Diagenesis of magnetic mineral assemblages in multiply redeposited siliciclastic marine sediments, Wanganui basin, New Zealand

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Abstract: In many sedimentary environments, early diagenetic sulphidization reactions cause extensive dissolution of detrital magnetic minerals which can alter or destroy the palaeomagnetic signal. Pliocene sediments from the Wanganui basin, North Island, New Zealand, have been subjected to multiple cycles of erosion and redeposition in sulphate-reducing environments before reaching their present setting. Despite this, the sediments retain a measurable and stable remanent magnetization. The only Fe-Ti oxide recognized from detailed sedimentary petrographic characterization of magnetic extracts and bulk sediments is ilmenite, with compositions that lie within the range from which paramagnetic behaviour is expected. There are no Fe-Ti oxide grains with compositions from which ferrimagnetic behaviour is expected (except for rare chromite). A direct link was made between magnetic behaviour and mineralogy by conducting electron probe microanalysis and back-scattered electron imaging of the same grains that were subjected to magnetic analysis. These studies demonstrate that stable magnetic behaviour is displayed by grains that appear to be homogeneously composed of ilmenite. This magnetic behaviour is attributed to the presence of ferrimagnetic Fe-enriched (hemo-ilmenite) microstructural domains that have been previously reported from ilmenite grains. These hemo-ilmenite domains appear to be dominantly responsible for the remanence of the Wanganui basin Pliocene sediments. Calculations of the reactivity of detrital iron-bearing minerals to sulphidization indicate that ilmenite is much less reactive than magnetite and other detrital magnetic minerals. Given the resistance of hemo-ilmenite, to dissolution, it is suggested that microstructural ferrimagnetic domains within ilmenite grains may be a source of palaeomagnetic information in sediments that have undergone diagenetic magnetic mineral dissolution during multiple episodes of erosion and redeposition.

Thick, generally rapidly deposited, Neogene and Quaternary marine sedimentary sequences have been uplifted above sea level and now crop out over large parts of New Zealand. Extensive studies of such sequences over at least the last half-century have allowed the development of a biostratigraphic framework that now serves as a standard reference for temperate southern latitudes (Hornibrook et al. 1989). Outcrop-based studies of rapidly deposited sequences can provide an unequalled perspective for sequence stratigraphic studies (e.g. Carter et al. 1991; Abbott & Carter 1994), for high-resolution studies of paleoceanclimatic and eustasy (e.g. Wright & Vella 1988; Kamp & Turner 1990; Turner & Kamp 1990; Pillans et al. 1994; Roberts et al. 1994), as well as for tectonic studies (e.g. Wright & Walcott 1986; Roberts 1992; Wilson & McGuire 1995). Correlation among coeval successions, and with the international time scale, is a vital part of such studies.

Magnetostratigraphy has been long recognized as a powerful tool for global correlation, but early studies of sediments were hampered by the insensitivity of magnetometers and their generally weak magnetization of sediments (see Kennett 1980). Despite this, magnetostratigraphic studies were completed for several important sequences in New Zealand (e.g. Kennett et al. 1971; Lienert et al. 1972; Kennett & Watkins 1974; Seward et al. 1986). With the development of cryogenic magnetometers and the widespread use of more rigorous schemes for interpreting demagnetization data, further

magnetostratigraphic studies have been completed (e.g. Wright & Vella 1988; Turner & Kamp 1990; Pillans et al. 1994; Roberts et al. 1994). However, the detrimental impact of pervasive reductive diageneis on the magnetic records carried by these sediments has been recognized only relatively recently (e.g. Roberts & Pillans 1993; Roberts & Turner 1993) and must be taken into account in interpreting palaeomagnetic results from such sequences. Rapidly accumulating continental shelf sediments generally undergo sulphate reduction during shallow burial, as a result of degradation of organic matter (e.g. Berner 1984; Canfield & Berner 1987). Dissolution of detrital Fe-Ti oxide minerals has been widely documented in magnetic studies of marine sediments (e.g. Kobayashi & Nomura 1972; Karlin & Levi 1983, 1985; Canfield & Berner 1987; Channell & Hawthorne 1990; Karlin 1990a, b; Leslie et al. 1990a, b; Roberts & Pillans 1993; Roberts & Turner 1993; Tarduno 1994). Most of the marine sediments that now crop out above sea level in New Zealand accumulated rapidly under sulphate-reducing conditions, and widespread dissolution of detrital magnetic phases is the most likely explanation for the weak magnetizations of these sediments (Roberts & Pillans 1993; Roberts & Turner 1993). The problem is exacerbated by the fact that these sediments, as well as most of the sedimentary units from which the sediments were derived, have been recycled through successive episodes of erosion and deposition (MacKinnon 1983) in sulphate-reducing environments (Smale 1990). The result is that a large portion of the available iron from detrital iron-bearing grains has been dissolved to form authigenic pyrite (see Berner 1970, 1984), thereby obliterating a large part of the detrital magnetic signal. Few studies have been conducted to determine the origin of the palaeomagnetic signal in sediments subjected to dissolution during multiple cycles of erosion and redeposition. A rock magnetic and sedimentary petrographic study has therefore been undertaken to determine the origin of the palaeomagnetic signal in this Pliocene sequence. These results have important implications for future studies of such sequences in New Zealand, as well as relevance to other sequences where the magnetic mineral fraction is strongly influenced by reductive diageneis.

Geological setting

The Wanganui basin lies in a back-arc position with respect to the Australia Pacific plate boundary zone. The basin is submerged in the south and has been tectonically uplifted above sea level in its northern and eastern parts, in response to uplift of the adjacent axial ranges of the North Island (Fig. 1). The basin has an area of c. 40,000 km² and contains a stratigraphic thickness of about 6 km of sediment that ranges from upper Miocene age in the north to present-day sediments that overlie to the south of the basin (Anderton 1981). Stern et al. (1992) described the basin as a lithospheric downwarp that resulted from frictional coupling at the interface of the underlying subduction thrust. The portion of the basin that lies above sea level is deeply dissected by rivers, which permits access to a nearly continuously exposed sequence of mid-ocean shelf to shoreline sediments. The Jurassic–Cretaceous greywackes and argillites of the Torlesse Supergroup are the dominant source of siliciclastic sediments deposited in the marginal basins of New Zealand. Widespread early diagenetic pyritization and dissolution of detrital iron-bearing phases has been documented in Torlesse rocks (e.g. Smale 1990), which were subjected to multiple cycles of erosion and redeposition during Mesozoic time (MacKinnon 1983). Further cycles of erosion and redeposition occurred in the Wanganui basin during Neogene time (e.g. Stern et al. 1992), which led to dissolution of much of the available iron in detrital magnetic grains. Development of arc-related volcanism in Quaternary time in the Central Volcanic Region of the North Island (Fig. 1) provided a ready source of volcanioclastic magnetic minerals that give rise to a generally stronger palaeomagnetic signal in Pleistocene sediments of the Wanganui basin (Turner & Kamp 1990; Roberts & Pillans 1993; Pillans et al. 1994).

Methods

About 360 conventional palaeomagnetic cores (25 mm diameter) were collected from 114 sites that crop out in the Wanganui and Rangitikei Rivers (Fig. 1), to determine an early to middle Pliocene magnetostratigraphy (Wilson 1993). Where possible, cores were drilled from fresh, unweathered mudstones, sandy mudstones or muddy sandstones. Magnetic remanence measurements were made using a cryogenic magnetometer. Thermal demagnetization has repeatedly been shown to be more suitable than alternating field (AF) demagnetization for isolating characteristic remanence components in Neogene marine sequences in New Zealand (Kennett & Watkins 1974; McGuire 1989; Turner et al. 1989; Turner & Kamp 1990; Roberts & Turner 1993; Pillans et al. 1994; Roberts et al. 1994). At least three samples from each site were subjected to stepwise thermal demagnetization at 50°C intervals, usually to a maximum of 300–350°C. Above this temperature, the natural remanent magnetization (NRM)
was greatly reduced and thermochemical alteration masked the remaining NRM.

Optical microscope and scanning electron microscope examinations of resin-impregnated polished sections of bulk sediment and magnetic separates, including electron probe microanalysis (EPMA) and back-scattered electron imaging (BSE), were performed to identify mineral types and proportions in sediments from the Wanganui basin and to relate the mineralogy to the observed magnetic behaviour. Magnetic separates were obtained by mechanically and ultrasonically disaggregating the sediment into a slurry with deionized water. The disaggregated sediment was then dried and sieved, and grain-size specific separates were prepared using a Frantz electromagnetic separator. A second set of separates was obtained by recirculating a slurry of disaggregated sediment past a permanent magnet with a peristaltic pump, using a device similar to that described by Petersen et al. (1986). Subsamples from the first set of separates were suspended within non-magnetic Plexiglas cylinders. Isothermal remanent magnetizations (IRM's) were imparted using a pulse magnetizer (up to peak fields of 800 mT) to assess the magnetic characteristics of the samples. After saturation was achieved, stepwise increasing backfields were applied to determine the coercivity of remanence (B_C). Polished grain mounts were then made out of the cylinders to directly determine the mineralogy of the grains that gave rise to the observed remanence. Grains from the second set of separates were subjected to magnetic hysteresis analysis up to maximum fields of 1 T. Subsamples from these separates were subjected to temperature-dependent susceptibility measurements. Polished sections were also made from the same grains from which hysteresis measurements were made, to allow direct determination of the magnetic minerals responsible for the observed hysteresis behaviour.

Results

Paleomagnetic behaviour

During thermal demagnetization, much of the signal was lost after heating to 150°C or 200°C. A stable linear remanence component was often observed between 150°C and 300°C, until thermal alteration prevented acquisition of useful data (Fig. 2). A weak remanence component commonly remained above 300–350°C. This component was inferred to be present in many samples because the demagnetization data were not directed to the origin of the vector component plot (Fig. 2c and d). Stable characteristic
Fig. 2. Orthogonal vector component plots of thermal demagnetization results for representative samples from the Wanganui basin. Filled (open) symbols indicate projections onto the horizontal (vertical) plane. (a) Reversed polarity sample from the Wanganui River section; (b) normal polarity samples from the Wanganui River section; (c) reversed polarity sample from the Rangitikei River section.

Fig. 3. Photomicrographs of pyrite and ilmenite grains. (a) Reflected light photomicrograph (crossed nicols) of pyrite framboids (brassy yellow) in a quartzofeldsparitic muddy sandstone from the Wanganui basin. Field of view is 80 μm. (b) Reflected light photomicrograph (crossed nicols) of a large ilmenite grain (dull metallic yellow) from the Wanganui basin, with solution weathering and pitting along weakness planes in the grain. The grain is 90 μm in height. (c) Back-scattered electron image of ilmenite grains in a magnetic extract from a sandy mudstone from the Wanganui basin with exsolution pitting (right-hand side) and weathering along cleavage and fracture planes (left-hand side). Field of view is 130 μm in height. (d and e) Reflected light photomicrographs (crossed nicols) of rims of microcrystalline hematite around pyrite framboids in muddy sandstones from the Wanganui basin. Field of view is 80 μm in height. (f) Back-scattered electron image of chromite grain (bright blue-white). The chromite is a late phase igneous mineral and is holding together several feldspar grains. The chromite grain is 90 μm in long dimension.
remanence components were isolated from 47% of the sample collection, and characteristic remanence directions were obtained from another 48% of the samples by means of remagnetization great circles analysis (Wilson 1993; Wilson & McGuire 1995).

Sedimentary petrography

Identification of stable remanence-bearing particles from thin sections of sediments is usually not feasible because the size and concentration of such grains is small. Sedimentary petrography can be extremely valuable, however, because it provides important information concerning grain types and concerning sediment diagenesis and authigenesis. Optical microscope observations indicate that 5-10% of the grains are opaque. Pyrite is common (Fig. 3), and is particularly abundant within foraminiferal tests. It occurs as frambooids and as euhedral grains: individual grains are smaller than 5 μm and they have a brassy yellow colour with metallic lustre. No other iron sulphide phases were identified. The pyrite (FeS₂) appears to be of uniform composition under BFI. Iron to sulphur ratios, measured using EPMA, vary between 1:1.91 and 1:2.12 (Table 1). The abundance of pyrite indicates that these sediments were deposited under sulphate-reducing conditions (see Berner 1970, 1984). Dissolution of detrital iron-bearing magnetic minerals should be ubiquitous in sediments that support active sulphate reduction and H₂S formation (Canfield & Berner 1987). Evidence for dissolution of detrital iron-bearing minerals is clear, particularly in ilmenite grains.

| Table 1. EPMA analyses of individual pyrite grains |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|     | Fe  | 46.02 | 46.28 | 46.62 | 46.85 | 45.16 | 47.52 | 47.1 | 46.25 | 45.17 | 45.06 | 45.66 |
| Mn  | 0.01 | 0.01 | 0.03 | 0.35 | 0.03 | 0.15 | 0.07 | 0.49 | 0.02 | 0.02 | 0.02 | 0.14 |
| Cu  | 0.02 | 0.02 | 0.03 | 0.06 | 0.01 | 0.02 | 0.05 | 0.02 | 0.05 | 0.05 | 0.05 | 0.02 |
| Sb  | 0.02 | 0.02 | 0.03 | 0.06 | 0.01 | 0.04 | 0.01 | 0.09 | 0.12 | 0.08 | 0.12 |
| As  | 0.02 | 0.02 | 0.03 | 0.06 | 0.01 | 0.04 | 0.01 | 0.09 | 0.12 | 0.08 | 0.12 |
| S   | 53.25 | 53.46 | 51.59 | 53.72 | 52.83 | 52.12 | 52.48 | 53.68 | 52.9 | 52.78 | 52.27 |
| Total | 99.54 | 98.91 | 98.38 | 100.7 | 98.64 | 99.77 | 99.87 | 101.0 | 97.73 | 98.98 | 98.2 |
| Fe:S | 1:2.02 | 1:1.97 | 1:1.93 | 1:2.00 | 1:2.04 | 1:1.91 | 1:1.94 | 1:2.02 | 1:2.09 | 1:2.04 | 1:1.99 |

| Table 2. EPMA analyses of single detrital chromite grains |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|     | SiO₂  | 0.1 | 0.13 | 0.11 | 0.05 | 0.18 | 2.51 | 0.01 |
| TiO₂  | 0.19 | 0.35 | 0.13 | 0.3 | 0.13 | 0.11 | 0.01 |
| Al₂O₃  | 24.76 | 8.46 | 10.76 | 24.08 | 25.49 | 11.77 | 29.19 |
| FeO  | 21.82 | 26.98 | 27.29 | 23.92 | 19.32 | 24.32 | 16.32 |
| Fe₂O₃  | 2.27 | 13.06 | 15.74 | 0.46 | 7.1 | 20.35 | 0.89 |
| MgO  | 0.42 | 0.38 | 0.35 | 0.36 | 0.18 | 2.51 | 0.21 |
| Cr₂O₃  | 8.95 | 2.35 | 3.8 | 8.81 | 13.04 | 7.31 | 13.02 |
| CoO  | 0.11 | 0.07 | 0.02 | 0.01 | 0.1 | 0.07 | 0.03 |
| Cr:O₂  | 41.68 | 41.78 | 42.15 | 47.94 | 37.32 | 34.63 | 39.89 |
| NiO  | 0.11 | 0.19 | 0.08 | 0.08 | 0.17 | 0.04 | 0.21 |
| ZnO  | 0.44 | 0.56 | 0.41 | 0.48 | 0 | 0 | 0 |
| Total | 101 | 94.51 | 101.1 | 106.5 | 101 | 103.6 | 99.68 |
| (total FeO) | 23.86 | 38.73 | 41.46 | 24.33 | 25.71 | 42.63 | 17.02 |
| % Ulvospinel | 77.84 | 19.29 | 5.9 | 99.34 | 17.86 | 2.37 | 47.43 |

(within magnetic extracts), which contain evidence of exsolution pitting and dissolution along cleavage and fracture planes (Fig. 3b and c). During later diagenesis, frambooidal pyrite grains were oxidized, and abundant microcrystalline hematite formed on the surface of the pyrite grains (Fig. 3d and e). Rare chromite was also identified in sediments from the Wanganui basin (Table 2), and is generally associated with aluminosilicate grains (Fig. 3f).

No spinel phase iron oxide (ulvospinel-magnetite solid solution series) grains were observed (except for rare chromite grains). However, rhombohedral iron oxide (ilmenite hematite solid solution series) grains were abundant within magnetic extracts. All such rhombohedral grains contain 46.7 52.3% TiO₂ and up to 9.4% MnO (Table 3a and b). Recalculation of the Fe²⁺ and Fe³⁺ ratios was carried out using the method of Stormer (1983), which indicates that the compositions of these grains are close to that of ilmenite (HIMSP 90–95; Hematite 95–100; Fig. 4).

**Table 3a.** EPM analyses of homogeneous individual ilmenite grains

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃*</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>NiO</th>
<th>Total</th>
<th>FeO</th>
<th>% Ilmenite</th>
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<td></td>
<td>0.09</td>
<td>48.83</td>
<td>0.05</td>
<td>7.09</td>
<td>2.09</td>
<td>0.25</td>
<td>0.04</td>
<td>0</td>
<td>99.84</td>
<td>47.78</td>
<td>93.04</td>
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**Table 3b.** EPM analyses of homogeneous individual ilmenite grains from magnetic extracts

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃*</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>NiO</th>
<th>Total</th>
<th>FeO</th>
<th>% Ilmenite</th>
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<tr>
<td></td>
<td>0.06</td>
<td>50.71</td>
<td>0.01</td>
<td>43.39</td>
<td>3.41</td>
<td>1.84</td>
<td>0.02</td>
<td>0.04</td>
<td>99.68</td>
<td>46.46</td>
<td>96.66</td>
</tr>
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* Calculated after Stormer (1983).
Compositions more ilmenite rich than Ilm$\text{Fe}_2\text{O}_3$-Hem$\text{Fe}_2\text{O}_3$$_3$$_2$ within the hematite-ilmenite solid solution series fall within the range of values that are expected to be paramagnetic at room temperature (see Nagata 1961), therefore one would not expect the observed grains to be able to carry a remanence. It should be noted that ilmenite has been widely documented in magnetic extracts from similar New Zealand marine sequences (Roberts & Pilans 1993; Roberts & Turner 1993), although the common presence of ilmenite has been attributed to the relative insensitivity of magnetic separation techniques to discriminate adequately between ferrimagnetic and paramagnetic phases.

**Rock and mineral magnetic studies**

IRM acquisition and back-field experiments were conducted to compare the magnetic properties of bulk sediment samples (e.g. Fig. 5a) with those of magnetic extracts. The IRM was weak and saturates at low inductions (<200 mT), which suggests that the magnetic carriers occur in low concentrations and have low coercivities. Saturation at fields below 300 mT is consistent with the dominance of ferrimagnetic grains. The magnetic extracts contain higher concentrations of magnetic grains, which therefore give rise to higher IRM intensities, but the range of $R_a$ values is similar to those of the bulk sediment samples (Fig. 5), suggesting that the extracts are representative of the magnetic grains that are responsible for the magnetization. To directly compare mineralogy and magnetic properties, magnetic extracts, obtained using a Frantz electromagnetic separator, were suspended within Plexiglas cylinders using a non-magnetic glue as a fixative and were subjected to IRM acquisition and back-field demagnetization studies. A blank sample of Plexiglas was subjected to the same analysis to confirm that the blank did not hold a measurable remanence. Results from the extracts were consistent with the magnetic properties of bulk sediment samples. The samples were then made into polished grain mounts to allow direct mineralogical identification of the remanence-bearing grains. EPMA and BEI analyses indicated that all samples contained only grains with compositions close to ilmenite (Table 3a and b, Figs 3c and 4). BEI analysis indicated that the grains (typically >40 μm in size) are compositionally homogeneous on the scale of the observations (the electron beam is about 1 μm in diameter). Because of uncertainty as to whether small concentrations of undetected ferrimagnetic particles were giving rise to the observed magnetic behaviour, further analyses were conducted on magnetic separates that were obtained using the method of Petersen et al. (1986). The grains obtained by this separation technique were dominantly large (>40 μm), which meant that magnetic measurements could be made directly on individual grains using a Micromag alternating gradient magnetometer. The single grains display magnetic behaviour that is indistinguishable from that of the bulk magnetic separates.
(Fig. 6) and EPMA analyses of carefully prepared polished grain mounts confirmed that the grains consist of ilmenite. Hysteresis parameters ($M_r/M_s$ and $B_r/B_s$) are consistent (Fig. 6) with those repeatedly observed in marine sedimentary rocks (e.g. Roberts & Pillans 1993; Tarduno 1994). The hysteresis behaviour of the bulk sediment is not identical to that of the magnetic extract. This is probably due to contributions from (super)paramagnetic phases that are present in the bulk sediment but which are absent in the extracts. Using the grain-size dependent framework of Day et al. (1977), which is strictly applicable only to magnetite or titanomagnetite compositions, the hysteresis data fall in the field for pseudo-single-domain grains. Temperature-dependent susceptibility measurements were made on bulk sediment samples, as well as on magnetic extracts, to obtain more information concerning magnetic mineralogy. As expected, low-field magnetic susceptibilities for most bulk samples are weak. On heating, no Hopkinson peaks are evident, but susceptibility decreases to near-zero values at about 580°C (Fig. 7a and b), which is consistent with the presence of magnetite (see Hunt et al. 1995). On cooling, susceptibilities are much higher, which is consistent with thermochemical alteration of iron-bearing minerals (clays and pyrite). Analyses of magnetic extracts produced noisy results because of the weak susceptibility; however, a decay in susceptibility is evident between 580 and 610°C (Fig. 7c), which is nearly reproducible on cooling, probably because of the absence of thermally unstable phases such as clays and pyrite grains within the magnetic extracts.

There are several anomalies in the above-described data. First, the magnetic behaviour is consistent with that expected for ferrimagnetic particles that are known to be faithful recorders of the geomagnetic field on geological time scales. However, the mineralogy of the same grains is demonstrably close to an ilmenite composition, which would be expected to be paramagnetic at ambient temperatures, and, therefore, would be unable to retain a remanent magnetization on any time scale. Second, the grains that displayed this anomalous magnetic behaviour are usually large (>40 μm), and such

**Fig. 6.** Hysteresis loops for bulk samples and extracts. **a** Bulk sediment sample (W085); **b** magnetic extract (from W085); **c** magnetic extract (from W069); **d** single ilmenite grain (from W069), from the Wanganui River section.
large grains would normally be expected to display multi-domain behaviour, which is not what is indicated by the hysteresis data (Fig. 6).

Third, grains with apparently paramagnetic compositions display thermomagnetic behaviour that is consistent with the presence of magnetite.

Discussion

Reconciling the apparent conflict between magnetic behaviour and mineralogical identifications

Data from magnetic extracts and bulk samples point to the unexpected result that grains with apparently paramagnetic compositions are contributing the dominant ferrimagnetic signal in Pliocene sediments of the Wanganui basin. This observation has been validated by making careful magnetic and mineralogical observations from the same grains, as outlined above. It is therefore concluded that this result is a genuine reflection of the magnetic mineralogy of the Wanganui basin Pliocene sediments and that this conflict needs to be reconciled. Lawson & Nord (1984) synthesized well-crystalline, optically homogeneous $\text{Ilm}_{20\%}$ Hem$_{80\%}$ samples with an average grain size of $40\mu m$ that falls within the range of compositions that is classically considered to be paramagnetic at room temperature. They found that these particles carry a measurable and stable remanence, which they attributed to the presence of Fe-enriched transformation-induced microstructural domain boundaries that arise during the ordering transition when the materials originally cooled from high temperatures (Lawson & Nord 1984). Dark-field transmission electron microscopy indicated that these Fe-enriched zones are variable, but submicron, in size (Fig. 8), and that they may be as small as a few atoms across in some cases (Lawson et al. 1981; Lawson & Nord 1984; Nord & Lawson 1989). The possibility of a self-reversed thermal remanent magnetization (TRM) within ferrimagnetic ilmenites (Ishikawa & Syono 1963; Allen & Shive 1974; Lawson et al. 1981; Lawson & Nord 1984; Nord & Lawson 1989; Hoffman 1992) is not directly relevant in the present study because, as detrital particles, the dominant remanence component, which might have been originally self-reversed, would align with the ambient geomagnetic field in the depositional environment. Although the grains identified as the likely remanence carriers in this study have somewhat higher Ti (and Mn) contents than those in the above-cited studies, the magnetic properties of the ilmenite grains in the Wanganui basin sediments can be attributed to a similar mechanism to that discussed by Lawson & Nord (1984) and Nord & Lawson

Fig. 7. High-temperature susceptibility results. (a) muddy sandstone; (b) sandy mudstone; (c) a magnetic extract from the Wanganui basin.
(1989). This interpretation is preferred to the possibility that the magnetic properties are due to discrete inclusions of magnetic iron oxides, because such inclusions were not observed under BLM. EPM results (Table 3a and b) indicate a near end-member ilmenite composition because this is the average composition detected across the width of the 1 μm electron beam, as was observed by Lawson & Nord (1984). Smaller, Fe-rich zones were detected by Lawson & Nord (1984) and Nord & Lawson (1989) only when dark-field transmission electron microscopy was used. The hysteresis properties measured in this study (Fig. 6) are also consistent with the observation of stable remanences in similarly large grains (c. 40 μm) by Lawson & Nord (1984). These properties are best explained by the presence of submicron Fe-enriched zones within the large grains. Relatively low values of \( M_r \), \( M_s \), of c. 0.26 (Fig. 6) probably result from a mixture of single-domain (SD) and superparamagnetic (SP) grains within these submicron zones. If the photomicrograph of Lawson & Nord (1984) is taken as a guide (Fig. 8), one would expect grain sizes within these zones to vary within the normal range of SD and SP sizes (i.e. a few atoms thickness to hundreds of nanometres). There is probably a relatively broad range of sizes within the SP and SD range in these Fe-rich zones, although the range is not sufficient to give rise to irregularly shaped hysteresis loops (Fig. 6) (see Roberts et al. 1995; Tauxe et al. 1996). A distribution of grain sizes in the SD range can also account for the distributed unblocking temperatures observed in stepwise thermal demagnetization data (Fig. 2), as has also been suggested by Roberts & Pillans (1993). A distribution of such grains would produce an overlap between the coercivity spectra of the primary and secondary remanence components, which may explain the frequent failure of AF demagnetization to isolate primary remanence directions in similar sediments in New Zealand. Also, a narrow grain-size distribution would be expected to give a well-defined Hopkinson peak near the Curie temperature for the phase under investigation: the absence of Hopkinson peaks in the high-temperature susceptibility results (Fig. 7) may therefore be attributable to the distributed grain-size spectrum.

Lawson & Nord (1984) suggested that the Fe-enriched zones within such ilmenite grains are enriched in a phase that lies toward the hematite end of the solid solution series. An additional puzzle concerning the magnetic properties of the Wanganui ilmenite grains is that high-temperature results suggest that the Fe-enriched zones have thermomagnetic properties that are close to those expected for magnetite (Fig. 7). As ilmenite is a product of the solid solution series between hematite and ilmenite, it would be surprising if a product of another solid solution series (i.e. the ulvöspinel series) were present. Temperature-dependent susceptibility results display somewhat variable results, with susceptibility decreasing to zero in a range of temperatures between 580 and 610°C (Fig. 7). Susceptibility values that persist to 610°C in a magnetic extract (Fig. 7c) are important because they suggest that the Fe-enriched material within the ilmenite grains may lie within the ferrimagnetic range of the hemo-ilmenite series rather than in the ulvöspinel series. Temperature-dependent susceptibility results also preclude maghemite as the mineral in the Fe-enriched zones. The lower magnetic moment of hemo-ilmenites with respect to magnetite (see Nagata 1961) is also consistent with the generally weak magnetizations documented in the Wanganui basin. Given the above evidence, it is concluded that the magnetization of the Wanganui basin Miocene sediments is dominated by ilmenite grains that contain submicron domains of a SD ferrimagnetic hemo-ilmenite phase.

**Impact of diagenesis on magnetic mineral assemblages in redeposited sediments**

Diagenesis has clearly had a major impact on the magnetization of Miocene sediments in the
Wanganui basin. This is attested to by the abundance of authigenic pyrite (Fig. 3a) which formed at the expense of detrital iron-bearing minerals. Detailed petrographic studies of bulk sediments, and of magnetic extracts, failed to identify any detrital magnetic or titanomagnetic grains. The only positively identified spinel phases were rare chromite grains (Fig. 3f).

Ilmenite is the only abundant detrital Fe Ti oxide in magnetic extracts and these grains have been extensively etched and pitted, presumably by sulphidic pore waters during early burial (Fig. 3b and c). Ilmenite is one of the least reactive iron-bearing minerals under diagenetic sulphide-reducing conditions: it is three orders of magnitude less reactive than magnetite and six orders of magnitude less reactive than hematite (Canfield et al. 1992).

From these observations, it appears that all of the commonly occurring detrital magnetic minerals (magnetite, titanomagnetite and hematite) have been completely dissolved during sulphidization in repeated cycles of erosion and redeposition in the Wanganui basin (as well as in earlier cycles of erosion and redeposition in the parent Torlesse rocks). A significant amount of ilmenite has survived pyritization, as has also been documented in other studies of detrital Fe Ti oxide minerals (e.g. Reynolds 1977; Roberts & Pillans 1993; Roberts & Turner 1993; Houslows et al. 1995; Reynolds et al. in press). Chromite also appears to be resistant to dissolution, as reported elsewhere (e.g. Leslie et al. 1989b; Houslows et al. 1995; Houslows 1996). Chromite, with similar compositions to those from the Wanganui basin (Table 2), has been reported to carry a strong and stable remanence (Kumar & Bhulla 1984a, b; Refai et al. 1989). Given the ability of chromite to resist diagenetic dissolution, it may be responsible for the remanence in some Wanganui basin sediments. However, a dominant magnetic signal due to chromite is considered unlikely, because chromite grains are rare in magnetic extracts and there is no widespread source of chromite in rocks from which the Wanganui sediments were derived.

The dominant magnetic mineral in Pliocene sediments of the Wanganui basin therefore appears to be a ferrimagnetic hemo-ilmenite phase that occurs as microcrystalline domains within ilmenite grains. This possibility has not been widely considered because such particles are not normally considered to be a source of remanent magnetization in sediments. However, in environments such as the Pliocene sediments of the Wanganui basin, where all other magnetic detrital Fe Ti oxide minerals have been dissolved, hemo-ilmenite domains within ilmenite grains might make a significant contribution to the sediment magnetism. The widespread occurrence of ilmenite grains within magnetic extracts in similar sediments from New Zealand (Roberts & Pillans 1993; Roberts & Turner 1993) may therefore be due to the presence of hemo-ilmenite domains. In addition to the dominant contribution of hemo-ilmenite domains within ilmenite grains, microcrystalline hematite has been identified on the surfaces of pyrite framboises in the Wanganui basin sediments (Fig. 3d and e). The hematite occurs on pyrite that did not form until early burial, therefore, the most likely time of hematite formation is during late-stage oxidation, probably after uplift when pore fluids may have been oxic. The hematite is extremely fine grained (Fig. 3d and e) and may be superparamagnetic, but an SD hematite fraction may be responsible for the weak high-temperature component that persists in many samples after thermal demagnetization up to 350°C (e.g. Fig. 2c).

Conclusions

Repeated magnetic and mineralogical measurements on magnetic grains from Pliocene marine sediments in the Wanganui basin indicate that the dominant carrier of remanent magnetization is hemo-ilmenite that occurs as submicron domains within large ilmenite grains. Ilmenite is much more resistant to dissolution during early diagenetic sulphidization than most ferrimagnetic Fe Ti oxide minerals which appear to have been completely dissolved. Ilmenite grains with compositions of those documented in this study are normally considered to be paramagnetic. The ferrimagnetic properties of these grains are attributed to microstructural inhomogeneities that arose during cooling of the original igneous source rock, following the mechanism described by Lawson & Nodal (1984). Although this remanence mechanism is unexpected, and would probably be unrecognized in sediments that contain significant magnetite, it may be widespread in other sediments that have undergone extensive diagenetic modification as a result of prolonged sulphidization.

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