

Cooling behaviour of partial thermoremanences induced in multidomain magnetite

Adrian R. Muxworthy*

Department of Earth Sciences, University of Oxford, Oxford, UK

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Abstract

The cooling behaviour of partial thermoremanences (pTRMs) below the acquisition temperature (T_2) is reported for the first time for well defined, sized, synthetic multidomain magnetite samples produced by hydrothermal recrystallisation. The pTRM cooling behaviour of low-stress magnetite samples is similar but not identical to that reported for higher stress crushed magnetite samples, that is, it displays a decrease in pTRM on cooling below T_2 , indicating domain re-organisation. This agrees with recent kinetic theories and domain observations, but strongly disagrees with the classical hysteretic models based on Néel's ideas which assume that the remanence increases with the increase in spontaneous magnetisation. It is demonstrated that the rate of decrease in remanence on cooling is not a viscous effect, and the rate of decrease increases with inducing field dependency. pTRM acquired from the Curie temperature T_c (pTRM $_{T_c}^{T_c}$) is found to be more stable to cooling than pTRM acquired from a temperature T_1 which is less than T_c (pTRM $_{T_2}^{T_1}$). It is suggested that for low-stress samples, pTRM acquired at high temperatures has a wider range of metastable stable states available than pTRM acquired at lower temperatures. The results support the theories that domain wall nucleation is relatively easy during cooling. Differences between the cooling behaviour of the low-stress samples and those previously published for crushed magnetite samples can be attributed to differences in the dislocation densities and the available metastable domain states. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

A thermoremanence acquired between the Curie temperature (T_c) and room temperature (rtp) is referred to as a TRM, whilst thermoremanence acquired over any other temperature range as a

partial thermoremanence or pTRM. According to 'classical' hysteretic multidomain (MD) thermoremanence models [1,2], during pTRM acquisition domain walls either block at some temperature T_b or will re-equilibrate to a remanence carrying or demagnetised state when the field is removed at a temperature T_2 , where $T_2 \leq T_b$. On cooling below T_2 it is assumed that pTRM will vary as the ratio of $M_s(T)/M_s(T_2)$ denoted by $m_s(T)$, where M_s is the spontaneous magnetisation and T the temperature. Because $M_s(T)$ increases with decreasing temperature [3], $m_s(T) \geq 1$ for all $T \leq T_2$, and so

* Present address: Institut für Geophysik, Universität München, Theresienstr. 41, 80333 Munich, Germany. Tel.: +49-89-2394-4325; Fax: +49-89-2394-4205; E-mail: adrian@geophysik.uni-muenchen.de

by classical theory, the ratio $p\text{TRM}/m_s(T)$ is constant on cooling below T_2 , however $p\text{TRM}/m_s(T)$ has been found experimentally to decrease on cooling below T_2 for MD magnetite [4–8]. Similar results have been found for cooling of isothermal remanences (IRMs) induced at 240°C in MD magnetite [9]. This decrease in the remanence on cooling indicates that domain re-organisation occurs, which violates the idea of a ‘blocked’ domain structure fundamental to the classical model. It should be noted that viscous decay [10] is not the cause of this decrease in either $p\text{TRM}$ or IRM, because no change is observed if the samples are held at a constant temperature for the same length of time [6,9].

In addition to measurement of $p\text{TRM}$ below T_2 , direct observations of domain structure in MD magnetite using optical techniques have found a temperature dependence of domain structure which disagrees with classical domain models [11–13]. The domain structures of synthetic crystals produced by hydrothermal recrystallisation were found to be highly temperature dependent at low temperatures ($< 100^\circ\text{C}$) violating Néel’s theories [11,12]. In natural crystals the number of domains was found to be relatively constant until 400°C, but gradually decreased on warming to 555°C [13]. Domain structures during TRM acquisition have also been observed, though not for magnetite due to its high T_c . Metcalf and Fuller [14,15] found that on cooling small, MD grains of $\text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$ from T_c in the earth’s field, the number of domains increased with decreasing temperature. In contrast, Halgedahl [16] observed for $\text{Al}_{0.1}\text{Mg}_{0.1}\text{Fe}_{2.2}\text{Ti}_{0.6}\text{O}_4$ grains that during cooling the domain structure denucleated domain walls. There is clearly an unresolved contradiction between the observations of Metcalf and Fuller [14,15] and Halgedahl [16], however this may be due to problems with domain wall visibility at high temperatures using the Bitter pattern method. Halgedahl [16] noted that domain walls often become visible during cooling, not due to nucleation, but simply due to the collection of more colloidal particles around domain walls due to increases in M_s , a possible reduction in wall width and a reduction in the thermal randomisation of the colloidal particles. The small Al and Mg con-

tent in Halgedahl’s samples reduced T_c from 150°C for $\text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$ to 75°C, which improved domain wall visibility near T_c , by reducing thermal randomisation processes. Whether or not nucleations or denucleations occur during cooling is still unclear, however, there is strong observational evidence, especially from the work of Halgedahl [16], that disagrees with Néel’s domain wall pinning theory for TRM acquisition. It is worth noting that it is incorrect to directly apply the results from the titanomagnetite studies, to magnetite, because of the greater importance of magnetostriction in titanomagnetite domain structure. Yet some of the TRM results from titanomagnetite, if correctly, considered can yield important information about the nature of TRM acquisition in magnetite [17].

Recent models of this $p\text{TRM}$ cooling behaviour have been less than comprehensive. Incorporating the temperature dependent domain wall nucleation ideas of Moon and Merrill [18,19], kinematic models have been developed to explain thermoremanence acquisition and its behaviour on cooling below T_2 [6,20]. McClelland and Sugiura [6] assumed that domain walls can be regarded as a statistical ensemble, with each element of the ensemble being in one of two possible states: demagnetised or TRM state. During cooling, the domain walls jump randomly between the two states, however in zero field the demagnetised state is preferred whilst in a field the TRM state is preferred. During TRM acquisition the net contribution from the statistical ensemble is a magnetised state, whilst on cooling below T_2 the net magnetisation demagnetises giving rise to the observed behaviour. Shcherbakov et al. [20] developed this theory by considering a theoretical micromagnetic approach, i.e. in effect they replaced the statistical ensemble of domain walls used by McClelland and Sugiura [6], with a statistical ensemble of dipole moments. Unfortunately the model of Shcherbakov et al. [20] makes some simplifications which rather invalidate the model; most importantly the model did not calculate the inter-cellular interaction effect. However, the model does predict a decrease in thermoremanence after cooling in zero field below T_2 , allows for the possibility of the irreversibility of $p\text{TRM}$

on heating and cooling, and shows the importance of thermal prehistory on remanence acquisition [21].

Attempts to model TRM acquisition using three-dimensional micromagnetic modelling have been limited to SD and vortex structures [22], and have found that nucleation and denucleation between these states only occur at high temperatures. However, the behaviour of these simple domain structures is thought not to be analogous to the behaviour of the larger MD grains [23], rendering comparisons between the model results for SD and vortex structures and the behaviour of larger MD grains speculative.

Clearly there are still unresolved problems in the field of TRM acquisition and the behaviour of pTRM. It is important to understand the mechanisms controlling MD TRM acquisition if, for example, we wish to improve palaeointensity determinations. Previous measurements of pTRM cooling below T_2 have been measured on annealed synthetic samples of unknown preparation [5], crushed, sized, natural magnetites [6] and peridotite samples with a near magnetite phase displaying MD characteristics [7]. In this paper, for the first time, the results of cooling pTRM induced in well defined, sized, synthetic MD magnetite samples produced by hydrothermal recrystallisation are reported. Hydrothermal crystals have lower dislocation densities than synthetic samples produced by crushing or by the crystals grown by the glass ceramic method [24], and their magnetic behaviour is closer to that predicted by theoretical models for ‘ideal’ crystals [23]. This makes them perfect for studying fundamental magnetic effects. The effects on cooling behaviour of variations in pTRM inducing field and grain size are investigated.

2. Sample description and experimental methods

The four synthetic sample sets ($H(7.5 \mu\text{m})$ – $H(76 \mu\text{m})$) considered in this study were made by hydrothermal recrystallisation [25]. Grain size distributions and magnetic parameters of the samples are summarised in Table 1. XRD analysis and Mössbauer spectroscopy confirmed that the

Table 1

Summary of mean grain size, standard deviation σ , and hysteresis parameters H_c , H_{cr} (remanent coercive force) and the ratio of M_{rs} to M_s at rtp, for the samples considered in this study

Sample name	Size (μm)	$\pm \sigma$ (μm)	H_c (mT)	H_{cr} (mT)	M_{rs}/M_s
$H(7.5 \mu\text{m})$	7.5	3.0	2.4	18.4	0.018
$H(39 \mu\text{m})$	39	9	1.5	24.7	0.010
$H(59 \mu\text{m})$	59	16	1.36	15.8	0.008
$H(76 \mu\text{m})$	76	25	0.96	19.9	0.006

samples were pure magnetite [26]. The samples have slightly wider grain distributions than the hydrothermal crystals prepared by Heider and Bryndzia [25]. The hydrothermal samples have low values for coercive force (H_c) and low saturation remanence to (M_{rs}) to saturation magnetisation (M_s) ratios suggesting that they have low dislocation densities, in agreement with previous studies [24]. The samples were dispersed (2–3% magnetite) in lightly pressed KBr pellets. Several pellets from each grain size range were prepared.

Thermomagnetic cooling curves were measured using a Princeton Measurements μ -VSM (Vibrating Sample Magnetometer). Two types of pTRM were induced in the samples; type 1 – samples are cooled from above T_c to T_2 in a field, where $\text{rtp} \leq T_2 < T_c$ ($T_c \downarrow T_2$, H=ON; pTRM $_{T_2}^{T_c}$). Type 2 – pTRM acquired by cooling from T_c to a temperature T_1 with the field switched off, and from T_1 to T_2 in a field, where $\text{rtp} < T_2 < T_1 < T_c$ ($T_c \downarrow T_1$, H=OFF; $T_1 \downarrow T_2$, H=ON; pTRM $_{T_2}^{T_1}$). In both cases below T_2 , the samples were cooled with the field switched off. The μ -VSM allowed the samples to be kept in an inert atmosphere of He during heating which reduced the possibility of oxidation. As an extra precaution against oxidation the pellets were coated in weak diamagnetic, high-temperature glue (Omega CC High Temperature Cement). Each sample was examined only once.

As the μ -VSM had no shielding from the earth’s magnetic field, it was necessary to induce the thermoremanences in fields greater than $\approx 42 \mu\text{T}$ to produce a ‘step-down’ in field when T_2 was reached. Most experimental evidence in the literature suggests that TRM intensity measured is

linear with applied field up to 200–400 μT [20,27,28]. Such a TRM is usually referred to as ‘weak-field’ TRM, while TRM induced in higher fields as ‘high-field’ TRM. A field of $\approx 200 \mu\text{T}$ would have been ideal for inducing pTRM, being ‘weak-field’ TRM and with a reasonable step-down in field at T_2 . Unfortunately, the low sensitivity of the $\mu\text{-VSM}$ meant that this was not possible. Initially an inducing field of 5 mT, that is, 5000 μT , was used, however, a few later samples were induced with pTRM in a field of 500 μT . TRM induced in fields as high as 5 mT is probably not analogous to thermoremanences induced in the earth’s field, and it is debatable that thermoremanences induced in 500 μT are analogous either, however, high-field thermoremanences are still of scientific interest, as they provide further contributions to thermoremanence theory even if the results are not directly applicable to naturally occurring thermoremanences. In fact most previous studies investigating the decrease in pTRM on cooling below T_2 have examined ‘high-field’ thermoremanences, i.e., $H > 400 \mu\text{T}$, e.g. Parry [4] and Sugiura [9] both used a field 1 mT, whilst McClelland and Sugiura [6] used a field of 0.84 mT. However the observed decrease is not a property confined to high-field thermoremanences, as Markov et al. [5], Sholpo et al. [7] and Shcherbakova et al. [8] have observed the same effect for an inducing field of 100 μT .

3. Results

3.1. Field dependence of pTRM decay on cooling below T_2

The pTRM inducing field in some of the experiments in this study was considerably higher than those used in all previous studies except for Markov et al. [5]. Because of this difference it was decided to examine the dependency of pTRM cooling behaviour on H . pTRMs acquired over the same temperature range, but with different inducing field (0.5 mT and 5 mT), are shown in Fig. 1 for type 1 and type 2 pTRM. As is standard in these types of diagrams, the increase in

the spontaneous magnetisation is compensated for.

The reported decrease in $\text{pTRM}/m_s(T)$ on cooling [5–7] is repeated here (Fig. 1). However the field dependency of behaviour is opposite to that reported by Markov et al. [5], who found that as H increased the observed demagnetisation in pTRM_{300}^{400} below T_2 decreased. In a similar experiment, Sugiura [9] measured the decrease of IRM on cooling from an acquisition temperature of 240°C. He also found that as the inducing field increased the relative demagnetisation of IRM decreased. However, the field dependency results from this study support the theories of McClelland and Sugiura [6] and Shcherbakov et al. [20], whilst those of Markov et al. [5] and Sugiura [9] disagree.

3.2. Viscous decay

To check that the decrease on cooling (Fig. 1) was not a viscous effect, $H(39 \mu\text{m})$ was induced with a $\text{pTRM}_{480}^{T_c}$ and held at 480°C for ≈ 30 min in zero field (earth’s field). The magnetisation was found to remain constant, confirming the theory that demagnetisation on cooling is truly temperature dependent. This corresponds to similar tests reported in the literature [6,9].

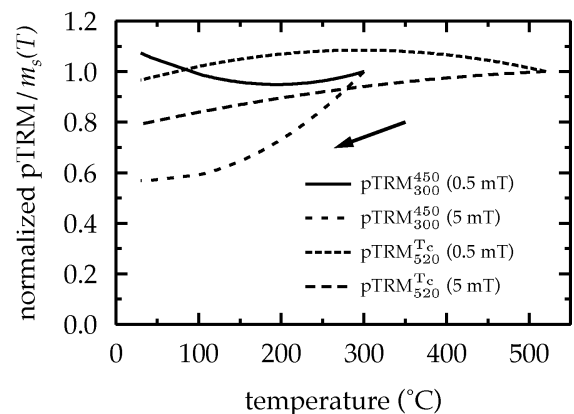


Fig. 1. Cooling behaviour of normalised type 1 ($\text{pTRM}_{520}^{T_c}/m_s(T)$) and type 2 ($\text{pTRM}_{300}^{450}/m_s(T)$) for hydrothermal sample $H(76 \mu\text{m})$, with variable inducing field. Measurement was made in the earth’s magnetic field.

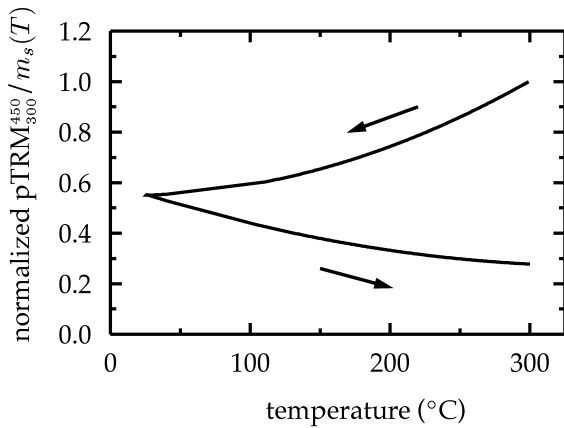


Fig. 2. Typical thermomagnetic curve depicted the irreversibility of pTRM to changes in heating/cooling direction. pTRM₃₀₀⁴⁵⁰ ($H=5$ mT) induced in hydrothermal magnetite sample $H(76 \mu\text{m})$. Measurement was made in the earth's magnetic field.

3.3. Test on irreversibility of thermoremanence

Both measurement of the magnetisation [6–8] and direct observation of the domain structure [11] find that cooling pTRM curves are irreversible to changes in the direction of heating/cooling below T_2 . A simple check for this phenomenon was done for a selection of samples (Fig. 2), where it is seen that hydrothermal recrystallised grains of magnetite behave in a similar manner as crushed grains of magnetite [6]. The size of the decay is similar to that reported by Shcherbakova et al. [8], for a natural sample induced with a pTRM₃₀₀⁴⁰⁰ in a field of 100 μT .

3.4. Effect of grain size and pTRM type

In this section, the dependency of pTRM cooling behaviour on grain size and pTRM type is investigated. For all experiments in this section a field of 5 mT was used to induce the pTRMs. The type 1 pTRM, i.e. pTRM _{T_2} ^{T_c} , was induced by cooling in field over the temperature range $T_c \rightarrow 520^\circ\text{C}$. The results are normalised and the temperature dependent behaviour of $m_s(T)$ compensated for (Fig. 3). It is seen in Fig. 3 that the

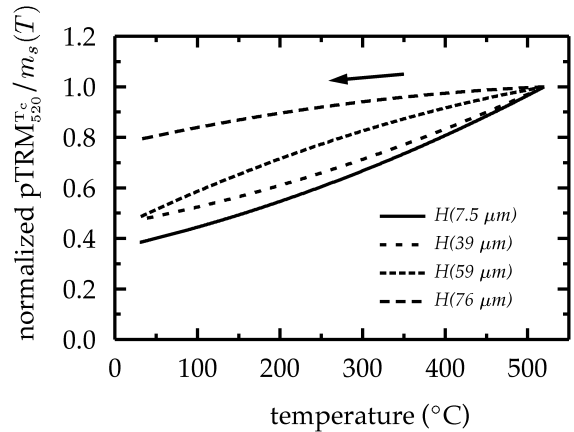


Fig. 3. Behaviour of normalised pTRM₅₂₀ ^{T_c} on cooling below 520°C in the earth's field. pTRM₅₂₀ ^{T_c} was induced in the hydrothermal samples $H(7.5 \mu\text{m})$, $H(39 \mu\text{m})$, $H(59 \mu\text{m})$ and $H(76 \mu\text{m})$ using a field of 5 mT. Measurement was made in the earth's magnetic field.

demagnetisation observed on cooling pTRM₅₂₀ ^{T_c} decreases with increasing grain size.

Two type 2 pTRMs, i.e. pTRM _{T_2} ^{T_1} , were induced by cooling the samples over the temperature ranges $550^\circ\text{C} \rightarrow 450^\circ\text{C}$ and $450^\circ\text{C} \rightarrow 300^\circ\text{C}$, having previously been cooled from T_c in the earth's field.

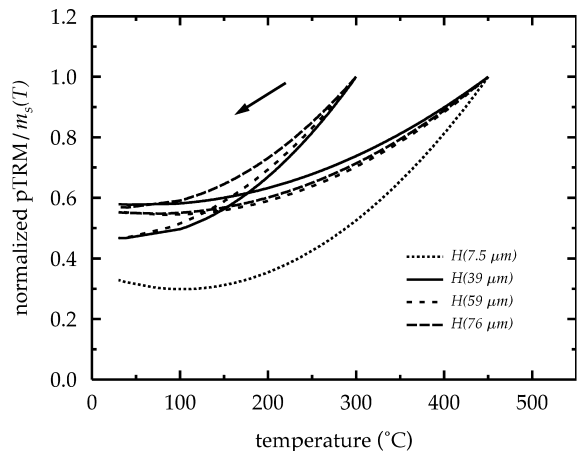


Fig. 4. Change of normalised pTRM/ $m_s(T)$ on cooling in the earth's field for two different pTRM _{T_2} ^{T_1} induced in hydrothermal samples using a field of 5 mT; pTRM₃₀₀⁴⁵⁰ induced in samples $H(7.5 \mu\text{m})$, $H(39 \mu\text{m})$, $H(59 \mu\text{m})$ and $H(76 \mu\text{m})$, and pTRM₃₀₀⁴⁵⁰ induced in samples $H(39 \mu\text{m})$, $H(59 \mu\text{m})$ and $H(76 \mu\text{m})$. Measurement was made in the earth's magnetic field.

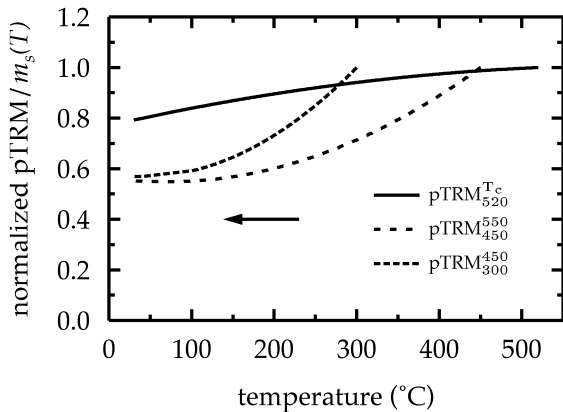


Fig. 5. Change of normalised pTRM/ $m_s(T)$ on cooling below T_2 in the earth's field for sample $H(76 \mu\text{m})$ induced with type 1 pTRM ($\text{pTRM}_{520}^{T_c}$) and type 2 pTRM (pTRM_{450}^{550} and pTRM_{300}^{450}). An inducing field of 5 mT was used. Measurement was made in the earth's magnetic field.

For type 2 pTRM (Fig. 4), it is seen that the demagnetisation during cooling pTRM $_{300}^{450}$ below 300°C and pTRM $_{450}^{550}$ on cooling below 450°C are both relatively independent of grain size. Only pTRM $_{450}^{550}$ induced in sample $H(7.5 \mu\text{m})$ (Fig. 4) displays a grain size dependency, and unfortunately no cooling behaviour was measured for sample $H(7.5 \mu\text{m})$ induced with pTRM $_{300}^{450}$. The rate of demagnetisation on cooling below T_2 is greater for pTRM $_{300}^{450}$ than for pTRM $_{450}^{550}$, but the amount of decay from T_2 to 20°C is similar.

Fig. 5 depicts both type 1 and type 2 pTRM for the $H(76 \mu\text{m})$ sample. Type 2 pTRM, i.e. pTRM $_{450}^{550}$ and pTRM $_{300}^{450}$, decrease more rapidly than type 1 pTRM, i.e. pTRM $_{520}^{T_c}$. This suggests that type 2 pTRM domain structures are more susceptible to domain reconfigurations during cooling below T_2 , i.e., they are less stable than type 1 pTRM.

4. Discussion

4.1. Field dependence of pTRM decay

The field dependency of behaviour depicted in Fig. 1 is opposite to that reported by Markov et

al. [5]. There is no clear reason for the disagreement, however there are a few possible contributory causes which may account for it. Firstly, the samples in this study were relatively stress-free stoichiometric magnetites, whilst Markov et al. [5] used synthetic magnetites (300–400 μm) of unknown origin. Secondly, the temperature range over which the pTRMs were acquired was different; in this study pTRM was acquired over the range T_c –520°C for type 1 pTRM and 450–300°C for type 2 pTRM, whereas Markov et al. [5] induced their pTRM (type 2 only) over the temperature range 400–300°C. However it is unlikely that pTRMs acquired over 450–300°C and 400–300°C should vary significantly in their response to applied field. Lastly, differences in initial domain state could play a significant role. In this study for type 2 pTRM, the samples were cooled from T_c in zero field (in fact the earth's field). This domain state is commonly referred to as the absolute zero state (AZS) [20]. The experiments of Markov et al. [5] were carried out before the importance of thermal history had been truly clarified [21]. Because of this Markov et al. [5] have not commented on the thermal histories of their samples, only that they were induced with pTRM $_{300}^{400}$. It is unknown if differences in thermal histories affect the field dependency of pTRM cooling behaviour. It should be noted in support of the results of Markov et al. [5], however, that the similar field dependency behaviour observed by Sugiura [9], was for IRMs induced in AZS MD grains.

It was noted above that the pTRM $_{300}^{450}$ was not induced in hydrothermal samples in a true AZS, because they had been cooled from T_c in the earth's field. However, pTRM $_{520}^{T_c}$ displayed a similar field dependency (Fig. 1) as pTRM $_{300}^{450}$ which suggests that the error in the AZS of pTRM $_{300}^{450}$ was not significant.

4.2. Effect of grain size and pTRM type

On cooling type 1 pTRM, the observed demagnetisation (Fig. 3) decreases with increasing grain size, in contrast to previous experimental observations which found an increase [6,9]. However there are differences in the detail; in this study

thermoremanences were induced in a larger field ($H=5$ mT) than either McClelland and Sugiura ([6], $H=0.84$ mT) or Sugiura ([9], $H=1$ mT). Secondly McClelland and Sugiura [6] and Sugiura [9] both used crushed magnetites, whereas the samples in this study were relatively stress-free.

It is suggested here, that the increased inducing field can partially explain the discrepancy between the literature and the results in this study. The larger inducing field would be expected to form domain configurations with fewer domains than those induced in the smaller field by McClelland and Sugiura [6]. On switching off the field at T_2 , the domain structure of MD grains partially reverses, the ‘reversible induced moment’ (RIM) of McClelland and Sugiura [6], i.e. the high self-demagnetising energy causes unblocked domain walls to demagnetise until pinned on a dislocation. Because hydrothermal crystals have lower internal stresses and less pinning sites than crushed crystals, hydrothermal samples are expected to have larger RIM than the crushed rocks of McClelland and Sugiura [6]. In this study over 90% of the moment was reversible on switching off the 5 mT field (Table 2), compared to McClelland and Sugiura [6] who found RIM values in their crushed samples in the range 50–95% depending on the selected pTRM temperature range for an inducing field of 0.84 mT. As the inducing field in this study was higher than that used by McClelland and Sugiura [6] it is difficult to draw direct comparisons.

As expected the size of the RIM was dependent on the inducing field (Table 2). The smaller crystals, e.g. $H(7.5 \mu\text{m})$, have smaller RIM than the larger crystals, e.g. $H(76 \mu\text{m})$ (Table 2), in agreement with the results of McClelland and Sugiura

[6]. There are two reasons for this; firstly the smaller grains have fewer domain walls to reverse, and secondly there is a relatively larger interaction between the domain walls and the crystals surfaces. It is even possible that small crystals are in a SD-like state after cooling from T_c in a field of 5 mT [28,29]. On cooling below T_2 , the smaller crystals are expected to be in relatively unstable high-magnetisation states, making them susceptible to domain reconfigurations. Due to the low number of domains, nucleation of even one wall contributes significantly to the domain structure. In larger grains with many more domains, the nucleation of one or two walls is less significant. On removal of the field at T_2 , the crushed samples of McClelland and Sugiura [6] have larger remanence per grain than hydrothermal crystals, because of the increased pinning site density, i.e., domain walls are trapped in states further from the demagnetised state. The demagnetisation process which occurs on cooling is expected to increase as the self-demagnetising energy domain structure increases, i.e. the process is more pronounced in crushed grains than for hydrothermal grains. Increased dislocation density aids the ability of domain walls to nucleate/denucleate [23].

Type 2 pTRM is relatively independent of grain size (Fig. 4), unlike type 1 pTRM which displays a strong grain size dependency (Fig. 3). This may reflect a narrower range of possible domain configurations open to type 2 pTRM.

In comparing type 1 and type 2 pTRM (Fig. 5), it is immediately obvious that type 1 pTRM is more stable on cooling than type 2. This is in disagreement with McClelland and Sugiura [6], but in agreement with Sholpo et al. [7]. This difference may be due to the nature of the samples, as the former used crushed samples, whereas the later used natural samples.

A pTRM acquired at a higher temperature range, i.e. $\text{pTRM}_{T_2}^{T_c}$, will form domain structures with higher self-demagnetising energies than a pTRM acquired at lower temperatures. It is postulated, that increases in the dislocation density will also cause domain structures with higher self-demagnetising energies to be formed, i.e., grains with high dislocation densities are expected to have less domains. This is supported by do-

Table 2
RIM for $\text{pTRM}_{520}^{T_c}$ for different applied fields, as a percentage of the total magnetic moment at 520°C

Sample	Field (mT)	RIM (%)
$H(7.5 \mu\text{m})$	5	91.7
$H(39 \mu\text{m})$	5	96.9
$H(59 \mu\text{m})$	5	97.5
$H(76 \mu\text{m})$	5	97.6
$H(76 \mu\text{m})$	0.5	93.3

main observations, on two sets of natural magnetites, where it was found that the samples displaying higher coercivity of remanence (often considered to be related to internal stress) also displayed on average less domains at higher temperatures [13]. Therefore a pTRM acquired in a crushed grain at high temperatures is expected to have less domains and consequently a very high self-demagnetising energy. During cooling domain structures with higher self-demagnetising energies are more likely to be demagnetised. Assuming that the results from micromagnetic calculations for pseudo-single domain grains are applicable to larger grains, then it is postulated that for MD grains the number of accessible metastable LEM structures decreases with temperature [30], even though the number of metastable LEM states increases [31]. Samples with low internal stress will have on average a smaller remanence per grain, however, as the energy barriers between the various LEM states are likely to be smaller on average than in stressed samples the domain configuration will have a wider range of available metastable LEM states. In low-stress samples with smaller self-demagnetising energies, LEM structures acquired at high temperatures are relatively stable to the self-demagnetising energy. Consequently pTRM acquired in low-stress samples is more stable if acquired at higher temperatures. Unstable domain structure will display the largest demagnetisation on cooling, i.e., $\text{pTRM}_{T_2}^{T_c}$ is less stable than $\text{pTRM}_{T_2}^{T_1}$ for crushed samples, and vice versa for natural and hydrothermal samples.

4.3. Implications of high inducing and residual field

The inducing field and residual field used in this paper were higher than those used in previous studies. Here the implications of these high fields are discussed.

The two inducing fields used (i.e., 0.5 mT and 5 mT) are both thought to have produced 'high-field' thermoremanences, i.e. where the TRM acquisition no longer displays a linear relationship with inducing field intensity. The 0.5 mT inducing field is believed to be just above the break in linear behaviour (0.2–0.4 mT) [28]. It is likely

that high-field thermoremanences are relatively less stable than weak-field thermoremanences, however, once a wall is pinned or blocked, according to Néel [1] the energy barrier will increase on cooling and the wall will remain blocked, regardless of whether the initial remanence is high- or weak-field thermoremanence or of some other origin, e.g. isothermoremanence, that is, the remanence should increase as M_s on cooling. The behaviour of high-field remanences in this study disagrees with the theory of Néel [1]. On comparison to previous studies, the 5 mT inducing field was a little higher than those used in other studies, but the 0.5 mT field was less than that used in several previous high-field thermoremanence studies [4,6,9]. All high-field pTRMs displayed a similar decrease in magnetisation on cooling. This effect has also been observed for weak-field pTRM [5,7,8]. It appears, therefore, that the cooling behaviour is independent of the type of inducing field whether it is low- or high-field thermoremanence. However, whether results from high-field thermoremanences are directly applicable to low-field thermoremanence studies is debatable, but the implications and interpretations still have relevance to natural thermoremanence studies.

As the measurements were made in the earth's field, and not in an absolute zero field as is desired, then this leads to the question: is it possible that the high-'zero field' approximation is the cause of demagnetisation on cooling below T_2 and that it is not a genuine MD effect independent of field? There are several arguments which suggest that the behaviour is an MD effect. Firstly, on switching off the inducing field, the field is stepped down from 5 mT to the earth's field orientated in a different direction. Domain walls which pin at this temperature are pinning in the presence of the earth's magnetic field. So as the earth's magnetic field is constant during cooling, the energy barriers and conditions due to the residual field should not change. This effectively reduces or increases the energy barriers compared to an ideal zero field situation, but does not change the energy barrier's behaviour on cooling. On cooling the energy, barriers should increase in an identical manner to that of the ideal zero field case, and the behaviour should be the

same, i.e. it is the step-down in field which is important.

Another argument in support of the idea that it is genuine MD effect is found by considering the viscous magnetisation experiment discussed above (Section 3.2). If the earth's field was the cause of the demagnetisation, then the effect of the earth's field would be greater at higher temperatures. However, when the temperature was held constant as 480°C, as discussed previously, the magnetisation was found to remain constant. This suggests that the earth's magnetic field did not cause significant demagnetisation of the remanence and that the decrease in magnetisation is a genuine MD temperature effect. Lastly, the same decrease on cooling has been seen in previous studies where the residual field was lower, suggesting that the earth's field was not the cause of the demagnetisation. In the limited number of previous studies of this type, the 'zero field' approximation was usually less than $\approx 10 \mu\text{T}$ [4–8].

However, it is also necessary to consider the induced moment due to the earth's magnetic field, i.e., the RIM in the earth's field. Unfortunately this was not directly measured as a function of temperature in this study. However, McClelland and Sugiura [6] did measure it as a function of temperature for a field of 0.84 mT. They found that it decreased with temperature, but not as rapidly as the decrease in pTRM due to cooling. Importantly they found that RIM and the remanence were effectively independent of each other. If the RIM due to the earth's magnetic field in this study was significant, then its effects would have been observed in two experiments. As the RIM due to the earth's field is proportionally larger in pTRM induced in a field of 0.5 mT compared to a field of 5.0 mT, then if the cooling behaviour of the RIM was the cause of the observed cooling decrease in magnetic moment, its effect would have been greater in the experiment where the sample was induced in a field of 0.5 mT and not 5.0 mT. However, in Fig. 1 it is seen that the 5 mT curves decrease more rapidly, suggesting that a RIM contribution is not significant to the behaviour. Secondly, as McClelland and Sugiura [6] found that RIM increased slowly with temperature up to $\approx 520^\circ\text{C}$, then if the RIM contribu-

tion was the cause of the cooling behaviour, then in Fig. 2 the warming curve would be expected to increase and not decrease as was observed. It would appear, therefore, that the MD effect was genuine, however, it should also be realised that the behaviour of RIM may also have contributed slightly to the observed behaviour, however this is also true for all other studies where there was a residual field.

5. Conclusions

The results presented in this paper agree with those previously published, in that they show a decrease in pTRM/ m_s on cooling below T_2 , indicating domain re-organisation. This agrees with the kinetic theories [6,20] and domain observations [11,12], and strongly disagrees with the classical hysteretic models [1,2] which assume that the domain structure is 'blocked'.

There are several fundamental points which arise from the results in this study; firstly that the dependency of inducing field on pTRM cooling behaviour agrees with the theory [6,20] in contrast to previous reports [5], secondly pTRM $_{T_2}^{T_c}$ appears to be more stable for 'low-stress' samples than pTRM $_{T_2}^{T_1}$ on cooling below T_2 , and thirdly the level of internal stress is thought to strongly effect the cooling behaviour of pTRM.

The results support the theories of McClelland and Sugiura [6] and Shcherbakov et al. [20], which are, however, too abstract to be quantitative. These theories do not incorporate variations in dislocation density, which is the probable cause for the difference between the results of this study and those of McClelland and Sugiura [6]. McClelland and Sugiura [6] and Shcherbakov et al. [20] suggest that domain wall nucleation is a relatively easy process, but it has been suggested elsewhere that it is not [17,23]. However, the arguments against easy domain wall nucleation in magnetite seem flawed. For example, Dunlop and Özdemir [23] applied the results of Halgedahl [16] to magnetite. Halgedahl [16] explained the behaviour of TRM acquisition in $\text{Al}_{0.1}\text{Mg}_{0.1}\text{Fe}_{2.2}\text{Ti}_{0.6}\text{O}_4$ by suggesting that domain nucleation is relatively difficult during cooling,

i.e., nucleation failure is more common. However, it is inappropriate to directly apply the results for $\text{Al}_{0.1}\text{Mg}_{0.1}\text{Fe}_{2.2}\text{Ti}_{0.6}\text{O}_4$ to magnetite due to the relative importance of the magnetostriction in Ti-rich minerals. From the results in this study, it appears that nucleation is relatively easy, with increased dislocation density facilitating domain wall nucleation in larger grains.

The results in this paper also support the postulation by Heider [12] that the demagnetisation processes on cooling are continuous rather than discrete as suggested by the simplified model of McClelland and Sugiura [6].

It is planned in a future study to investigate the effect of stress on this phenomenon in more detail, using a suite of samples where the degree of internal stress is more readily controlled, and the residual field is significantly lower.

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