotite and magnetite-bearing remagnetized Triassic limestone

Giovanni Muttoni

Lamont-Doherty Earth Observatory, Palisades, New York

Abstract. Remagnetized samples of the Triassic Prezzo Limestone from northern Italy contain a mixture of pyrrhotite and magnetite, as deduced by thermal unblocking characteristics of triaxial isothermal remanent magnetizations (IRM's) and low-temperature cycling of saturation IRM's. Hysteresis loops are commonly "wasp-waisted" and remanent coercivity curves contain a break in slope, as a result of the contrast in coercivity between remanence-carrying pyrrhotite and magnetite. The relative proportion of the high to low remanent coercivity fractions, as deduced by the study of the remanent coercivity curves, seems to control the degree of "wasp-waistedness" of the hysteresis loops. Samples that are dominated by one of the two coercivity end members have lower B_{cr}/B_c values as well as hysteresis loops that have a less pronounced constricted waist compared to samples with higher B_{cr}/B_c values. Maximum B_{cr}/B_c values (and thus maximum degrees of "wasp-waistedness" in the hysteresis loops) are attained when the low remanent coercivity fraction contributes 15-35% to the bulk remanent coercivity curves.

Introduction

Hysteresis loops give information concerning the coercivity spectrum and domain state of ferri- and ferromagnetic materials. A set of non-interacting single domain (SD) magnetic particles with uniaxial symmetry gives hysteresis loops with saturation remanence (M_{rs}) values that are equal to about half the saturation magnetization (M_s) [Stoner and Wohlfarth, 1948]. Lower values of M_{rs}/M_s are expected for low coercivity multidomain (MD) grains, due to the less effective mechanism of remanence acquisition for these grains.

A problem arises when dealing with rocks that contain magnetic minerals with contrasting coercivities. Day et al. [1977] showed that, for (titano)magnetite samples that comprise a mixture of <20% of a hard coercivity fraction with a low coercivity fraction, the coercive force (B_c) is dominated by the soft fraction and the coercivity of remanence (B_{cr}) increases with increasing amounts of the hard fraction. Mixtures of hard and soft coercivity minerals may give "wasp-waisted" hysteresis loops (i.e., loops that are constricted in the middle section and wider above and below the middle section). As pointed out by Roberts et al. [1995], "wasp-waisted" hysteresis loops were first described in the literature in the 1920's [e.g., Gumlich, 1920]. During recent years, as the study of the response of magnetic materials to applied fields has become more common in paleomagnetic research, examples of "wasp-waisted" hysteresis loops from a variety of natural and artificial materials are being reported more widely. "Wasp-waisted" loops have recently been reported from: non-remagnetized Mesozoic hematite and magnetite-bearing limestones [Channell and McCabe, 1994], remagnetized Paleozoic magnetite-bearing limestones with a non-uniform B_{cr}/B_c distribution [Jackson et al., 1993; Sun and Jackson, 1994; McCabe and Channell, 1994], basaltic glass containing single domain magnetite that co-exists with a superparamagnetic (SP) fraction [Pick and Tauxe, 1994], as well as from Pleistocene lake sediments from northern California, archeomagnetic samples from Bulgaria, and a wide range of other natural occurrences [Roberts et al., 1995]. Numerical simulations of composite hysteresis loops using single domain/superparamagnetic (SP) assemblages have also been generated by Tauxe et al. [1995].

The Triassic Prezzo Limestone from northern Italy contains a mixture of pyrrhotite and magnetite, as deduced by Muttoni and Kent [1994] and the present study. The aim of this paper is to test whether a pyrrhotite-magnetite mixture can give "wasp-waisted" hysteresis loops. Hysteresis parameters from 48 Prezzo Limestone samples are presented here.

Geology and paleomagnetism

The Prezzo Limestone is latest Anisian (middle Triassic) in age and consists of up to 90 m of 20-25 cm-thick beds of gray to black limestones that alternate with black marls. The sampling site (site 1 of Muttoni and Kent [1994]) is located in the upper Daone Valley (Giudicarie Alps, Trentino, Italy) near the late Eocene-Oligocene (42 to 30 Ma) Adamello batholith.

The vector end point demagnetization diagrams of Muttoni and Kent [1994] sometimes show up to 3 antiparallel demagnetization trajectories that co-exist in a single specimen and that all seem to be carried by a 320°C maximum unblocking temperature phase (the definition "maximum unblocking temperature phase" is hereafter abbreviated to MTP for the sake of brevity.) These antiparallel paleomagnetic directions are much better grouped *in situ* rather than after tilt correction and they yield a mean pole which lies close to the early Cenozoic portion of the European Apparent Polar Wander Path. These paleomagnetic directions were interpreted by Muttoni and Kent [1994] as a remagnetization associated with the Adamello intrusion and they were acquired after the main phase of deformation in the country rock (i.e., during late Cretaceous to early Paleogene time.) By contrast, samples of the Prezzo Limestone, collected some 50 km to the west of the Adamello batholith, display the presence of an overwhelming 570°C MTB, interpreted as magnetite, and which carry a pre-folding characteristic component that is likely to be primary in origin [Muttoni and Kent, 1994].

Paper number 95GL03073
0094-8534/95/95GL-03073$03.00

Laboratory techniques

The ferrimagnetic phases were identified with the aid of thermal unblocking characteristics of triaxial isothermal remanent magnetizations (IRM's), according to the method of Lowrie [1990]. IRM's were obtained by imparting a 1.4T field along the sample z-axis, a 0.4T field along the y-axis, and finally a 0.12T field along the x-axis. Low-temperature cycling of a saturation IRM (SIRM) was performed by Christopher Hunt (Institute for Rock Magnetism, University of Minnesota) with a Quantum Design MPMS super-conducting susceptometer. Hysteresis loops (up to ±1.4T) were obtained from small rock chips (a few tens of mg in mass) which were taken from selected cores. The parameters M_S, M_{rs} and B_c were determined after correction for the para- or diamagnetic contribution to the total magnetic moment (83% (17%) of the samples displayed a dia-magnetic (paramagnetic) slope.) Samples were then demagnetized in an alternate field and given an SIRM which was demagnetized in a stepwise backfield from 0T to a maximum of -1.4T. The curves thus obtained (referred hereafter to as remanent coercivity curves) give the remanent coercivity spectrum of a sample. The coercivity of re-manence (B_{cr}) is the particular value of field required to reduce the maximum remanence to zero. Both hysteresis loops and remanent coercivity curves were obtained with a MicroMag 2900 Alternating Gradient Magnetometer.

Rock magnetic data

Thermal decay of the IRM's

Thermal decay of the IRM's (and of the natural remanent magnetizations) is dominated by a magnetic phase with narrowly distributed unblocking temperatures between 300 and 320°C, interpreted as pyrrhotite by Muttoni and Kent [1994] (Fig. 1). The shape of the thermal decay curves of the hard (1.4T) and soft (0.12T) coercivity fractions are similar, with

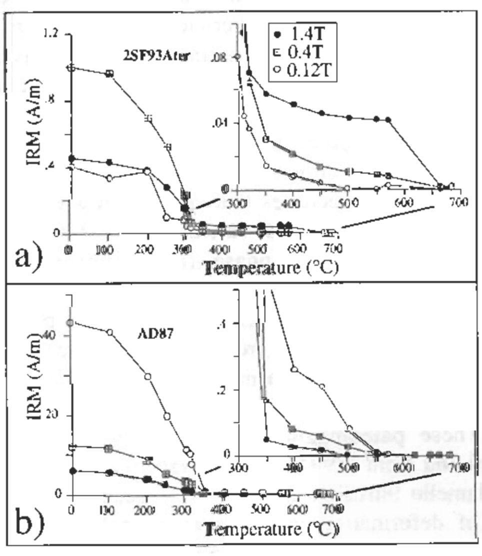

Figure 1. Thermal decay curves of three axis IRM's for: (a) Prezzo Limestone samples dominated by fine-grained pyrrhotite (0.4T curve) together with less abundant coarse grained pyrrhotite (0.12T curve) and magnetite, and (b) Prezzo Limestone samples dominated by a coarse-grained pyrrhotite fraction that co-exists with less abundant fine-grained pyrrhotite and magnetite.

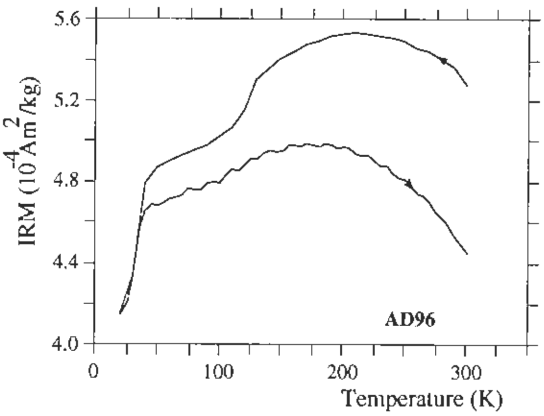

Figure 2. Thermal variation of room temperature saturation IRM (mass-normalized) on cooling and heating for one representative Prezzo Limestone sample that contains pyrrhotite and magnetite. Both the Verwey (110-120K) and the 30-34K transitions are present.

the 0.4T coercivity fraction dominating in some of the specimens (Fig. 1a) and subordinate to the 0.12T fraction in others (Fig. 1b). These new data suggest that the example illustrated for the same rock from site 1 in Figure 8 of Muttoni and Kent [1994], where the 1.4T coercivity fraction dominates, is not representative of the magnetic behavior of these samples. The representative examples reported in Figure 1a, b suggest the presence of a 300-320°C MTP with relatively uniform coercivities (i.e., grain sizes). Above 320°C, a small but still detectable portion of the IRM indicates the presence of, in some cases, a 500-570°C MTP (Fig. 1b). In other cases, the unblocking curves change slope at about 450-500°C and reach unblocking temperatures as high as 680°C (Fig. 1a). Initial (volume) susceptibility shows a sharp increase generally above 400°C, and is sometimes followed by a decrease at higher temperatures. One interpretation of the results is that, due to thermal alteration during the heating procedure, a 320°C MTP transforms into (or forms) a high susceptibility 450-500°C MTP, which in turn may transform into (or form) a low snsceptibility 680°C MTP, most probably hematite. These observations are reminiscent of the results of Dekkers [1990] who, after monitoring pyrrhotite behavior during heating, described the progressive oxidization of pyrrhotite into magnetite and eventually into hematite. Because the susceptibility increases substantially at temperatures somewhat above 400°C (i.e., when a large fraction of the 450-500°C MTP is unblocked), it is concluded that at least a portion of this 450-500°C MTP does not result from mineral alteration during heating, but rather it represents a primary phase that co-exists with the ubiquitous 320°C MTP.

Low-temperature cycling of SIRM

Four selected samples of Prezzo Limestone were subjected to low-temperature cycling of SIRM. The descending branch of the curves (i.e., from room temperature to the liquid helium temperature) reveals three peculiar features (Fig. 2):

1) *A broad peak in the 200K range.* This feature corresponds to a maximum in M_S for pyrrhotite according to Rochette et al. [1990].

2) *A decrease in the intensity of the SIRM at about 110-120K.* This discontinuity is interpreted by several authors (e.g., Özdemir et al. [1993] and references therein) as a

magnetite-diagnostic feature. In magnetite, a discontinuity occurs at 110-120K due to the trans-formation of the crystal structure from cubic to a lower symmetry. This discontinuity is widely known as the Verwey transition [Verwey, 1939].

3) *A sharp decrease in the intensity of the SIRM at about 30-34K.* Like the first feature, this discontinuity is interpreted by Rochette et al. [1990] as a pyrrhotite-diagnostic feature. At room temperature, the spontaneous magnetization of pyrrhotite is confined to the crystallographic basal plane. On cooling at low temperatures, an inferred change of easy axis direction within the basal plane should cause a discontinuity in the intensity of remanence between 30 and 34K [Rochette et al., 1990].

The ascending branch of the curves (i.e., from the liquid helium temperature to room temperature) does not reproduce the descending branch. Multidomain magnetite grains loose some of their initial remanence when they are cycled back to room temperature after being cooled below ≈130K in zero field [Kobayashi and Fuller, 1964]. There is about a 20% loss in remanence for all of the samples from the Prezzo Limestone that have been subjected to low-temperature cycling. This loss in the intensity of the remanence may be diagnostic of the presence of MD magnetite.

In conclusion, thermal decay curves of IRM's and low-temperature cycling of SIRM have been successfully applied to determine the co-existence, within single samples of the Prezzo Limestone, of 320°C MTP pyrrhotite, and of 400-570°C MTP multidomain (titano)magnetite.

Hysteresis loops and remanent coercivity curves

Both hysteresis loops and remanent coercivity curves from the Prezzo Limestone are, in most cases, indicative of a composite magnetic assemblage. The hysteresis loops are "wasp-waisted" in shape, and the remanent coercivity curves are sometimes characterized by a break in slope, usually at low applied backfield values (Fig. 3; in the remanent coercivity curves, the arrow indicates the slope break.) When visible, this break in slope divides the remanent coercivity curve into an initial steep portion, which is controlled by the low remanent coercivity fraction, and a succeeding less inclined portion, which is controlled by the high remanent coercivity fraction, and which eventually reaches saturation at fields usually as high as 0.7T or more. This is interpreted to reflect the co-existence of pyrrhotite and magnetite with contrasting coercivities. The low coercivity fraction (i.e., MD magnetite and possibly coarse grained pyrrhotite, as revealed by the 0.12T curve in Fig. 1), mainly controls the B_c values, whereas the high coercivity fraction (i.e., fine grained pyrrhotite as indicated by the 0.4T curve), contributes mostly to the B_{cr} values.

The inflection in the remanent coercivity curve can be used to estimate the percentage contribution of the low remanent coercivity component. For example, if the inflection occurs at $M_{rs} = 0$, then the low remanent coercivity fraction contributes 50% to the total re-manence. The percentage contribution of the low remanent coercivity fraction (L_c) to the bulk remanent coercivity curve is then simply calculated as $L_c = (M_{rlc}/2M_{rs})*100\%$, where M_{rlc} is the value of the magnetic remanence at the slope break.

In Figure 3, for each of the Prezzo Limestone samples, the coercivity contrast, expressed by the B_{cr}/B_c ratio, is plotted *versus* the correlative value of L_c. Sample "A", which plots far to the left in the B_{cr}/B_c vs. L_c diagram, has a relatively low coercivity contrast and it is dominated by the high remanent coercivity end member (L_c≈1-2%). This sample gives rise to a loop with a less pronounced waist than those of samples "B", "C" and "D", which have higher B_{cr}/B_c and L_c values. For

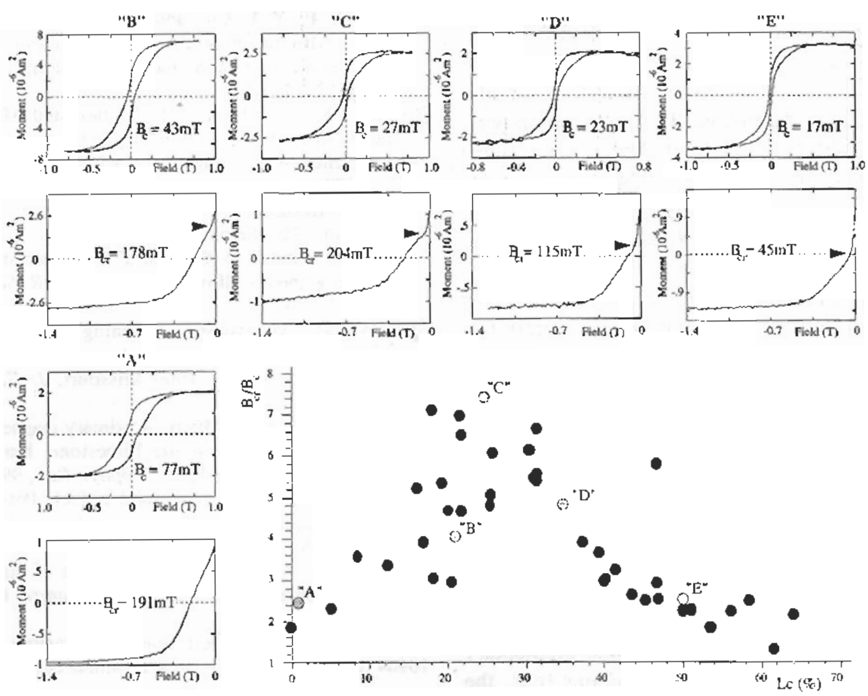

Figure 3. Hysteresis loops (corrected for the para- or diamagnetic contribution to the total magnetic moment) and remanent coercivity curves of representative Prezzo Limestone samples (sample "A" is AD96, sample "B" is 2SF94AB1A, sample "C" is SF110A, sample "D" is AD80, sample "E" is SF96A.) In the central portion of the figure is the B_{cr}/B_c vs. L_c plot. See text for discussion.

samples "B", "C" and "D" the contribution of the low remanent coercivity fraction is higher, and reaches values of $L_c \approx 21\%$, $L_c \approx 25\%$ and $L_c \approx 34\%$, respectively. Sample "E", which plots far to the right of the diagram, has a low B_{cr}/B_c value and it is dominated by the low remanent coercivity fraction (the value of L_c is about 50%). This latter sample gives rise to a less pronounced "wasp-waisted" hysteresis loop of a different type than those of samples that plot to the left of the B_{cr}/B_c vs. L_c diagram. As deduced from Figure 3, the high degrees of "wasp-waistedness" for the Prezzo Limestone samples are accounted for by high B_{cr}/B_c values, which are attained when the low remanent coercivity fraction contributes 15-35% to the bulk remanent coercivity curves.

Discussion and Conclusions

Rock magnetic experiments have unambiguously determined the presence of pyrrhotite and MD (titano)magnetite within individual Prezzo Limestone samples. These results are positive because other authors have tried to infer the presence of these two minerals in remagnetized carbonate rocks and have obtained uncertain results [Jackson et al., 1993]. This mixture gives rise to a strong contrast in coercivity, as evident in the "wasp-waisted" shape of hysteresis loops and remanent eoercivity curves that are charaeterized by a major slope break, generally at soft coercivities. The degree of "wasp-waistedness" inereases with inereasing B_{cr}/B_c values, as pointed out also by Roberts et al. [1995]. Maximum B_{cr}/B_c values are attained when the low remanent coercivity fraction contributes 15-35% to the bulk remanent eoercivity curves. When the contribution of the low remanent coereivity fractiou is either small (i.e., $L_c<15\%$) or large (i.e., $L_c>35\%$), however, the shape of the hysteresis loops is sensibly less "wasp-waisted". In the former case, the hysteresis loops are more open in shape and have M_{rs}/M_s values of about 0.45, whereas in the latter case the average values of M_{rs}/M_s are somewhat less (i.e., 0.2-0.3).

Hysteresis parameters are often plotted on a $\log(M_{rs}/M_s)$-$\log(B_{cr}/B_c)$ diagram of the type described by Day et al. [1977]. When plotted on such a diagram, the Prezzo Limestone samples display restricted M_{rs}/M_s vs. distributed B_{cr}/B_c values (power-law fit $M_{rs}/M_s=0.41(B_{cr}/B_c)^{-0.22}$, r=0.29). This is reminiseent of the results of Channell and McCabe [1994] for magnetite and hematite-bearing Mesozoic Tethyan limestones.

As already pointed out by other investigators (e.g., Tarduno and Myers [1994]), the presenee of "wasp-waisted" hysteresis loops alone does not provide an unambiguous test for remagnetization. A non-uniform distribution of eoereivities that result in a "wasp-waisted" loop can easily be associated with either secondary or primary processes of magnetization acquisition. Secondary processes may involve the growth of a late authigenic phase forming over a primary phase. This example is precisely the case of the remagnetized Triassic Prezzo Limestone of the present study, in whieh magnetite is probably the surviving primary phase, and at least a portion of pyrrhotite successively formed as a consequence of hydrothermal circulation aetivated by the Cenozoic Adamello batholith. Moreover, "wasp-waisted" loops have been found in mixtures of detrital and/or biogenic magnetite and pigmentary hematite that carry primary paleomagnetic directions (e.g., the reddened varieties of the Mesozoic Tethyan limestones of Channell and McCabe [1994]), as well as in recent basaltic glass [Pick and Tauxe, 1994] and basaltic lava flows [Radhakrishnamurty, 1993], which are presumably non remagnetized.

Acknowledgments. Dennis V. Kent, Andrew P. Roberts and Lisa Tauxe have greatly improved the manuscript. Chris Hunt performed low-temperature experiments.

References

Channell, J. E. T., and C. McCabe, Comparison of magnetic hysteresis parameters of unremagnetized and remagnetized limestones, *J. Geophys. Res.*, 99, 4613-4623, 1994.

Day, R., M. D. Fuller, and V. A. Schmidt, Hysteresis properties of titanomagnetites: Grain-size and compositional dependence, *Phys. Earth Planet. Inter.*, 13, 260-267, 1977.

Dekkers, M. J., Magnetic monitoring of pyrrhotite alteration during thermal demagnetization, *Geophys. Res. Lett.*, 17, 779-782, 1990.

Gumlich, E., Die magnetischen eigenschaften von ungleichmäßigem material, *Arch. Elektrotech.*, 9, 153-166, 1920.

Jackson, M., P. Rochette, G. Fillion, S. K. Banerjee, and J. Marvin, Rock magnetism of remagnetized Paleozoic carbonates: Low-temperature behaviour and susceptibility characteristics, *J. Geophys. Res.*, 98, 6217-6225, 1993.

Kobayashi, K., and M. D. Fuller, Stable remanence and memory of multidomain materials with special reference to magnetite, *Philos. Mag.*, 18, 601-624, 1964.

Lowrie, W., Identification of ferromagnetic minerals in a rock by coercivity and unblocking temperature properties, *Geophys. Res. Lett.*, 17, 159-162, 1990.

McCabe, C., and J. E. T. Channell, Late Paleozoic remagnetization in limestones of the Craven Basin (northern England) and the rock magnetic fingerprint of remagnetized sedimentary carbonates, *J. Geophys. Res.*, 99, 4603-4612, 1994.

Muttoni, G., and D. V. Kent, Paleomagnetism of latest Anisian (Middle Triassic) sections of the Prezzo Limestone and the Buchenstein Formation, Southern Alps, Italy, *Earth Planet. Sc. Lett.*, 122, 1-18, 1994.

Özdemir, Ö., D. J. Dunlop, and B. M. Moskowitz, The effect of oxidation on the Verwey transition in magnetite, *Geophys. Res. Lett.*, 20, 1671-1674, 1993.

Pick, T., and L. Tauxe, Characteristics of magnetite in submarine basaltic glass, *Geophys. J. Int.*, 119, 116-128, 1994.

Roberts, A. P., Y. L. Cui, and K. L. Verosub, Wasp-waisted hysteresis loops: Mineral magnetic characteristics and discrimination of components in mixed magnetic systems, *J. Geophys. Res.*, 100, 17909-17924, 1995.

Rochette, P., G. Fillion, J.-L. Mattei, and M. J. Dekkers, Magnetic transition at 30-34 Kelvin in pyrrhotite: Insight into a widespread occurrence of this mineral in rocks, *Earth Planet. Sc. Lett.*, 98, 319-328, 1990.

Radhakrishnamurty, C., The magnetic properties of basalts, *Mem. Geol. Soc. India*, 20, 208 pp., 1993.

Stoner, E. C., and E. P. Wohlfarth, A mechanism of magnetic hysteresis in heterogeneous alloys, *Philos. Trans. R. Soc. London, Ser. A*, 240, 599-642, 1948.

Sun, W., and M. Jackson, Scanning electron microscopy and rock magnetic studies of magnetic carriers in remagnetized early Paleozoic carbonates from Missouri, *J. Geophys. Res.*, 99, 2935-2942, 1994.

Tarduno, J. A., and M. Myers, A primary magnetization fingerprint from the Cretaceous Laytonville Limestone: Further evidence for rapid oceanic plate velocities, *J. Geophys. Res.*, 99, 21691-21703, 1994.

Tauxe, L., T. A. T. Mullender, and T. Pick, Pot-bellies, wasp-waists and superparamagnetism in magnetic hysteresis, *J. Geophys. Res.*, in press, 1995.

Verwey, E. J. W., Electronic conduction of magnetite (Fe_3O_4) and its transition point at low temperatures, *Nature*, 144, 327-328, 1939.

G. Muttoni, Lamont-Doherty Earth Observatory, Palisades, N.Y. 10964 (email: gio@lamont.ldeo.columbia.edu)

Received: March 17, 1995 Revised: June 29, 1995
Accepted: August 14, 1995