

ROCK MAGNETISM OF LOWER/MIDDLE PLEISTOCENE MARINE SEDIMENTS,
WANGANUI BASIN, NEW ZEALAND.

Andrew P. Roberts

Department of Geology, University of California, Davis, California

Brad J. Pillans

Research School of Earth Sciences, Victoria University, Wellington, New Zealand

Abstract. Rock magnetic studies were carried out in order to identify the remanence carrying minerals and the domain state of magnetic grains in Lower/Middle Pleistocene marine sediments from the Wanganui Basin, southwestern North Island, New Zealand. Isothermal remanent magnetization (IRM) acquisition and stepwise thermal demagnetization of a three-axis composite IRM suggest that titanomagnetite (or titanomaghaemite) is the dominant remanence carrier in these sediments. Other rock magnetic data suggest that these grains occur in a range of sizes in the superparamagnetic to pseudo-single domain range, which helps account for the wide range of observed palaeomagnetic behaviour. Isolated occurrences of ferrimagnetic iron sulphides cannot be ruled out.

Introduction

The Wanganui Basin of southwestern North Island, New Zealand, contains a thick succession of Plio-Pleistocene siliciclastic marine sediments that are now uplifted above sea level. The Early/Middle Pleistocene was a time of known large-amplitude glacio-eustatic sea level fluctuations. Deposition of cyclic packages of unconformity bound sequences in the Wanganui Basin are interpreted to represent successive sea level cycles [Pillans et al., 1993; and references therein]. Recent magnetostratigraphic studies in the Wanganui Basin [Turner and Kamp, 1990; Pillans et al., 1993] provide important chronological constraints which allow detailed correlation of sea level controlled sequences across the basin, as well as correlation with the international Pleistocene timescale.

The sediments of the Wanganui Basin were deposited rapidly (c. several 10's of cm/kyr). The ubiquity of framboidal pyrite indicates that sedimentation occurred in a sulphate-reducing environment. Magnetite dissolution should be ubiquitous in sediments that support active sulphate reduction and H₂S formation [Canfield and Berner, 1987]. Diagenetic dissolution of detrital titanomagnetite grains and the presence of ferrimagnetic iron sulphide minerals have been documented in similar sediments elsewhere in New Zealand [Roberts and Turner, 1993]. The possible presence of several magnetic remanence carriers, which may have locked in their remanences at different times, and the likelihood of dissolution of detrital ferrimagnetic grains in sulphate-reducing environments make it necessary to carry out detailed rock magnetic investigations in order to establish the validity of the magneti-

zation record in such sediments. Pillans et al. [1993] collected samples from approximately 60 sites of fresh, unweathered siltstones and mudstones from fine-grained parts of the sea level controlled sequences. Samples from ten sites, which displayed various types of palaeomagnetic behaviour, were subjected to detailed rock magnetic analysis in order to identify the remanence carriers and their domain state.

Demagnetization of Natural Remanent Magnetization (NRM)

Preliminary analyses indicated that thermal demagnetization is more efficient than alternating field (AF) demagnetization in removing secondary magnetization components and in isolating characteristic remanence directions. Many samples displayed spurious behaviour at peak alternating fields above 30 mT, while below this level, sufficient isolation of the characteristic remanence was not achieved, as also reported by other workers in New Zealand sedimentary successions [e.g. Turner and Kamp, 1990]. The most notable aspect of the thermal demagnetization behaviour is that in all cases, the remanence unblocks at relatively low temperatures, with less than 20% of the NRM remaining at 300-350°C [Pillans et al., 1993]. Thermal alteration of magnetic minerals prevents acquisition of data above 350°C. Pillans et al. [1993] observed three types of behaviour during thermal demagnetization, designated as types A, B and C. Type A samples are stably magnetized and characteristic remanence directions can be readily isolated. Type B samples are less stably magnetized and are strongly overprinted by secondary components of magnetization. Type C samples are so unstably magnetized that no useful palaeomagnetic data can be obtained. Normal and reversed polarity characteristic remanence directions from type A samples are antipodal to each other and are interpreted as recording a primary remanence [Pillans et al., 1993].

In type A samples, a "soft" normal polarity component is removed below 250°C. These sediments have not undergone significant burial, therefore the overprint is likely to be a Brunhes Chron component acquired at temperatures not significantly higher than room temperature. In type B samples, the normal overprint persists at higher demagnetization levels, and is usually not removed before thermal alteration occurs at around 350°C. The following rock magnetic analyses were made, on conventional palaeomagnetic samples, to determine whether the variations in palaeomagnetic behaviour (summarised for each site studied in Table 1) are due to variations in magnetic mineralogy or domain state.

Copyright 1993 by the American Geophysical Union.

Paper number 93GL00802
0094-8534/93/93GL-00802\$03.00

IRM Acquisition and Demagnetization

IRM acquisition curves are shown for each site in Figure 1A. All sites display behaviour typical of ferrimagnetic min-

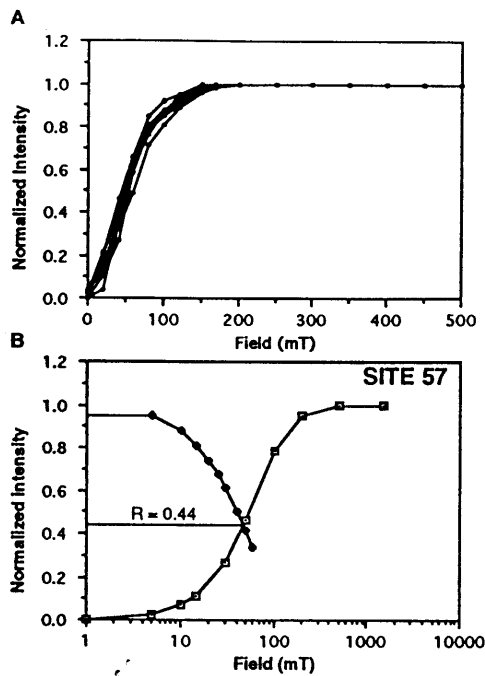


Fig. 1 (A) Normalized IRM acquisition curves for each site studied. (B) Acquisition and AF demagnetization of IRM for site 57. R ratio (Table 1) is after Cisowski [1980].

erals. The IRM is completely saturated at 200 - 250 mT, therefore the presence of antiferromagnetic minerals, such as haematite or goethite can be ruled out. AF demagnetization curves for the saturation IRM (SIRM) are nearly symmetrical to the acquisition curves in all cases (e.g. Figure 1B). The R ratio (Table 1) is the projection of the intersection point of the two curves onto the ordinate axis [Cisowski, 1980]. For non-interacting single domain (SD) particles, the R ratio should equal 0.5 [Wohlfarth, 1958]. Maher [1988] reported an average R ratio of 0.36 for interacting synthetic magnetite grains that lie in the superparamagnetic (SP) to SD size range. The R values determined here lie in a narrow range between 0.40 - 0.47 (Table 1), suggesting that the magnetic minerals in these samples are fine-grained and weakly interacting.

Hysteresis Measurements

Hysteresis parameters were measured (up to 1 T) on a Micromag alternating gradient magnetometer which enables sensitive measurement of small samples (< 50 mg). At least

three sub-samples from conventional palaeomagnetic samples were analysed in order to estimate the variability of hysteresis parameters (Table 1; Figure 2). The ratios of saturation remanence to saturation magnetization (M_{rs}/M_s) and coercivity of remanence to coercive force (B_{cr}/B_c) are useful indicators of the size of magnetic grains, as outlined by Day et al. [1977].

The data vary widely within the field expected for pseudo-single domain (PSD) grains [Day et al., 1977]. Some of the data are indicative of mixtures of PSD and SP grains (Figure 2). This observation is supported by measurements of the frequency dependence of magnetic susceptibility, χ_{fd} (the loss in low field susceptibility, χ , when measured at high frequency (4.7kHz), compared to low frequency (470 Hz), expressed as a percentage of the low frequency measurement). Significant frequency dependence is indicative of grains near the SD/SP boundary. The values obtained here are relatively low (Table 1), however, Maher [1988] has shown that magnetite assemblages containing significant SP populations can have similar values of χ_{fd} to those obtained here.

Rocks normally contain magnetic minerals with a distribution of grain sizes. It is therefore likely that these rocks contain SD grains as well as the ultra-fine SP grains and the relatively coarser PSD grains. The measured hysteresis parameters reflect contributions from all of these grains, and the presence of SP and PSD grains will bias the results on Figure 2 away from the values expected for a uniform distribution of SD grains. Multi domain (MD) grains do not appear to contribute significantly, given the distribution of data on Figure 2 and the range of R values (Table 1) of Cisowski [1980].

Thermal Demagnetization of IRM

Coercivity spectra obtained from IRM acquisition often give ambiguous information concerning the mineralogy of remanence carriers. Stepwise thermal demagnetization of an IRM is a more conclusive means of identifying magnetic minerals because minerals which have similar maximum coercivities usually have different characteristic unblocking temperatures [Lowrie and Heller, 1982]. Lowrie [1990] extended this method by applying successively smaller fields to the three orthogonal axes of a sample. Thus, stepwise demagnetization of the composite IRM allows the detection of variations in the temperature dependence of three different coercivity fractions.

In this study, applied fields of 1.4 T, 0.4 T and 0.125 T, respectively, were used to distinguish between possible high, intermediate and low coercivity minerals. Thermal demagnetization was carried out at 50°C steps up to 650°C. Susceptibility was measured at each step to monitor for mineralogical

Table 1. Data from rock magnetic experiments.

Site	Palaeomagnetic ¹ behaviour	NRM ² 10 ⁻⁷ Am ² kg ⁻¹	ARM ³ 10 ⁻⁶ Am ² kg ⁻¹	SIRM ⁴ 10 ⁻⁴ Am ² kg ⁻¹	χ_{sp} ⁵ 10 ⁻⁸ m ³ kg ⁻¹	χ_{fd} ⁶ %	SIRM/ χ_{sp} kAm ⁻¹	R ⁷	B_{cr} ⁸ mT	B_c ⁹ mT	M_{rs}/M_s ¹⁰	N ¹¹
1	4A	25.5	4.87	5.43	10.4	1.8	5.22	0.40	76 - 79	47 - 50	0.32 - 0.41	3
5	5B+1C	1.6	4.29	0.88	9.1	2.4	0.97	0.47	30 - 52	11 - 14	0.09 - 0.11	3
8	4C	1.9	3.30	1.23	8.4	1.5	1.46	0.43	34 - 43	9 - 13	0.06 - 0.12	3
12	5C	1.7	2.62	0.74	8.4	2.4	0.88	0.45	35 - 55	8 - 14	0.08 - 0.10	4
16	4A	0.9	5.14	0.85	9.7	1.1	0.88	0.45	29 - 32	8 - 12	0.04 - 0.11	4
20	4A	2.4	2.96	0.90	8.3	0	1.08	0.47	30 - 46	6 - 13	0.09 - 0.10	3
55	2B	1.7	3.00	1.02	8.9	1.1	1.15	0.41	36 - 53	10 - 16	0.05 - 0.16	4
56	6A	2.4	5.40	2.10	7.4	1.3	2.84	0.44	48 - 53	15 - 17	0.10 - 0.16	3
57	5C	1.0	3.01	0.78	8.3	1.6	0.94	0.44	29 - 45	9 - 13	0.06 - 0.07	3
63	3A+2B	1.9	4.04	1.56	7.9	3.7	1.98	0.45	31 - 52	13 - 14	0.12 - 0.14	3

¹ A, B, C as described in text; numerals indicate number of demagnetized samples of type A, B, C; ² natural remanent magnetization; ³ anhysteretic remanent magnetization, acquired in AF of 100 mT with bias field of 0.05 mT; ⁴ saturation IRM; ⁵ mass specific magnetic susceptibility; ⁶ frequency dependent magnetic susceptibility (see text); ⁷ R ratio of Cisowski [1980]; ⁸ coercivity of remanence; ⁹ coercive force; ¹⁰ ratio of saturation remanence to saturation magnetization; ¹¹ single determination; ¹¹ number of sub-samples from which 8-10 were determined.

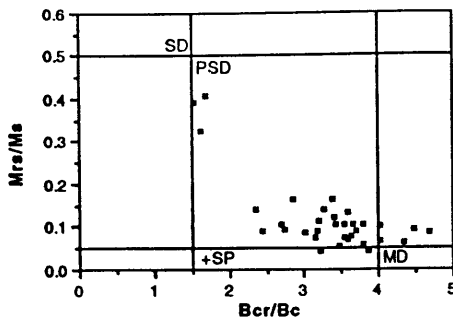


Fig. 2 Plot of high-field hysteresis parameters, M_{re}/M_s vs B_{cr}/B_c , with expected fields shown for SD, PSD (+SP) and MD states, after Day et al. [1977].

changes due to thermal alteration. All sites display similar results (Figure 3A), except site 1 (Figure 3B). Changes in the slope of the thermal demagnetization curve are used to identify magnetic minerals with this type of plot [Lowrie, 1990].

For all sites, most of the remanence is held by the < 0.125 T coercivity fraction (Figure 3A). The intensity decays in a quasi-linear fashion from room temperature to 350 - 400°C, where the slope of the curve changes. A high temperature phase, with a maximum unblocking temperature between 550 and 600°C, also exists. Because of the sharp increase in susceptibility at 350 - 400°C, the high temperature phase is likely to be magnetite formed by thermal alteration of clay minerals, or by oxidation of pyrite, rather than original magnetite.

Several low coercivity minerals have maximum unblocking temperatures in the range from 300 - 400°C. However, ferrimagnetic iron sulphides can be ruled out in these sites because pyrrhotite has a maximum unblocking temperature of c. 325°C [Dekkers, 1989] and greigite loses most of its magnetization between 200 - 350°C [Snowball, 1991]. Furthermore, the greigite identified in similar depositional environments in New Zealand [Roberts & Turner, 1993] typically shows a decrease in χ during thermal demagnetization above 200°C and is characterized by SIRM/ χ values that are higher

than most natural magnetite assemblages, consistent with observations by Snowball [1991]. This behaviour is not evident for the majority of sites analysed here (Figure 3A; Table 1). The mineral most likely to display soft coercivities (Figure 1A) and thermal stability to 350 - 400°C (Figure 3A) is a moderate Ti titanomagnetite/maghaemite.

Site 1 displays different thermomagnetic behaviour to all of the other sites studied (Figure 3B). More of the IRM resides in the 0.125 - 0.4 T coercivity fraction and a change in slope of the IRM curve occurs between 250 - 350°C. As with the other sites, increased susceptibilities above 400°C suggest growth of a new magnetic phase. Ferrimagnetic iron sulphide minerals, titanomagnetite and titanomaghaemite can display low unblocking temperatures and similar coercivity spectra to those obtained at site 1 [Lowrie, 1990]. Because the sediments of the Wanganui Basin were deposited under sulphate-reducing conditions, it is likely that intermediate ferrimagnetic iron sulphides, that form during the sedimentary pyritization process, may be preserved at some localities and the possibility of their presence at site 1 cannot be ruled out. Hysteresis data indicate that magnetic grains from site 1 are smaller than those from all other sites studied (Figure 2; Table 1). A narrow grain size range may account for the narrow range of blocking temperatures observed (Figure 3B), if the magnetic carrier is a moderate Ti titanomagnetite.

This clearly illustrates the difficulty in unambiguously identifying magnetic carriers that have soft coercivities and maximum unblocking temperatures between 300 - 400°C. However, site 1 clearly shows different thermomagnetic characteristics to all of the other sites which, on the basis of the above evidence, are almost certainly dominated by a ferrimagnetic iron oxide mineral (titanomagnetite/haematite).

Tuffs, which are derived from large volcanic eruptions in the Taupo Volcanic Zone to the north, occur sporadically throughout the Wanganui Basin. Considerable reworking of tuffs is indicated by the presence of volcanic glass throughout the sediments studied, and also by mixed glass populations identified from electron microprobe analyses of the glass [Pillans et al., 1993]. Many large oxidized titanomagnetite

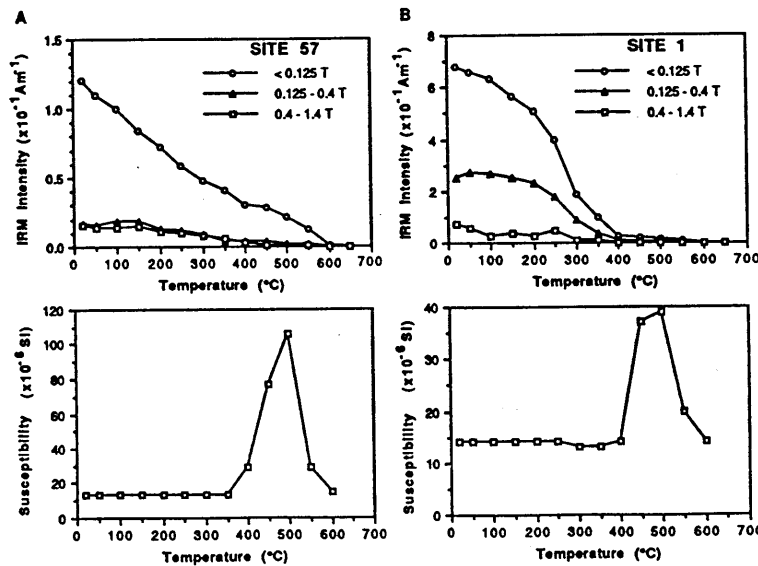


Fig. 3 Stepwise thermal demagnetization of a three component IRM (acquired in fields of 1.4, 0.4 and 0.125 T, respectively). Bulk susceptibilities are also shown for each step. (A) site 57, and (B) site 1.

grains, with a wide range of compositions, were identified from these tuffs by electron microprobe analysis. Given that volcanogenic material has been reworked throughout the sediments studied, it is likely that fine-grained titanomagnetite is also present. This observation supports the IRM demagnetization results that indicate that titanomagnetite/maghaemite is the dominant remanence carrier in Lower/Middle Pleistocene sediments of the Wanganui Basin.

Conclusions

Moderate Ti titanomagnetite/maghaemite appears to be the dominant remanence carrier in all but one of the sites studied here. Magnetic properties at site 1 may be equally explained by moderate Ti titanomagnetite, titanomaghaemite or ferri-magnetic iron sulphide minerals (greigite or pyrrhotite).

There is no obvious difference between well behaved sites and relatively poorly behaved sites, based on rock magnetic data (Table 1). Grain size distributions of magnetic grains may therefore hold the key to understanding the observed palaeomagnetic behaviour, because the rock magnetic parameters measured cannot discriminate between uniform distributions of intermediate sized grains and mixtures of coarse and fine grains (e.g. Figure 2).

Rock magnetic data suggest that grain sizes vary widely in the SP - PSD range in sediments of the Wanganui Basin (Figure 2). The palaeomagnetic behaviour can be explained if type A sites have narrow grain size distributions, while type B sites have broader grain size spectra. The overlapping remanence components at type B sites can be accounted for if the secondary component is carried by small SD grains that have lower blocking temperatures, with shorter relaxation times, than those holding the primary component [cf. Van Velzen and Zijdeveld, 1990]. This may explain the failure of AF demagnetization to isolate the primary remanence component because the two components have overlapping coercivity spectra. Lack of evidence for high-coercivity minerals (Figure 1) argues against a mixture of minerals with different coercivities. The primary component is likely to be carried by larger, stable SD and PSD grains.

Despite the likelihood of diagenetic dissolution of detrital iron-bearing grains in sulphate-reducing environments [Canfield and Berner, 1987], it appears that a significant number of titanomagnetite/maghaemite grains have survived dissolution and retain a coherent early magnetization. This is consistent with other studies that indicate that detrital ferrimagnetic grains can survive diagenetic dissolution if they are stable and occur in sufficient concentrations [e.g. Karlin, 1990].

Acknowledgements. We are grateful to Prof. Ken Verosub for use of his laboratory and for reviewing the manuscript; Dr Gillian Turner and Gary Wilson for helpful reviews of the manuscript; and the helpful comments of two anonymous reviewers. Support for fieldwork was provided by the Internal Grants Committee, Victoria University, Wellington.

References

Canfield, D.E., and R.A. Berner, Dissolution and pyritization

- of magnetite in anoxic marine sediments, *Geochim. Cosmochim. Acta*, 51, 645-659, 1987.
- Cisowski, S., Interacting vs. non-interacting single domain behavior in natural and synthetic samples, *Phys. Earth planet. Inter.*, 26, 56-62, 1980.
- Day, R., M.D. Fuller, and V.A. Schmidt, Hysteresis properties of titanomagnetites: grain size and composition dependence, *Phys. Earth planet. Inter.*, 13, 260-266, 1977.
- Dekkers, M.J., Magnetic properties of natural pyrrhotite. II. High- and low-temperature behaviour of Jrs and TRM as function of grain size, *Phys. Earth planet. Inter.*, 57, 266-283, 1989.
- Karlin, R., Magnetite diagenesis in marine sediments from the Oregon continental margin, *J. geophys. Res.*, 95, 4405-4419, 1990.
- Lowrie, W., Identification of ferromagnetic minerals in a rock by coercivity and unblocking temperature properties, *Geophys. Res. Lett.*, 17, 159-162, 1990.
- Lowrie, W., and F. Heller, Magnetic properties of marine limestones, *Rev. Geophys. Space Phys.*, 20, 171-192, 1982.
- Maher, B.A., Magnetic properties of some synthetic sub-micron magnetites, *Geophys. J. Int.*, 94, 83-96, 1988.
- Pillans, B.J., A.P. Roberts, G.S. Wilson, S.T. Abbott, and B.V. Alloway, Magnetostratigraphic, lithostratigraphic and tephrostratigraphic constraints on Lower/Middle Pleistocene sea level changes, Wanganui Basin, New Zealand, *Earth planet. Sci. Lett.*, in press, 1993.
- Roberts, A.P., and G.M. Turner, Diagenetic formation of ferrimagnetic iron sulphide minerals in rapidly deposited marine sediments, South Island, New Zealand, *Earth planet. Sci. Lett.*, 115, 257-273, 1993.
- Snowball, I.F., Magnetic hysteresis properties of greigite (Fe₃S₄) and a new occurrence in Holocene sediments from Swedish Lapland, *Phys. Earth planet. Inter.*, 68, 32-40, 1991.
- Turner, G.M., and P.J.J. Kamp, Palaeomagnetic location of the Jaramillo subchron and the Matuyama-Brunhes transition in the Castlecliffian stratotype section, Wanganui Basin, New Zealand, *Earth planet. Sci. Lett.*, 100, 42-50, 1990.
- Van Velzen, A.J., and J.D.A. Zijdeveld, Rock magnetism of the Early Pliocene Trubi Formation at Eraclea Minoa (Sicily), *Geophys. Res. Lett.*, 17, 791-794, 1990.
- Wohlfarth, E.P., Relationships between different modes of acquisition of remanent magnetization of ferromagnetic particles, *J. Appl. Phys.*, 29, 595-596, 1958.

B.J. Pillans, Research School of Earth Sciences, Victoria University, Wellington, New Zealand.

A.P. Roberts, Department of Geology, University of California, Davis, CA 95616.

(Received January 4, 1993;
accepted March 24, 1993.)