Absence of natural viscous remanent magnetization in multidomain high-titanium magnetites: evidence for domain-wall interactions

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Accepted 2003 January 27. Received 2003 January 20; in original form 2002 March 15

SUMMARY

We have studied viscous remanent magnetization (VRM) acquisition in lava clasts from volcaniclastic breccias from Ruapehu, North Island, New Zealand. The age of these deposits ranges from 2.5 to >65 ka BP VRM parallel to the direction of the present Earth's field is present in most clasts. However, VRM is not recorded in lava clasts in which high-titanium titanomagnetite of composition in the range x = 0.44-0.65 (~TM55) is the only or the dominant magnetic mineral present. Experiments demonstrate that these TM55-bearing samples have low blocking/unblocking temperatures, which would have been reset by viscous processes to give VRM if the material was in a single-domain state. Our experiments show that our TM55 samples can acquire low-temperature pTRMs in the laboratory. Analytical electron microscopy confirms the composition and demonstrates that these TM55 grains are up to 100 µm in size and that there are no observable exsolution structures. The grains are therefore in a multidomain state. Previous theoretical work has predicted that multidomain (MD) magnetic material will not acquire VRM if changes in remanence result in a complete reorganization of the whole-grain domain structure, as the activation energy of this process considerably exceeds the kinetic energy available at ambient temperatures ($\sim 20 \,^{\circ}$ C) even over timescales greater than the age of the Earth. Previous laboratory experiments have been reported that show the acquisition of VRM in crushed and sized MD magnetite and titanomagnetite. These results have been used by several authors to conclude that MD VRM proceeds by motion of small segments of individual walls rather than by whole-grain domain reorganization. Our experiments suggest that the previously reported VRM effects in synthetic MD titanomagnetites may be due to contamination by a minute fraction of very fine and very viscous particles rather than due to inherent MD properties. We conclude that, on our natural material, MD TM55 does not acquire VRM. In this material, there is evidently no mode of remagnetization available for VRM acquisition other than thermal activation between whole-grain LEM states, and there is insufficient kinetic energy available at 20 °C to effect this activation. This is the first demonstration of this effect.

Key words: domain wall interactions, multidomain remanence, natural breccias, Ruapehu volcano, titanomagnetite, viscous remanent magnetization.

INTRODUCTION

Viscous remanent magnetization (VRM) is acquired by exposure of a magnetic material to applied magnetic fields at ambient temperature. Most rocks acquire some VRM during exposure to the Earth's magnetic field. This VRM is usually identified by a component of magnetization parallel to the direction of the Earth's magnetic field at the site, and this component is demagnetized between ambient temperatures and a maximum temperature, which is likely not to exceed 150–200 °C. The details of the acquisition process have long been debated. Néel (1949) set out the theory of acquisition of remanence by single-domain (SD) grains which provides the framework for understanding acquisition of VRM in SD material. Dunlop (1973) and Moskowitz (1985) have given comprehensive reviews of VRM in single- and multidomain magnetic materials, and this paper outlines the key theories and experimental results in a later section. Rocks can carry a permanent record of the ancient magnetic field direction because the magnetic minerals which they contain have large energy barriers to changes of magnetization. For single-domain grains, smaller grains have lower energy barriers. Viscous magnetization is acquired by thermal activation of a small proportion of grains. Pullaiah *et al.* (1975) published nomograms that depict the temperature–time relationships and which enable readers to determine the maximum laboratory unblocking temperature of VRM acquired over a large range of timescales.

Several authors have queried whether the kinetics of this thermal activation can adequately be described by Néel's (1949) theory. Middleton & Schmidt (1982) published revised nomograms, which were modified to incorporate experimental data from their study of thermal overprinting in the Milton monzonite. These revised nomograms predict considerably higher laboratory unblocking temperatures for VRM than do those of Pullaiah et al. (1975). Walton (1980) and Moon & Merrill (1986) have developed different theoretical models for thermal activation that predict different relationships between blocking and unblocking temperatures over different timescales. However, the weight of experimental evidence now seems to support the validity of Néel's thermofluctuational SD theory following a number of well-constrained experiments both in the laboratory and in natural settings on material with a wellcontrolled domain state. Thermal demagnetization experiments by Williams & Walton (1988) on laboratory VRM in well-dispersed SD magnetite grains gave results that fit very well with the predictions of Pullaiah et al. (1975). Dunlop & Ozdemir (1993) demonstrated a similar result in their study of VRM in SD magnetite. Tyson Smith & Verosub (1994) published a study of natural VRM acquired in blocks of Columbia River Basalt with SD magnetite remanence carriers that had been incorporated into a landslide 800 yr ago. They found that laboratory unblocking temperatures of VRM were consistent with Pullaiah et al.'s predictions.

The acquisition of VRM in large multidomain grains is far less well understood. Results of laboratory experiments are in conflict as is shown in a later section.

Tyson Smith & Verosub (1994), in their study of TVRM of basalt blocks in a landslide, point out that there are very few situations where estimates of exposure time to the Earth's field and the temperature at which exposure took place can be determined with any accuracy. The ideal place to study VRM is in breccia deposits of a known age, where the VRM will be imprinted in a different direction from the primary ChRM of the material, enabling differentiation between VRM and ChRM by directional analysis and enabling the determination of the maximum unblocking temperature of the VRM component.

In this paper, we present results of a study of volcaniclastic breccias deposited between 2.5 and >65 ka BP. In some of this material, the only magnetic mineral is titanomagnetite with compositions in the range x = 0.44-0.65 (~TM55) in an multidomain magnetite (MD) state, and we have investigated the acquisition of VRM (or lack of acquisition) in this material and in other mineralogies containing pure magnetite and other mixed magnetic mineralogies.

GEOLOGY, SAMPLING AND PALAEOMAGNETIC METHODS

Ruapehu ring plain

This study was initially designed to investigate whether previously unidentified pyroclastic flows are present on the ring plain surrounding the volcano of Ruapehu, North Island, New Zealand. In this study, between 10 and 13 individual lava clasts were collected from each of 10 unconsolidated breccia units which had been identified as debris or stream deposits by Donoghue *et al.* (1995). These deposits have ages ranging from 2.5 to >65 ka. The blocks were oriented by gluing a plastic plate on to a surface of the block, marking strike and dip lines on the plate and then measuring strike and dip with a compass-clinometer. 1 in diameter cores were drilled from each block in the laboratory. Some blocks disintegrated during the

drilling process, and the smallest number of usable samples at a site was seven (site RRP3).

All samples were thermally demagnetized in temperature steps of 60, 90, 120, 150, 200, 250, 300, 400, 500 and 600 °C using an Magnetic Measurements (MMTD) oven with a residual field of less than 5 nT. Remanence was measured using a Cryogenic Consultants Ltd cryogenic magnetometer or a Molsin spinner magnetometer. Vector components were analysed using the SuperIAPD program written by Trond Torsvik incorporating the LINEFIND algorithm of Kent *et al.* (1983). Magnetic mineralogy was determined by the following techniques: (1) high-temperature susceptibility measurements made in an argon atmosphere obtained using a CS2 furnace attachment to a KLY2 Kappa bridge; (2) analysis of blocking temperature spectra from thermal demagnetization data; (3) SEM and wavelength dispersive microprobe analysis.

Samples were collected from sites located at 39.5° S, 175.5° E. The time-averaged axial geocentric dipole field has an inclination of -58° at this latitude.

RESULTS

Site RRP4

This site is a massive, 50 cm thick breccia unit displaying slight reverse grading, and lies stratigraphically between two tephra marker layers (Pourahu member and Shawcroft lapilli, dated at *ca.* 10 000 and 11 00 BP, respectively, Donoghue *et al.* 1995) and we assign an age of *ca.* 10 500 BP to this unit. It is part of the Tangatu formation of Donoghue *et al.* (grid ref. T20/417981). NRM intensities vary from 12.6 A m⁻¹ to 815 mA m⁻¹ at this site. There is a considerable variation of behaviour on thermal demagnetization, reflecting the variation of lithology of the blocks within the breccia.

Type-1 behaviour.

Samples that display this type of behaviour have few or no unblocking temperatures below about 200 °C (Figs 1a and c). Samples that exhibit this behaviour are referred to as having a discrete blocking temperature spectrum. In each of these samples, only one component of magnetization is revealed on demagnetization (Figs 1b and d, respectively). We refer to this component as component A.

Type-2 behaviour.

In five samples, remanence is lost throughout the demagnetization sequence (Fig. 1g), and such samples are referred to as having a distributed blocking temperature spectrum. Remanence is completely demagnetized between 500 and 600 °C. In each of these five samples, there is a significant change in direction of the remanent vector during demagnetization, and two components of remanence can be identified on a vector plot (e.g. RRP4-5; Fig. 1h). We refer to the higher blocking temperature (T_b) component as component A and the lower T_b component as B.

Type-3 behaviour.

Two further samples from this site, RRP4-8 and RRP4-9 (Figs 2a and c), have distributed blocking temperatures, but 85–90 per cent of the remanence is demagnetized by heating to 200 $^{\circ}$ C. There is also only one component of remanence in these samples, which we refer to as component A.

The low- T_b component B is is statistically significantly, although not tightly, grouped at the 99 per cent confidence level (Dec. = 325° ,







Table 1. Site mean directions for all breccia sites from the Ruapehu ring plain. *N* indicates number of individual sample directions used, *R* is the resultant length of *N* unit vectors, *k* is precision parameter, a_{95} is the cone of 95 per cent confidence about the mean, R^* 99 per cent is as described in text, 'random 99 per cent' indicates whether the grouping is random at the 99 per cent confidence level, R^* 95 per cent is as described in text, 'random 95 per cent' indicates whether the grouping is random at the 95 per cent confidence level. A star (*) indicates there are too few samples for a statistical analysis of randomness. Bold type indicates data from the three key sites discussed in the text.

Site	Dec.	Inc.	Ν	R	k	a95	R* 99	Random	R^*	Random
							per cent	99 per cent?	95 per cent	95 per cent?
					High-T	compone	nt A			
RRP1	350	+37	9	1.18	1	180	5.61	yes	4.76	Yes
RRP2	26	-23	10	5.31	1.9	49	5.94	yes	5.03	No
RRP3	34	30	7	4.68	2.6	47	4.89	yes	4.18	No
RRP4	312	-41	9	4.48	1.77	57	5.61	yes	4.76	Yes
RRP5	194	+15	9	2.56	1.2	98	5.61	yes	4.76	Yes
RRP6	352	-3	10	1.29	1	180	5.94	yes	5.03	Yes
RRP7	68	+27	9	3.36	1.4	76	5.61	yes	4.76	Yes
RRP8	160	-31	11	3.93	1.4	68	6.25	yes	5.28	Yes
RRP14	122	-3	9	3.12	1.4	82	5.61	yes	4.76	Yes
RRP19	289	-15	8	2.93	1.4	86	5.26	yes	4.48	Yes
Mean of sites	21	-3	10	2.37	1.20	106	5.94	yes	5.03	Yes
					Low-T	componei	nt B			
RRP1	068	-66	4	3.3	4.3	50	3.49	Yes	3.10	No
RRP2	016	-55	4	3.30	4.3	51	3.49	Yes	3.10	No
RRP3	026	-38	7	6.19	7.4	24	4.89	No	4.18	No
RRP4	325	-57	5	4.45	7.23	30	4.02	No	3.50	No
RRP5	338	-52	6	5.12	5.66	31	4.48	No	3.85	No
RRP6	354	-30	3	2.8	9.9	41	*	*	*	*
RRP7	334	-45	8	6.6	5.0	27	5.26	No	4.48	No
RRP8	037	-63	8	7.17	8.5	20	5.26	No	4.48	No
RRP14	033	-57	3	2.43	3.5	79	*	*	*	*
RRP19	351	-47.5	5	4.69	12.9	22	4.02	No	3.50	No
Mean of sites	004	-55	10	9.38	14.5	13.1	5.94	No	5.03	No

Inc. $=-57^{\circ}$, $a_{95} = 30^{\circ}$; Table 1) and its direction is indistinguishable from the present Earth's field direction (PEF; Dec.= 0°; Inc. = -58°). In contrast, the directions of component A are randomly distributed (randomness defined using the test of Watson 1956, Table 1).

We interpret the behaviour from samples from this site as follows. Component A is a component of magnetization that predates the *ca*. 11 ka emplacement of this breccia unit. This component is now randomly oriented. All three sample types contain this component. Component B has been acquired since deposition of the breccia and is only seen in type-2 samples.

Site RRP5

This site is a 24 cm thick laminated breccia unit containing some pumice lapilli and lies 1.2 m above site RRP4, between the Ngamatea and Pourahu tephra marker layers (the upper unit is not dated, but the age of unit RRP5 must be less than *ca*. 10 000 yr). It is part of the Tangatu formation of Donoghue *et al*. (grid ref. T20/417981). NRM intensities vary from 5.5 A m⁻¹ to 240 mA m⁻¹ at this site. All three types of demagnetization behaviour are again found at this site: one sample has type-1 behaviour (RRP5-2, Figs 1e and f), five samples have type-2, two-component behaviour (e.g. RRP5-7, Figs 1i and j) and one sample has type-3 behaviour (RRP5-5B, Figs 2e and f). In a similar fashion to site 4, component A is randomly distributed (Table 1 and Fig. 3a), while component B is significantly well grouped at the 99 per cent confidence level and is statistically indistinguishable from the PEF (Table 1 and Fig. 3b).

At this site, in the type-3 sample RRP5-5, approximately 10 per

cent of the remanence is carried by magnetite while 90 per cent is carried by the predominant TM60. In this sample, a low- T_b component is removed up to 120 °C, but this is of small magnitude and is not in the direction of the PEF (Fig. 2f).

Site RRP19

This site is part of a *ca*. 5000 BP lahar deposit on the Ohakune mountain road (grid ref. S20/234035). NRM intensities vary from 15 A m^{-1} to 200 mA m^{-1} at this site. Only two types of demagnetization behaviour are displayed here: four samples have two-component type-2 behaviour (e.g. RRP19-8, Figs 1k and 1) and four samples have predominantly type-3 behaviour (e.g. RRP19-1, 19-6, Figs 2g, h, i and j). Again, component A is randomly distributed (Table 1) and component B is significantly well grouped at the 99 per cent confidence level and is statistically indistinguishable from the PEF (Table 1).

Of the type-3 samples, RRP19-5 has the most magnetite coexistent with the dominant TM60. In this example (Fig. 2l), the vector shallows in the first two demagnetization steps before component A is isolated, giving a curved trajectory. This suggests that an upward directed component which is steeper than B but which has overlapping blocking temperatures with B is removed in these two initial steps.

Other RRP sites

Of the remaining seven sites in the Ruapehu study, samples have predominantly type-1 or type-2 behaviour. Three sites contain one



Figure 3. Stereographic equal-angle projections of (a) low unblocking temperature component B for six samples from site RRP5, (b) high unblocking temperature component A for nine samples from site RRP5; (c) site mean directions for the low unblocking temperature components from all sites; (d) site mean directions for the high unblocking temperature components from all sites. Mean direction is indicated as a star at the centre of the 95 per cent circle of confidence. Open symbols represent upward-pointing vectors; closed symbols represent downward-pointing vectors.

sample with type-3 behaviour (RRP1, RRP2, RRP14) while the other four sites do not contain any samples with type-3 behaviour.

The type-2 samples have two remanence components. For each site, the low-temperature component B is statistically significantly grouped at the 95 per cent confidence level (Table 1), and passes the significance test at 99 per cent confidence for all sites except RRP1 and RRP2 where only four estimates of the component direction can be made. For each site, the high-temperature component A is randomly distributed at 99 per cent confidence levels. For two sites, RRP2 and RRP3, the grouping of component A is non-random at the 95 per cent confidence level.

All RRP sites

Table 1 includes a statistical analysis of all site mean directions of components A and B. The site means for component B are well grouped with an overall mean direction of 004/-55, very close to the PEF direction of 000/-58. The site means for component A are randomly distributed. Distribution of site means for components A and B are shown in Figs 3(c) and (d).

Maximum unblocking temperature of component B versus the age of the deposit

The maximum unblocking temperature of component B in the type-2 sites is not consistent at an individual site. For example, at the youngest site, RRP3 (grid ref. T20/464095), which was emplaced 2.5 kya, component B is removed by themal demagnetization to 90 °C for sample RRP3-10a (Fig. 4a) but persists up to 200–250 °C in sample RRP3-11 (Fig. 4b). Sites RRP7 and 8 (grid ref. S20/163129) are the oldest sites sampled, and are believed to have been emplaced more than 65 kya (Dr Vince Neal, private communication, 1996). At these sites, the blocking temperature spectra are often not favourable for accurate determination of the maximum $T_{\rm ub}$ of component B. In samples where this can be accurately determined, the maximum

unblocking temperature varies from 120 to $150 \degree C$ (RRP8-5) to over 300 $\degree C$ (RRP8-8) (Figs 4c and d).

The oldest site that contains blocks with a high-titanium magnetic mineralogy is site RRP14 (grid ref. T20/467101), from the Te Heuheu formation which has an age within the range 14.7–22.5 ka (Donoghue *et al.* 1995). There is no evidence of acquisition of VRM in this mineralogy over this timescale.

High-temperature susceptibility

Type 1 and 2 samples from all sites show variations in susceptibility through a heating and cooling cycle typical of slightly nonstoichiometric magnetite, with Curie temperatures of 580-600 °C (e.g. RRP3-7; not illustrated). On cooling, the Curie temperature is less sharply defined and is often reduced to 550-580 °C. During the cooling part of the run, the susceptibility value is reduced to between 70 and 20 per cent of the initial susceptibility.

Fig. 5 shows variations in susceptibility for four type-3 samples. Analytical electron microscopy has been carried out on four of these specimens.

RRP19-1. The susceptibility increases sharply during the initial part of the heating cycle, and then drops even more rapidly once the temperature has exceeded about 130 °C. Extrapolation of the steepest part of the descent curve gives a Curie temperature of 190 °C. This is consistent with a titanomagnetite mineralogy (Fe_{3-x}Ti_xO₄) with x = 0.6 (TM60), although on this evidence alone we cannot rule out the presence of titanohematites or titanomaghemites. There is no evidence of any phase with Curie temperatures higher than 190 °C in the heating curve. After heating to 700 °C, some alteration of the magnetic mineralogy has occurred, as there is a gradual increase in susceptibility below 600 °C, and the sharp change in susceptibility seen on heating has been smeared out towards higher temperatures.

RRP19-5. Again susceptibility increases markedly between room temperature and about 120 °C, and then falls at a similar rate. In contrast to sample RRP19-1, in this sample the decrease in susceptibility



Figure 4. Examples to illustrate the range of maximum unblocking temperatures of VRM in samples. Symbols as in Fig. 1.



Figure 5. Variation of low-field susceptibility with temperature. The thick curve indicates heating and the light curve indicates cooling.

continues up to above 600 °C. The cooling curve follows the heating curve almost exactly. This type of susceptibility versus temperature curve probably arises from a range of titanomagnetite compositions and Curie temperatures ranging between 200 and 600 °C.

RRP5-5. The heating curve for this sample is similar to that from sample RRP19-1, with a dominant and rapid drop in susceptibility between 120 and 180 °C. However, in this sample, there is a 'tail', as 20 per cent of the susceptibility remains above 200 °C, and then reduces gradually to reach zero at about 600 °C. This experiment demonstrates that the dominant magnetic mineralogy is probably TM60, but that a smaller amount of lower titanium content and higher Curie temperature titananomagnetites are present.

RRP4-9. The heating curve indicates that three distinct magnetic phases are present. There is a low-temperature sharp increase and decrease of susceptibility up to about 180 °C, indicative of TM60. Above 200 °C the susceptibility is almost constant until about 300 °C, when a rapid decrease in susceptibility occurs. Extrapolation of this descent curve gives a Curie temperature of about 330 °C, which suggests the likely presence of another titanomagnetite phase with $x \approx 0.4$. There is a small amount of a further phase with a Curie temperature of about 450 °C. These Curie temperatures are displaced to higher temperatures on the cooling curve, and the transitions are less well defined.

Electron microprobe analysis of type-3 samples

Polished thin sections were prepared from samples RRP4-9, 5-5, 19-1 and 19-5. Initial analyses were carried out using a JEOL JSM840A scanning electron microscope with an Oxford Instruments ISIS300 analytical facility to determine magnetic grain sizes and iron and titanium contents. A more detailed analysis was carried out using a wavelength dispersive JEOLJXA-8800 microprobe, which allowed oxygen to be measured directly, so that the oxidation state and degree of non-stoichiometry of the iron-titanium oxides could be determined. Using an accelerating voltage of 10 kV enabled grains as small as 1 µm diameter to be measured. Pure metals and oxides were taken as standards, minimizing matrix corrections, which were made using a $\phi - \rho - z$ procedure. Pure magnetite (Fe₃O₄) should have 42.8 per cent Fe atoms to 57.2 per cent oxygen atoms. Pure hematite or maghemite (Fe₂O₃) should have 40 per cent Fe atoms to 60 per cent oxygen atoms. Maghemitization of initially pure magnetite will result in Fe and O proportions intermediate between those of the pure end-members. The composition of titanomagnetite (Fe_{3-x}Ti_xO₄) is usually referred to in terms of the value of *x*, or as TM60 for a composition with *x* = 0.6, for example.

Iron-titanium oxides of size ranging from a few microns to over 50 µm have been identified in all four samples. The average compositions in terms of the atomic weights of Fe, Ti, Al, Mg, Cr and O determined by wavelength-dispersive microprobe analysis are shown in Table 2 and reflect the presence of slightly non-stoichiometric titanomagnetite containing Al and Mg impurities as the dominant iron oxides. Many of these titanomagnetites contain regions of ilmenite, recognized by higher titanium content, lower Fe content and higher O content. The ilmenite has not formed as exsolution lamellae within the titanomagnetites, as high-resolution profiles across the titanomagnetite crystals do not show variations in titanium composition. The ilmenite often forms as a single region with a smooth curved outline (e.g. crystals 19-1D and 19-5A; Fig. 6). This suggests that high-temperature oxidation occurred during the formation of these samples, and that this may have occurred in a magma chamber over timescales long enough to allow diffusion of titanium across distances of tens of microns, as we do not find fine-scale exsolution structures. Sample 19-1 contains the highest proportion of titanium (7.5 per cent), while 19-5 (7.3 per cent), 5-5 (6.2 per cent) and

Table 2. Averaged compositions from wavelength-dispersive microprobe analysis, given as atomic weight per cent of each atomic species. N is the number of separate crystals analysed, between three and five analyses per crystal were carried out.

Sample	Ν	Fe atomic wt per cent	Ti atomic wt per cent	Al atomic wt per cent	Mg atomic wt per cent	O atomic wt per cent	Total
RRP19-1	4	31.08	7.51	1.18	1.37	58.12	99.27
RRP19-5	3	31.99	7.34	1.13	1.21	57.83	99.51
RRP5-5	1	32.21	6.22	1.74	1.79	56.91	99.78
RRP4-9	6	33.94	4.76	1.85	1.43	57.61	99.61



Figure 6. Electron micrographs of titanomagnetite crystals (a) RRP19-1D and (b) RRP19-5A. The darker region is identified as ilmentite. The scale bar is 20 µm in both cases. White dots indicate analyses.

4-9 (4.7 per cent) contain decreasing amounts. The amount of Al substitution varies inversely with titanium content (Table 2). SEM analysis identified the presence of a substantially different low-titanium phase in sample 5-5 with an iron:titanium ratio of 22.6:1 in contrast to the main phase with an iron:titanium ratio of 3.8:1. This is likely to represent the close to pure magnetite phase which demagnetizes completely by 500 °C (Fig. 2e). These grains were less than 5 µm in size, and we did not find any examples of them during our microprobe analysis.

If the only constituents of our titanomagnetites were Fe, Ti and O, then we could estimate the x value of the titanomagnetites by the following relationship:

$$x(Ti) = 3$$
(atomic wt per cent of Ti)/(atomic wt per cent of Ti
+ atomic wt per cent of Fe). (1)

In this paper, we wish to estimate x to enable us to predict the Curie temperature of the minerals that constitute our samples, and to compare our predictions of T_c with the values determined experimentally from blocking temperature spectra and high-temperature susceptibility data. If we can show that our predictions fit the observed T_c values then we can be sure that our electron optical study has identified the important remanence-carrying minerals. Curie temperatures in titanomagnetites decrease systematically with increasing x (see Dunlop & Özdemir 1997). Titanomagnetites in sample 19-1 contain Al and Mg ions in addition to Ti, and are also slightly non-stoichiometric. The presence of Al produces a reduction of Curie temperature as it is diamagnetic, whereas replacement of Ti with Mg does not have a significant effect (O'Reilly 1984). In contrast, non-stoichiometry increases the Curie temperature in titanomagnetites (O'Reilly 1984). It is not clear how the Curie temperature in temperature in titanomagnetites (O'Reilly 1984).

perature will change in response to the combination of substitution of these cations and non-stoichiometry. Since there is no accepted way of incorporating these parameters into a calculation of expected Curie temperature, we have calculated an 'apparent' x value, which we call x'. We use the relationships between Curie temperature and xvalue for iron-titanium oxides from Fig. 3.11 of Dunlop & Özdemir (1997), to predict an apparent Curie temperature based on our x' value. Table 3 shows these 'apparent' values of x (x') calculated on the basis of three assumptions. First, that only the titanium should be considered, i.e. using eq. (1) with the total percentage of cations in the denominator (x'(Ti)). The second assumes that titanium plus aluminium should be considered and uses the following equation:

$$x'(Ti + Al) = 3$$
(atomic wt per cent of Ti
+ Al)/(atomic wt per cent of total cations). (2)

The third assumes that titanium, aluminium and magnesium all contribute to the reduction in Curie temperature and uses the following equation:

$$x'(Ti + Al + Mg) = 3$$
 (atomic wt per cent of Ti
+ Al + Mg) / (atomic wt per cent of total cations). (3)

We have then used the values of x' for these three models to estimate a Curie temperature, which is given in Table 3. In the next section we compare the values of T_c estimated from blocking temperature spectra, high-temperature susceptibility experiments and our probe data. This approach is obviously not intended to reflect the real physical controls on Curie temperature, but proves useful, as is described in the next section.

Sample			Ti	Ti + Al		Ti + Al + Mg	
	Measured $T_{\rm c}$ (°C)	<i>x</i> ′	$T_{\rm c}$ (°C)	<i>x</i> ′	$T_{\rm c}$ (°C)	<i>x</i> ′	<i>T</i> _c (°C)
RRP19-1	180	0.55	240	0.65	170	0.76	70
RRP19-5	220	0.47	290	0.57	230	0.66	160
RRP5-5	200	0.44	320	0.56	235	0.74	70
RRP4-9	330	0.29	420	0.44	320	0.53	250

Table 3. Estimated Curie temperatures from microprobe data. See the text for details. Values in bold indicate estimated values that fit with the measured Curie temperatures.

Estimates of titanomagnetite composition

We obtain consistent estimates of Curie temperature from blocking temperature spectrum analysis and measurements of hightemperature susceptibility for our four samples. Both methods give a single value of about 180°C for T_c for sample 19-1 (Figs 2g and 5a; tabulated in Table 3). For sample 19-5, the shape of the blocking temperature spectrum (Fig. 2k) suggests that a phase with $T_{\rm c}$ close to 220 °C dominates the remanence, and a smaller amount of higher Curie temperature phases carry remanence which is not demagnetized until 550 °C. The high-temperature susceptibility curve (Fig. 5b) indicates that there is probably a continuous range of compositions of titanomagnetite with Curie temperatures ranging from just above 200 °C up to 580 °C. For sample 5-5B, both methods confirm that the dominant phase has a Curie temperature of about 200 °C (Figs 2e and 5c), and that a subsidiary phase with T_c of up to 500 °C is present. For sample 4-9, the remanence is dominated by a phase that demagnetizes by 170 °C (Fig. 2c; this phase is identified in the high-temperature susceptibility data Fig. 5d), however, the high-temperature susceptibility measurements show that the most abundant phase has a Curie temperature of about 340 °C, although it only contributes less than 25 per cent of the remanence. We thus describe the 'dominant Curie temperature' for each sample to be 180 °C for 19-1; 220 °C for 19-5; 200 °C and above for 5-5; 330 °C for 4-9.

When we compare these measured values of T_c with the calculated values from microprobe data in table 3, we find that the Curie temperature estimated from the value x'(Ti + AI) gives a good match to the measured Curie temperatures for all four samples. This fit does not suggest that we have properly understood the way that cation substitution and non-stoichiometry affects Curie temperature. However, the fact that our estimates of x' for all four samples give estimated values of T_c that have approximately the same proportionality to the actual T_c values confirms that we have analysed the correct minerals in our microprobe analysis, and that the remanence is carried by titanomagnetites with compositions in the range x = 0.65-0.44, with Al and Mg substitution. For ease of reference, we will refer to this range as ~TM55.

INTERPRETATION

Component A is the original, now randomized, component of magnetization in all of these lava clasts, and predates the emplacement of the deposits in which it is found. It is found in all samples in this study.

Component B has been acquired since deposition of the breccia and is only seen in type-2 samples. The maximum unblocking temperature of this component is 200 °C. Component B is not seen in type-1 samples because they do not have grains with blocking temperatures in this temperature range. In volcaniclastic deposits, low- T_b components parallel to the PEF may have two possible origins. The first possibility is that the deposit was co-eval with pyroclastic activity on the volcano, and that the material was hot at the time of deposition. The low- T_b part of the primary component A would be demagnetized by heating in a pyroclastic flow, and then these grains would become remagnetized in the direction of the ambient PEF on cooling after deposition, acquiring a new uniformly directed component B. The equilibrium temperature of the deposit can be determined from the minimum temperature required to remove this low- T_b overprint B (e.g. McClelland & Druitt 1989). Thermally activated overprints are known as pTRMs. The second possibility is that the deposit was emplaced at ambient temperatures from a cold debris flow, and was not associated with pyroclastic flow; so in this scenario, component B is a VRM acquired at ambient temperatures during exposure to the ambient Earth's magnetic field since deposition of the breccia (between 2.5 ka for RRP3 to >65ka for RRP7).

An interesting and important feature of component B is that it is not seen at any of our sites in any samples that have predominantly high-titanium magnetic mineralogy (~TM55), although it is seen in all samples which have a low-titanium magnetite mineralogy with a distributed blocking temperature spectrum. If a given breccia was deposited from a pyroclastic flow and component B was a pTRM acquired on cooling of the flow from an equilibrium temperature, then all clasts would have been heated and acquired pTRM (component B), if grains with the appropriate blocking temperatures existed. The high-titanium samples have distributed T_b spectra, which would be ideal to record a pTRM, so the absence of component B in these samples is evidence that these deposits were not emplaced at elevated temperature.

We are then left with the interpretation of component B as a VRM which is present in these samples in low-Ti titanomagnetite or magnetite, but absent in high-titanium titanomagnetite.

Following this interpretation of component B as a VRM, we can consider the effects of a combined mineralogy in a sample that contains both \sim TM55 and magnetite. In such combined mineralogy samples, the low-blocking temperature magnetite grains may acquire a VRM, but ~TM55 grains with the same blocking temperatures may not. We have previously described samples from this study with a mixed magnetic mineralogy (e.g. RRP5-5, RRP19-5, Figs 2f and l). In these two samples, 10-20 per cent of remanence remains after the \sim TM55 is demagnetized, and this remanence persists up to 500-600 °C (i.e. is carried by magnetite). In these two samples, a small low- T_b component exists which is demagnetized by 120 °C for 5-5 and by 90 °C for 19-5. This direction is not in the PEF direction, but when the demagnetization data is plotted on a stereonet, the first few data points lie on a great circle between the A component and the PEF direction. Hence, the low blocking temperature fraction consists of the original A component in the ~TM55 overprinted by component B (VRM) in the magnetite, these two components have overlapping blocking temperature spectra. On thermal demagnetization, both components are demagnetized together, and the resultant vector is not in a geologically meaningful direction. This



Figure 7. pTRM experiments demonstrate that blocking and unblocking temperatures are very similar. pTRM was induced at 120 $^{\circ}$ C in a field of 60 μ T to partially overprint the NRM. The vector diagrams are presented with directions plotted with respect to the axes of the core, not in geographic coordinates. Symbols are as in Fig. 1. The symbol marked NRM indicates the direction of NRM before imposition of the pTRM. 'pTRM to 120' indicates the resultant direction combining pTRM and remaining NRM. (a) Sample RRP5-5a1. The inducing field was in the vertical direction. (b) Sample RRP5-5a2. The inducing field was in the horizontal direction marked south on this diagram.

demonstrates that a combined mineralogy of this type can give rise to false directional data.

Why, then, is VRM absent in high-titanium titanomagnetite? We have carried out a simple experiment to test one hypothesis, which is described in the following section.

Test of pTRM acquisition in high-titanium samples

A possible explanation of the lack of VRM acquired by the hightitanium magnetite phase could be that the material has nonequivalent unblocking and blocking temperatures. One can imagine a scenario where the remanence demagnetizes with distributed unblocking temperatures, but the blocking temperatures of these grains are all grouped close to the Curie temperature, and are in excess of the blocking temperatures that would be activated by a few thousand years exposure to ambient fields at ambient temperatures. This would mean that the \sim TM55 remanence could not acquire VRM or low-temperature pTRM, even though the unblocking temperature spectrum suggests it should be able to.

We carried out an experiment to test whether samples with a high-titanium magnetic mineralogy which do not carry a VRM, are in fact able to record a pTRM. Only sample RRP5-5 yielded enough residual material to carry out pTRM experiments.

We used three subsamples from this block, and these were not demagnetized prior to this experiment as we wished the pTRM to be superimposed over the NRM as it would be in nature. A pTRM was imposed by heating to 120 °C at approximately 90° to the NRM direction, the orientation of each sample was different during imposition of pTRM to test for any possible anisotropy effects. The unblocking temperature spectrum of NRM from RRP5-5 shows that about 80 per cent of the remanence is demagnetized between 100 and 200 °C, and 50 per cent of the demagnetization occurs in a very narrow interval between 100 and 150 °C. The pTRM was induced at 120 °C so that it would activate approximately half of the titanomagnetite grains, if there is reasonable equivalence between blocking and unblocking. The inducing field was 60 µT. The resulting two-component remanence was then thermally demagnetized in steps of 90, 120, 150, 180, 200 and then 50 °C steps to 450 °C. Bulk susceptibility was monitored at each step of the experiment.

In all three samples, after imposition of a 120 °C pTRM, bulk susceptibility does not change (within the error), suggesting that no

chemical alteration or exsolution has occurred. The pTRM overprint is almost completely removed by thermal demagnetization to $120 \,^{\circ}$ C (demonstrated by the return of the remanence direction to close to the initial NRM direction, Figs 7a and b), but a small 'tail' persists up to 140 $^{\circ}$ C. The initial remanence is almost demagnetized by heating to 200 $^{\circ}$ C (Figs 7a and b). The demagnetization spectrum of the NRM showed that 10 per cent of the remanence was carried by lowtitanium magnetite with a Curie temperature above 500 $^{\circ}$ C. In this pTRM experiment, the magnetite component is not remagnetized or affected by the pTRM, so the remanence directions return to the NRM direction once the samples are demagnetized to above 140 $^{\circ}$ C.

This experiment demonstrates that these Ruapehu samples do indeed have a large proportion of the grains with blocking temperatures which are less than 120 °C, and that blocking and unblocking temperatures are very similar, although not all of the overprint is removed at the acquisition temperature. This means that we cannot explain the lack of VRM in ~TM55 by saying that there are no blocking temperatures available which would be activated by VRM over 11 ka. What is known about the relationship of blocking and unblocking temperatures suggests that the scenario outlined at the beginning of this section is unlikely, in any case. Single-domain grains have blocking and unblocking temperatures that are very similar (Dunlop & Ozdemir 1993), while multidomain magnetite grains are known to have distributed unblocking temperatures that can considerably exceed the blocking temperature. A theoretical explanation for the lack of VRM in this material is outlined in a later section.

THEORY OF VISCOUS REMANENT MAGNETIZATION

In magnetic materials that are important for palaeomagnetic studies, viscosity arises predominantly from three sources which are described below (see Moskowitz 1985, for a detailed review).

Thermofluctuations

At room temperature, thermal fluctuations will occasionally exceed the activation energy barriers that pin domain walls in MD grains or constrain spins to lie along the easy axis in SD grains, allowing the remanence to be partially reset; VRM has traditionally been assumed by rock magnetists to arise from this effect. The original theoretical formulation that describes this thermofluctuational effect was derived by Néel (1949). Néel showed that the influence of thermal fluctuations on the moments of small grains enables the moments to reverse themselves spontaneously so that thermodynamic equilibrium establishes itself rapidly. The relaxation time, τ , is the characteristic time for this spontaneous reversal to occur and is given by

$$1/\tau = C \exp[-vK(T)/2kT].$$
(4)

For SD grains, v is the grain volume, K(T) is the anisotropy energy, k is Boltzmann's constant and C is a frequency factor equal to 10^{10} Hz. The product $v \cdot K(T)$ is the activation energy required to initiate a change in magnetic direction. A magnetic system is in thermodynamic equilibrium if the time available is greater than the relaxation time of grains in the system, i.e. the magnetization direction is able to change in direct response to a change in the external field. The magnetic system becomes 'blocked' and magnetization does not respond to changes in external field if the relaxation times are greater than the time available. The relaxation time varies very rapidly with temperature, so there is a blocking temperature (strictly a blocking temperature interval) for an individual grain when the relaxation time is close to the time available. Pullaiah et al. (1975) used the relaxation time equation to calculate time-temperature relationships for magnetite and hematite, and published 'nomograms' that allow estimation of the change of blocking temperature over different timescales. These curves can be used to determine the laboratory temperatures required to demagnetize VRM acquired at ambient temperatures (~20 °C) over different timescales for magnetite and hematite. The exposure times at 20 °C experienced by our Ruapehu ring plain deposits range from 2.5 to >65 ka, and Pullaiah et al.'s predictions suggest that we should have to heat to 125-150 °C in the laboratory over 300 s to remove these VRMs if they were carried by SD magnetite. Our experiments demonstrate that the dominant mineral in our samples can be represented by TM55. We have recalculated time-temperature relationships for TM55 using a very simple assumption that activation energy is proportional to $v \cdot J_s$ $(T)^2$, and using the temperature dependence of J_s (T) for TM61 given by Sahu & Moscowitz (1995), scaled for the higher Curie temperature of TM55. The resulting nomogram is shown in Fig. 8. The nomogram lines are steeper than for magnetite, and we predict that we should have to heat to 80-90 °C in the laboratory over 300 s to remove VRMs acquired at 20 °C between 2.5 and 65 ka in SD TM55. This prediction conflicts with our observation that there is no VRM carried by this composition.

For MD grains, if thermofluctuational changes in magnetization can be described by eq. (4), it is not clear what the 'activation volume', v, should be for MD VRM acquisition. If MD VRM is acquired by small segments of domain walls undergoing Barkhausen jumps in position then the activation volume could be quite small, and the MD viscosity may be of a similar magnitude to SD VRM. Experimental observations of domain states have shown that the same magnetic grain can have a number of different, equally stable, domain configurations, for example Heider et al. (1988) demonstrated that the same grain can have between two and five domains at room temperature following successive thermal cycles. These different domain states have been described as being local energy minima or LEM states (Moon & Merrill 1985). If the whole domain structure needs to be reorganized so that the grain is in a different LEM state for VRM to be acquired, then the activation volume will be very large compared with that of submicron SD grains and MD grains will be



Figure 8. Nomogram for TM55.

very much less viscous than SD grains. Dunlop (1973) took reasonable values of material properties for a 200 Å SD particle and a 1 μ m particle (which he defined as MD) and calculated that the viscous acquisition constant S_{sd} for single domains was approximately 300 times that for multidomains, assuming that the MD activation volume is equal to the whole-grain volume. Viscosity in large (>100 μ m) MD grains thus may be many orders of magnitude smaller than SD VRM.

One would expect that laboratory experiments should easily differentiate between these two widely different predictions of MD versus SD VRM. However, evidence is conflicting, and is outlined in more detail later in the paper.

Moskowitz and other authors have pointed out that diffusional aftereffects and disaccomodation can also contribute to timedependent changes in magnetization of magnetite and titanomagnetite.

Diffusional aftereffects

When a multidomain grain containing many domain walls is magnetized (in any kind of remanence acquisition process) the domain walls are assumed to lie in a local energy minimum position. However, diffusion of dislocations and defects, and of impurities within the grain can occur and can ultimately change the energy balance within the grain. This will result in the relocation of the wall in a new energy minimum position, and if this process occurs in an external magnetic field (e.g. the Earth's field), the new magnetization recorded by the grain or part of grain will be parallel to the external field, i.e. VRM. This type of viscosity is called a diffusion aftereffect and Néel (1952) published a theoretical treatment of the phenomenon. The magnetic aftereffect causes a change in the intensity of magnetization (Moskowitz 1985).

Disaccomodation

Disaccomodation is also a diffusion-related effect, but in contrast to the diffusional aftereffect, it is due to the diffusive reordering of vacancies and Fe²⁺ ions. This effect causes a change in susceptibility and will lead to the stabilization of magnetization (the ΔT effect of Tivey & Johnson 1981) as the diffusion causes a deepening with time of potential wells within which the domain walls lie.

Disaccomodation and the diffusion aftereffect are competing processes (Moskowitz 1985). Disaccomodation deepens potential wells with time, inhibiting wall displacement, while the diffusion aftereffect produces more wall displacements with time.

Viscous acquisition coefficient, S

The viscous acquisition coefficient S is defined by the following equation:

$$J_{\rm vrm}(t) = S\log t,\tag{5}$$

where $J_{\rm vrm}(t)$ is the magnetization after time *t* and *S* is the viscous acquisition coefficient. This definition assumes that there is a logarithmic relationship between VRM acquired and time of acquisition. However, Dunlop (1983) points out that non-logarithmic VRM acquisition is common among the many experimental studies of VRM.

Previous experiments on the grain size dependence of VRM

A variety of studies have been published which have produced conflicting evidence for the acquisition of VRM in MD titanomagnetites.

Some studies show a significantly higher viscosity in SD material compared with MD. For example, a study of artificial magnetites and natural soils by Mullins & Tite (1973) showed that MD VRM is two orders of magnitude weaker than SD VRM in these materials. Dunn & Fuller (1972) described VRM in lunar materials, and noted that a rock containing SP and SD grains had high viscosity while a crystalline rock containing mostly MD iron had negligible viscosity. Dunlop (1983) measured VRM acquisition in 0.04–100 μ m magnetites at room temperature and at elevated temperature for the SD grains. He found that substantial room-temperature VRM is acquired in PSD magnetite, but that 100 μ m magnetite gives a significantly lower value of *S*.

In contrast, other studies show similar viscosity coefficients for SD and MD material. For example, Tivey & Johnson (1984) characterized VRM acquisition and decay in pure magnetite and determined that both submicron SD grains and MD grains of ~45 μ m can acquire substantial VRM at room temperature and in fields up to 100 μ T over short, laboratory timescales. Sporer (1984) studied VRM in MD titanomagnetite (Fe_{3-x}Ti_xO₄) with varying titanium content *x* (0 < *x* < 0.72) with grain sizes from 20 to 200 μ m. All of his experiments were undertaken with an initial AF demagnetized state, and VRM was acquired at room temperature and liquid nitrogen temperature. His data shows the viscosity coefficient *S* increasing by a factor of 10 as the titanium content increases from *x* = 0 up to 0.6.

The conflict between these studies may be a result of the use of samples with different histories. Tivey & Johnson (1984) and Dunlop (1983) used synthetic samples that had been ball-milled from much larger single crystals, which will have introduced defects and local wall-pinning centres. Sporer's (1984) samples are described as polycrystalline titanomagnetite. So far, there are no reliable experimental studies on unstressed or relatively defect-free titanomagnetites which would be more representative of natural titanomagnetites in rocks. Finally, as Dunlop (1983) has pointed out, 115

it is difficult to know whether observed VRM effects in synthetic material are inherent or due to contamination by a minute fraction of very fine and very viscous particles.

Laboratory experiments, which necessarily take place over a limited timescale, can only activate a narrow range of SD grain sizes or MD pinning characteristics, and the results from such experiments cannot necessarily be extrapolated to acquisition processes on natural timescales taking place over thousands of years.

Measurements of VRM acquisition on natural breccia deposits of known age therefore provide a very valuable test of theories of VRM acquisition over natural timescales and in natural uncrushed magnetic materials in SD and MD domain state.

Contribution of new data to theory

Our new data of acquisition of VRM in natural magnetite and titanomagnetite demonstrates that \sim TM55 in our samples does *not* acquire any significant VRM over timescales of 2.5 to >65 ka, while it can and does acquire low-temperature pTRM at 100–150 °C over laboratory timescales.

Samples RRP19-1 and RRP19-6 provide good examples where laboratory unblocking temperatures exist that should record VRM if it were acquired by thermofluctuations which follow time–temperature relationships predicted for SD ~TM55 shown in the nomogram of Fig. 8. The breccia at this site was deposited 5 ka BP, so it would be expected to have a VRM in the population of grains that demagnetized by 110 °C in a laboratory experiment. In sample RRP19-1, 15 per cent of the remanence demagnetizes by heating to 60 °C, 29 per cent by heating to 90 °C, but there is *no* VRM in the PEF direction. Sample RRP19-6 contains 9 per cent remanence with T_{ub} less than 60 °C, 19 per cent with T_{ub} less than 90 °C and again there is no evidence of VRM. This laboratory evidence thus suggests that the ~TM55 is not in an SD state, but is MD.

There are several lines of evidence that point to our \sim TM55 being in an MD state. A wavelength-dispersive microprobe analysis, which can directly analyse for oxygen, demonstrates that there are many large >20 µm titanomagnetite grains with *x* approximately equal to 0.55. There is no evidence of microscale exsolution and consequent subdivision of grains into smaller magnetic units.

At ambient temperatures, if VRM in MD grains proceeds by thermal activation between local energy minima states and a reorganization of the whole domain structure is required, then the energy barriers between LEM states are too great to be surmounted by the kinetic energy available, even on timescales up to the age of the Earth (Dunlop *et al.* 1994). This would mean that MD material should not acquire VRM, if reorganization of the whole domain structure is required. MD material could acquire VRM if segments of domain walls can be activated, thus changing the remanence of the material, without altering the overall domain configuration.

A complete absence of VRM acquisition in MD material has not been reported in any of the laboratory experiments described above. However, all of the reported laboratory VRM experiments on MD material have been carried out using material that has been crushed from very large crystals, and there is a real possibility that all of this material has been contaminated by very fine magnetic grains adhering to the large grain surfaces. Dunlop & Özdemir (1997) called for viscosity measurements on synthetic material grown to the required size by modern techniques such as hydrothermal recrystallization (Heider & Bryndzia 1987).

Our results, using the natural laboratory of breccias exposed to the Earth's field for thousands of years, demonstrate that MD \sim TM55

does not acquire VRM, at least in the present circumstances. In this material, there is evidently no mode of remagnetization available for VRM acquisition other than thermal activation between LEM states, and there is insufficient kinetic energy available at 20 °C to effect this activation. This is the first demonstration of this effect.

The processes of disaccomodation and diffusion aftereffect may not operate in this type of situation. Both processes are diffusioncontrolled, and the diffusion rate will decrease exponentially with time. Our material was probably incorporated into the Ruapehu ring plain deposits thousands of years after the initial cooling and magnetization of the lava. All diffusional effects must have gone to completion before the material was moved and exposed to the Earth's field in a new direction.

CONCLUSIONS

(1) Natural rock samples that contain titanomagnetites with compositions in the range x = 0.44-0.65 (\sim TM55) have been demonstrated to *not* acquire VRM during exposure to the Earth's magnetic field for time periods of 2.5 to >65 ka.

(2) This \sim TM55 is in a multidomain state and is close to being stoichiometric.

(3) Thermofluctuational magnetic transitions in MD \sim TM55 thus seem to progress by complete domain reorganization of the whole grain, rather than by small segments of domain walls undergoing Barkhausen jumps in position. The latter scenario would give rise to MD VRM.

(4) This evidence that isothermal magnetization change in MD grains proceeds by whole-grain domain reorganization fits with the predictions of McClelland & Sugiura (1987) and McClelland *et al.* (1996) that acquisition of TRM in multidomain material is controlled by incremental changes in the whole-domain structure.

(5) The magnetite in our natural materials is not in a simple SD state, and cannot be used to test thermofluctuational theory in SD magnetite.

ACKNOWLEDGMENTS

Field sampling and laboratory analysis was carried out with the support of ROPA grant ROPA/96/98(GR3/R138). Dr Kate Hobson is thanked for field assistance. Dr Jan Alexander is thanked for logistical assistance during some of the writing of this paper.

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