Experimental procedure to detect multidomain remanence during Thellier–Thellier experiments

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Abstract

Reliability checks in Thellier-type experiments usually focus on the detection of chemical alteration of the magnetic mineral component or the formation of new magnetic phases during the heating process. However, a major problem in Thellier-type experiments is the presence of multidomain (MD) particles which can lead either to complete failure of palaeointensity determinations or to serious misinterpretation.

We present a modification of the Thellier–Thellier experiment that detects the presence of MD particles by verifying the law of additivity of pTRMs. The law of additivity is valid for regular pTRMs (i.e. the upper temperature of pTRM acquisition is reached by cooling from the Curie temperature) for both SD and MD particles, whereas it is not valid for pTRM* (the upper temperature of pTRM acquisition is reached by heating from room temperature) in the case of MD particles. As the partial thermoremanences imparted in Thellier–Thellier experiments are of the pTRM* type, additivity as a prerequisite for the validity of the obtained result is not given if the remanence is carried predominantly by MD particles.

The proposed method is applied to seven synthetic samples covering a grain size range of 23 nm to 12.1 μm. The obtained palaeointensity estimates show a significant error for all samples with grain sizes >0.7 μm due to the failure of the law of additivity. Our experiment is able to detect this failure.
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1. Introduction

Absolute palaeointensity estimates determined on rocks carrying a thermoremanent magnetisation (TRM) are vital for the reconstruction of the ancient geomagnetic field and, by implication, the state of the geodynamo in the geological past. Among the many proposed experimental procedures the Thellier and Thellier (1959) method and its modifications proved to be the most successful. This method relies on a set of basic assumptions known as Thellier's laws. Main causes of violation of these laws are chemical alteration, which can be detected by pTRM checks introduced by Coe (1967), and thermoremanence carried by multidomain (MD) particles. For the reliability of the obtained results it is of crucial importance to assess the influence of these two effects.

MD remanence, causing a difference between blocking and unblocking temperatures (T_b and T_{ub}, respectively) and thus an MD tail (Shashkanov and Metallova, 1972), invalidates Thellier–Thellier experiments if $T_b > T_{ub}$. In this case, linearity of the NRM-TRM plot is destroyed (Fabian, 2001). As Shcherbakov et al. (1993) pointed out, MD pTRM is also dependent on the thermal prehistory of the sample. One of the main consequences is that the law of additivity in the case of MD particles is in fact valid for the regular pTRM, i.e. the maximum temperature of pTRM acquisition is reached by cooling the sample from its Curie temperature T_C in zero field. The pTRM used in Thellier–Thellier experiments, however, is of the pTRM* type, i.e. the maximum temperature of pTRM acquisition is always reached by heating the sample from room temperature and the sample is never heated beyond that temperature. Shcherbakov et al. (1993) showed that additivity does not hold for pTRM* applied to MD samples. Thus, it should be possible to distinguish between MD and SD grains by checking the validity of the law of additivity of pTRM*.

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So far, determination of the domain state for the selection of suitable samples for Thellier–Thellier experiments relies usually on hysteresis measurements using the theoretical limits of H_{CR}/H_C and M_{RS}/M_S (Day et al., 1977). However, interpretation of these data is not straightforward, as natural samples often consist of mixtures of SD, MD or SP particles. Moreover, the results depend not only on domain state but also on factors like internal stress of the grains (Dunlop, 2002).

On the other hand, detection of MD remanence hitherto is pursued by measuring the tail of pTRMs. McClelland and Briden (1996) proposed to check for MD behaviour by introducing additional heating steps to the Thellier–Thellier experiment, i.e. the sample is demagnetised by heating to a temperature $T_i > T_0$ and cooling in zero field, then a $pTRM^*(T_i, T_0)$ is imparted followed by a demagnetisation of this $pTRM^*$ by heating the sample again to T_i and cooling in zero field. This test was subsequently used for a modified Thellier technique (MT3) by Leonhardt et al. (2000) to exclude samples dominated by MD particles and more recently by Riisager and Riisager (2001). However, although there is a MD tail resulting from $pTRM^*$ as well, it is nonetheless much smaller than the tail of a regular pTRM as was demonstrated by Shcherbakova et al. (2000).

Another domain state criterion based on the observation of a tail of a regular pTRM was proposed by Shcherbakov et al. (2001). The authors introduced the parameter A_a which is the tail of $pTRM(T_1, T_2)$ normalised to $pTRM(T_1, T_2)$ intensity. However, as they also pointed out, the disadvantage of this criterion is the need to heat the samples to T_C, potentially causing serious chemical alteration, in order to acquire a regular pTRM. Another drawback is the fact, that this test can only be performed on sister samples of the sample used for the Thellier–Thellier experiment, as the NRM is completely demagnetised.

To overcome this disadvantages we propose an MD check in the present paper which makes use of the failure of the law of additivity in the case of MD $pTRM^*$.

2. Sample description and experimental methods

In order to evaluate the efficiency of the test, complete Thellier–Thellier experiments plus the additivity checks at various temperature intervals were performed on synthetic magnetite samples of different grain sizes. Seven commercially available synthetic samples were used for this study: Three PSD samples with a grain size below 1 μm (threshold according to Dunlop and Özdemir (1997)) and three MD samples (grain size up to 12.1 μm) from *Wright Industries Inc.* (New York) and one SD sample which was obtained by reducing maghemite available from *Alfa Aesar* (Karlsruhe). The properties of these samples are summarised in Table 1.

In order to diminish intergrain magnetostatic interaction, the samples were dispersed in CaF_2 and a magnetite content of about 3 wt.% was obtained. To avoid major chemical changes during the Thellier–Thellier experiment, the samples were sealed in evacuated quartz glass tubes and were heated for 3 h to 700 °C in order to stabilise them thermally. For the experiments a laboratory total TRM(700 °C, 20 °C) in a field of 60 μT resembling the NRM of a natural sample and thus simply called NRM in the following, was then imparted. The laboratory field used for $pTRM^*$ acquisition during the Thellier–Thellier experiment was also 60 μT.

The rock magnetic characterisation of the samples was performed by measuring hysteresis parameters, $M_S(T)$ curves and, as a proxy for SP grains, the viscous decay coefficient defined as $S_d = (IRM_{t_0} - IRM_t)/\log(t/t_0)$ (Worm, 1999) with a variable field translation balance (VFTB). Additionally, low temperature saturation IRM (LTSIRM) warming curves were measured with an MPMS. All samples show a sharp Verwey transition (Fig. 1) and Curie temperatures between 577 and 586 °C (Table 1). The grain size of the samples is also reflected in the LTSIRM plot, where the magnitude of the change in magnetisation at the Verwey transition increases with increasing grain size. This dependence is valid up to a grain size of ≈ 10 μm (Heider et al., 1992).

Table 1
Grain size and rock magnetic parameters

Type	Name	Nominal grain size (μm)	Mean grain size (μm)	T_C (°C)	T_V (K)	M_{RS}/M_S	H_{CR}/H_C	S_d/SIRM (%) @920 mT
Alfa Aesar	MGH1	0.023	–	577	120	0.19	2.03	2.1
3006	W1	–	0.7	578	117	0.06	4.54	3.6
4000	W2	0.5	<0.5	578	116	0.14	2.44	2.3
31,182	W3	–	0.5	582	126	0.07	3.54	2.8
33,093	W4	7	5.7	586	126	0.03	5.90	0.8
42,093	W5	11	8.3	577	126	0.03	5.09	0.3
112,982	W6	–	12.1	583	115	0.02	8.37	0.04

Samples W1–W6 were obtained from *Wright Industries Inc.* Nominal grain size is the size given by the manufacturer. The mean grain size was determined on SEM pictures by picking 500 grains for each sample and using a log-normal fit.
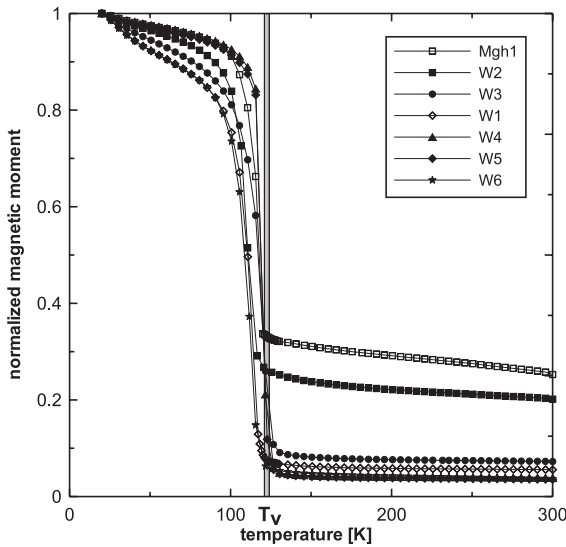
Fig. 1. Low temperature SIRM warming curves of the synthetic samples. T_V marks the temperature interval of the Verwey transition for pure magnetite (Muxworthy, 1999). T_V of the samples shows only minor deviations probably due to a small degree of maghemitisation.

Although having a grain size in the SD range, sample MGH1 shows a M_{RS}/M_S ratio well below the theoretical value of 0.5 for uniaxial anisotropy. This might either be due to particle interactions caused by incomplete separation of the grains or to a certain content of super-paramagnetic (SP) grains (Dunlop, 2002). As a rough estimate, published data from Worm (1999) shows that for a significantly decreased M_{RS}/M_S ratio (below 0.4) due to SP grains, S_d/SIRM exceeds 7%. In contrast to Worm (1999) who used an IRM acquired at 78 mT, we measured the decay of saturation IRM, which results in a considerably larger decay coefficient according to the author. For the samples used in this study however, the maximum S_d/SIRM never rises above 3.6% (Table 1). This value is even lower than the above mentioned threshold for the IRM(78 mT) viscous decay. Thus, our conclusion is that incomplete grain separation is the main cause for the decrease of the M_{RS}/M_S ratio in the grain size range of sample MGH1 and that the contribution of SP particles can be neglected.

For this investigation we use the modified Thellier and Thellier (1959) experiment after Coe (1967) with additional tail checks after McClelland and Briden (1996) referred to as MT3 (Leonhardt et al., 2000). In order to check the additivity of two certain pTRMs an additional demagnetisation step is introduced: In the course of the Thellier–Thellier experiment the two pTRMs* (pTRM*(T_1, T_0) and pTRM*(T_2, T_0) with $T_1 > T_2$ and T_0: room temperature) are imparted on the sample. The acquired pTRM*(T_1, T_0) is then partly demagnetised by heating in zero field up to temperature $T_2 < T_1$ and the remaining remanence M_{rem} is measured.
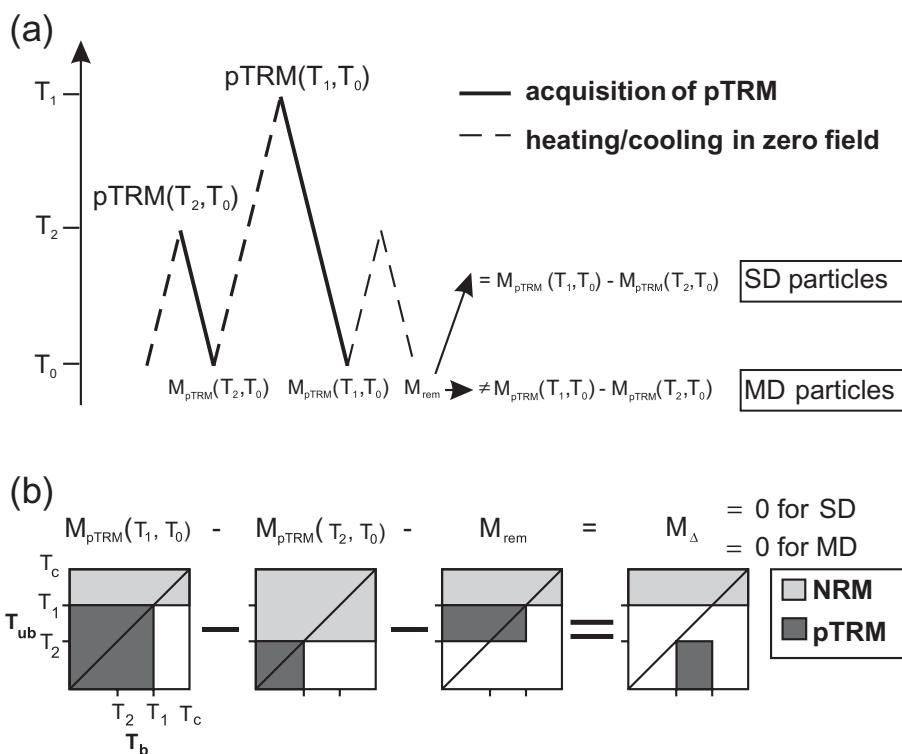

Fig. 2. Scheme of the proposed additivity check. (a) Sketch of the experimental procedure. (b) Diagram equation of the proposed additivity check using the phenomenological representation of Fabian (2000). The equation shows that the additivity check error M_Δ is only caused by remanences with $T_{ub} < T_b$. See text for further details.

If the law of additivity is valid, $M_{rem} = M_{pTRM}(T_1, T_0) - M_{pTRM}(T_2, T_0)$. In case of MD remanence, the remaining remanence will be less than the difference of the two separate pTRMs. The value of deficiency is referred to as M_Δ. Fig. 2 shows the procedure by using the phenomenological model of Fabian (2000). Failure of the test in the case of MD remanence is caused by MD particles having an unblocking temperature T_{ub} below their respective blocking temperature T_b. The procedure is not sensitive to particles with $T_{ub} > T_b$. However, Dunlop and Özdemir (2000) showed that there is a symmetry of high-T_{ub} and low-T_{ub} tails in MD magnetite, i.e. the distribution function of unblocking temperatures $f(T_{ub})$ has always a high-T as well as a low-T tail. Moreover, only remanences with $T_{ub} < T_b$ cause a non-linearity in the NRM-TRM plots (Fabian, 2001).

3. Results

The results of the Thellier experiments are shown in Fig. 3 and Table 2. The NRM-TRM plots include the pTRM checks and the additivity checks (AC) which are displayed in an analogous manner. As the remaining remanence M_{rem} after the AC step should equal the difference between pTRM*(T_1, T_0) and pTRM*(T_2, T_0),

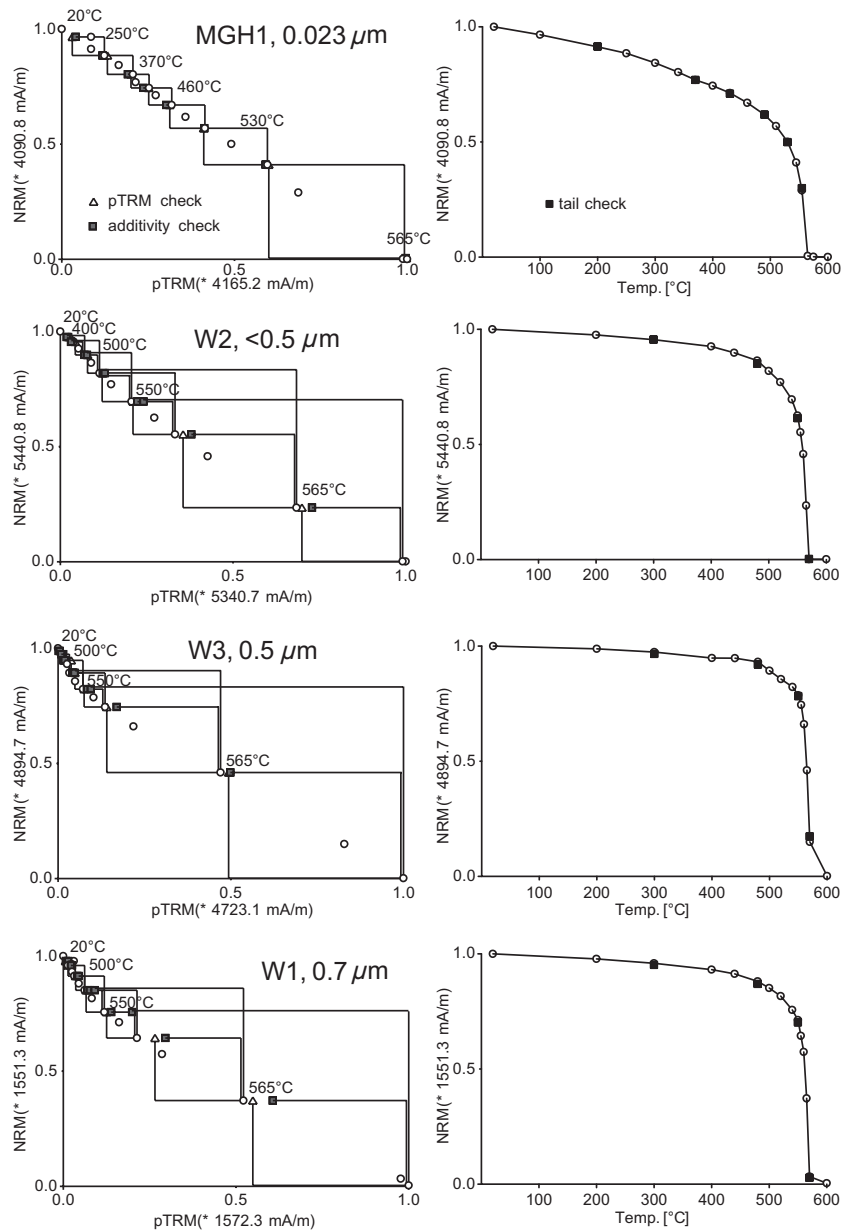

Fig. 3. Results of the Thellier experiments. Each additivity check is plotted as a filled square and a horizontal line starting at pTRM*(T_1, T_0). The value of M_{rem} is represented by the length of this horizontal line.

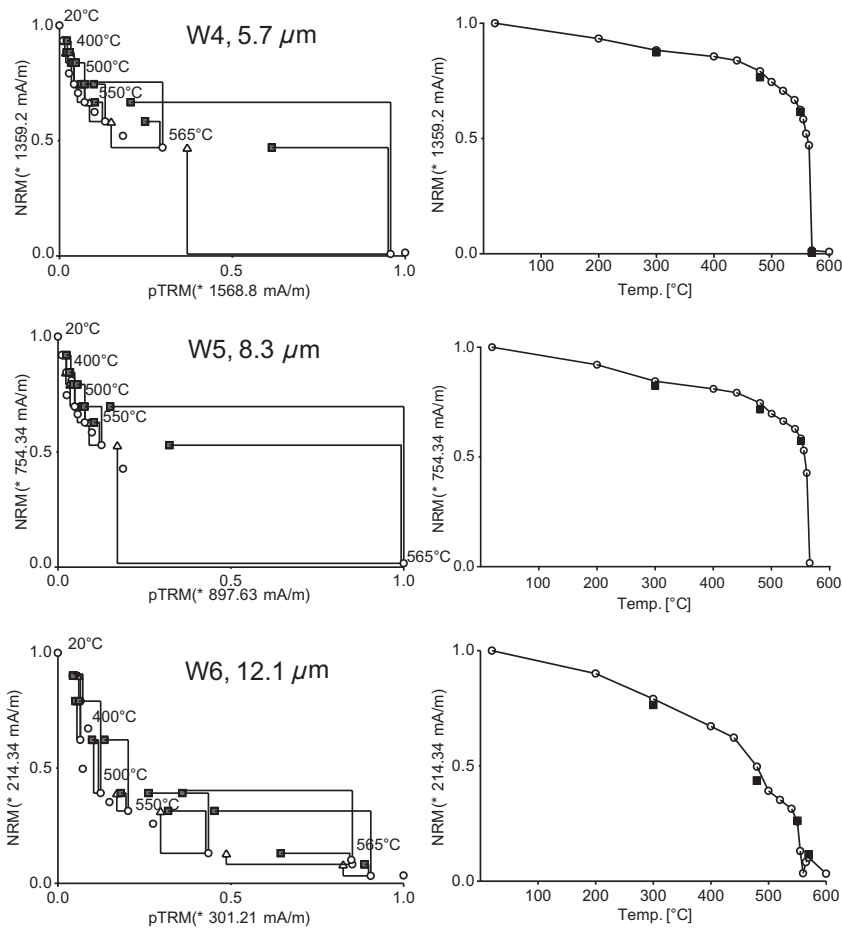Fig. 3 (continued)

Table 2
Results of the palaeointensity experiment

Sample	Max. AC error M_Δ (%)	Max. pTRM check error (%)	Max. tail check error (%)	TRM (mA/m)	NRM (mA/m)	(NRM−TRM)/ NRM (%)	$\Delta F/F$ (%)
MGH1	1.6	1	0.97	4133	4091	−1.0	1.6
W2	3.1	2	1.3	4968	5441	8.7	7.0
W3	3.7	2	2.3	4413	4895	9.8	8.4
W1	9.2	5	1.2	1475	1551	4.9	12.0
W4	27.8	7	2.6	1361	1359	−0.15	35.0
W5	16.4	5	3	825	754	−9.4	48.2
W6	21.3	10	6.1	222	214	−3.7	66.9

AC error and pTRM check error are normalised to the complete TRM, the tail check error is normalised to the NRM. The TRM value is the magnetisation after the last pTRM acquisition step and after correction of the pTRM check error with the method of Valet et al. (1996). (NRM−TRM)/NRM indicates the deviation from the expected Koenigsberger (1936) ratio Q_{nt} of 1. The last column shows the deviation of the palaeointensity estimate from the expected value of 60 µT determined on the near linear part of the NRM/TRM plot.

the measured M_{rem} is plotted as a filled square and a horizontal line starting at pTRM*(T_1, T_0). The length of this line represents the value of M_{rem}.

The MGH1 sample shows the expected behaviour for SD samples: A linear NRM-TRM plot, positive tail checks and also positive ACs. The pTRM checks confirm that no chemical alterations occurred. All other samples show a varying degree of concave curvature of

the NRM-TRM plots potentially causing erroneous palaeointensity estimates. According to Fabian (2001) this curvature is caused by remanences having a $T_{ub} < T_b$. As already mentioned in the previous section, these remanences also cause failure of the AC.

Only sample W6 with the largest grain size shows a tail check error exceeding the threshold of 5% of the NRM given by Leonhardt et al. (2000). Despite sealing

them in evacuated quartz glass tubes, *Wright* samples show a certain degree of chemical alteration as can be seen from the pTRM checks. This error seems to increase with increasing grain size and is largest in the case of sample W6 (10% of total TRM), in the case of the other samples it never exceeds 7%. This dependence on grain size might be caused by the fact, that thermal stabilisation by heating the samples takes longer for larger grains. If a pTRM check error occurs, this means that an alteration of existing or the formation of new particles with a T_b in the temperature range of the pTRM check took place. This does not only affect the acquired remanence but also the loss of remanence during the AC. Thus, the ACs are also biased by chemical alteration.

The ACs show no significant deviations for sample MGH1 confirming the law of additivity for the SD sample. The rest of the samples displays AC errors which are increasing with grain size.

4. Discussion and conclusions

The modified Thellier–Thellier experiment on synthetic samples carrying a laboratory TRM shows that the proposed additivity check is capable of identifying remanence carried by MD particles. A palaeointensity determination for samples W1, W4, W5 and W6 using the low temperature or high temperature part of the NRM-TRM plot would yield a significantly too high or too low palaeointensity estimate, respectively (Table 2). The result for sample W1 implies that already PSD sized particles can cause wrong palaeointensity estimates due to failure of the law of additivity.

In the case of chemical alterations the data can be corrected using the method of Valet et al. (1996). In this case the ACs have to match the respective pTRM values after check correction to yield a positive result. By using this correction method, the AC allows alteration and MD behaviour to be evaluated independently.

In the absence of chemical alteration or after correction for alteration the Koenigsberger (1936) ratio ($Q_{nt} = NRM/TRM$) yields correct palaeointensity estimates within an error margin of maximum 10% (Table 2). This was already shown in the numerical approach to Thellier–Thellier experiments by Fabian (2001).

Sample W1 is the sample with the smallest grain size where the error of a palaeointensity estimate in the near linear part of the NRM-TRM plot in the temperature interval between 550 and 600 °C exceeds 10%. As this sample shows a maximum AC error of 9.2% of total TRM, we propose a value of 7% as the limit for a positive AC. If the check error exceeds this threshold, palaeointensity estimates will suffer from significant errors.

The failure of the pTRM tail check to detect MD behaviour for all samples apart from sample W6 is probably due to the fact, that pTRM* has a much smaller tail than a regular pTRM as already discussed in the introduction.

Acknowledgements

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