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THE EFFECT OF MAGNETITE PARTICLE SIZE ON PALEOINTENSITY DETERMINATIONS OF THE GEOMAGNETIC FIELD

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The Thellier method for paleointensity determinations has been applied to prepared samples containing magnetites whose mean particle sizes range from single domain, SD, to multidomain, MD. Linear (ideal) PNRM–PTRM curves are obtained for samples containing SD and submicron magnetite particles. However, for MD particles non-linear (concave-up) PNRM–PTRM curves are observed such that a linear approximation to the lower blocking-temperature data leads to apparent paleointensities that are higher than the actual paleofield; however, the ratio of the end-points, NRM/TRM, yields the correct (laboratory) intensity. The non-linear (concave-up) PNRM–PTRM curves for the MD particles are explained in terms of the lack of symmetry of the domain-wall movements during the two heatings of the Thellier experiment. Low stabilities with respect to alternating fields and with respect to temperature cycles below magnetite's isotropic temperature are diagnostic in detecting samples most likely to exhibit non-linearities due to the MD effect.

1. Introduction

It is usually much more difficult to obtain a reliable estimate of the intensity of the earth's magnetic field from a certain rock or other remanence-bearing artifact than it is to obtain the direction of that field. Folgheraiter (1899) suggested the possibility of obtaining paleointensities from thermoremanent magnetization, TRM, of baked clays by comparing their original or natural remanence, NRM, which is assumed to be a pure TRM, with a laboratory TRM, obtained by heating the sample above its highest Curie temperature, T_C, and cooling it in the known laboratory field. Both the NRM and the laboratory TRM are assumed to be linearly proportional to the external field. A paleointensity estimate can then be obtained from the equation:

$$\frac{|J_n|}{|J_t|} = \frac{|h|}{|h_L|} \tag{1}$$

where J_t is the TRM produced in the laboratory in a field of strength h_L; J_n is the measured NRM, and h is the unknown field intensity.

Physical and chemical changes are known to occur subsequent to the acquisition of the primary TRM, which may affect the intensity of the remanence, sometimes even in cases where the remanence direction remains unaltered. The probability that such a change has occurred during a rock's history increases with the rock's age, making reliable paleointensity determinations from older rocks very difficult.

In addition, it was recognized early (Folgheraiter, 1899) that one of the major sources of error in obtaining paleointensities is caused by chemical and physical alterations of the sample when it is heated in the laboratory. Indeed, Folgheraiter was discouraged from intensity studies because repeated TRM's were not self-consistent. The rate and extent of mineralogical and chemical reactions increase rapidly with temperature, and they may irreversibly affect the chemical and physical properties of the magnetic minerals and thus alter their TRM capacity and blocking tem-

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peratures. Often, however, most of the physical and chemical changes occur upon the first heating to above T_C, such that internal consistency of subsequent TRM's might crown the result of the first laboratory TRM with false confidence. For these reasons it is imperative that any reliable method for paleointensity determinations have some sort of consistency checks to detect the presence and development of unwanted effects!

Since 1899, several methods for paleointensity determinations have been proposed (Thellier, 1938; Thellier and Thellier, 1959; Wilson, 1961; Van Zijl et al., 1962; Carmichael, 1967; Shaw, 1974). In principle, all these methods are similar in so far as they compare the NRM with a laboratory induced TRM, using specific bracketed segments of partial-NRM and partial-TRM to arrive at an estimate for the paleointensity. Each method has certain checks to assess whether the NRM is a pure TRM and whether the laboratory heating(s) alter(s) the sample's magnetic behaviour. Coe and Grommé (1973) compared three of the more common paleointensity methods in their study of historic lavas that erupted in known fields, and they find that the Thellier method yields the most reliable results. Therefore, this paper is limited to studying the Thellier method for paleointensity determinations.

The remanence of many continental igneous rocks resides in titanomagnetites with relatively low Ti content. For stoichiometric magnetite the upper size limit for single-domain, SD, particles is usually considered to be less than 0.1 μm (see review by Evans, 1972; Butler and Banerjee, 1975). However, magnetic particles larger than 1 μm are common in volcanic rocks and their fraction increases markedly in intrusive rocks. In addition, stable remanence, comparable to that of many igneous rocks, has been observed in natural and synthetic magnetite particles larger than the SD limit and also in particles larger than 1 μm (Roquet, 1954; Morrish and Yu, 1955; Rimbert, 1959; Parry, 1965; Dunlop, 1973; Levi, 1974). The electron-microscope studies of Evans and Wayman (1970) suggest that the unusually stable remanence of the Modipe gabbro is carried by magnetite particles whose particle-size distribution peaks near 0.25 μm. In addition, Soffel (1971) observed domain walls in titanomagnetite particles of composition $(Fe_2TiO_4)_{0.55} \cdot (Fe_3O_4)_{0.45}$ with diameters as small as 1.3 μm, suggesting that for Ti-free magnetite domain walls can exist in substantially smaller grains. These results show that stable remanence resides in particles larger than SD; that is, in pseudosingle-domain, PSD, and multidomain, MD, particles. (PSD refers to particles whose sizes and magnetic properties are intermediate between those of "truly" SD and "truly" MD particles.)

It is often difficult to analyze a rock to determine the particular reason for the failure of a paleointensity determination, largely because rocks typically contain magnetic minerals that vary widely in their shapes, sizes, and sometimes compositions. This research was conducted in what appears to be the first well-controlled experiment where magnetic minerals of known compositions, sizes and shapes have been given a pure TRM in a known field and then subjected to a paleointensity method to determine whether or not a reliable estimate of the known field intensity can be extracted from that mineral. Magnetite (Fe_3O_4) was chosen for this study for reasons of experimental convenience and because magnetite commonly occurs in continental rocks. Each sample was prepared to contain a narrow distribution of particle sizes and shapes, varying from SD to PSD to MD. The purpose of the study is to isolate the effects of particle size and domain state on the Thellier method for paleointensity determinations.

2. The Thellier method

The Thellier method for paleointensity determinations (Thellier and Thellier, 1959; Coe, 1967a,b) consists of a sequence of paired heatings to a given temperature $T_1 < T_C$. The two heatings are used to determine: (1) the partial-NRM (PNRM $\equiv \Delta J_n$) that would be lost upon heating from room temperature, T_R, to T_1 in zero field; and (2) the partial-TRM (PTRM $\equiv \Delta J_t$) that would be acquired by cooling the sample in a known field, $\boldsymbol{h}_L$, from T_1 to T_R. Ideal behaviour in the Thellier sense is defined such that:

$$\frac{|\Delta J_n(T_2,T_1,\boldsymbol{h})|}{|\Delta J_t(T_2,T_1,\boldsymbol{h}_L)|} = \frac{|\boldsymbol{h}|}{|\boldsymbol{h}_L|} \qquad (2)$$

is obeyed for any temperature interval T_2,T_1. The notation $\Delta J(T_2,T_1,\boldsymbol{h})$ refers to the magnetization acquired during cooling from T_2 to T_1 in a constant magnetic field, $\boldsymbol{h}$. The subscripts n and t respectively

refer to NRM and TRM. In the Thellier method the temperature of the paired heatings is progressively increased from T_R until all blocking temperatures are exceeded, generating a data set $[\Delta J_n(T), \Delta J_t(T)]$ for the different temperature steps. Each point gives an independent determination of $|\boldsymbol{h}|/|\boldsymbol{h}_L|$, providing the necessary self-consistency check. It is convenient to represent the data graphically by plotting ΔJ_n vs. ΔJ_t for the different temperatures [Arai (1963) in Coe (1967b); see also Figs. 1 and 2]. The data of an ideally behaving sample will form a line whose slope is $|\boldsymbol{h}|/|\boldsymbol{h}_L|$ from which the paleointensity can be directly determined. The following assumptions are implied by the Thellier method:

(1) PTRM's acquired in different temperature intervals are independent and additive.

(2) J_n is a TRM with negligible secondary components of magnetization.

(3) Both J_n and J_t are in the region where the TRM is linearly dependent on the external field.

(4) J_n and J_t are independent of cooling rates.

(5) The sample-demagnetizing field due to its surroundings (e.g., the remainder of the lava flow) has a negligible effect on the acquisition of the primary TRM.

(6) Heating in the laboratory causes no physical or chemical changes of the sample that alter in any way its TRM properties.

Deviations from linearity of the ΔJ_n–ΔJ_t curves are usually attributed to the failure of one or more of the above assumptions. Effects on the shapes of ΔJ_n–ΔJ_t plots caused by the violation of some of the above assumptions have been discussed in detail by Coe (1967b, 1973).

Experimentally, it is known that only a small fraction of paleointensity experiments yields reliable results. (It has been said that only rocks which acquire remanence in known magnetic fields yield reliable paleointensities!) Since the Thellier method is so time-consuming and because of the relatively few samples yeilding linear ΔJ_n–ΔJ_t curves over their entire spectrum of blocking temperatures, it is important to understand the causes for non-ideal (non-linear) ΔJ_n–ΔJ_t curves and the effects of such non-ideal behaviour on paleointensity determinations. It would also be helpful to establish criteria that would help maximize the success of paleointensity determinations. In this paper it will be shown that the presence of MD particles of magnetite causes non-linear ΔJ_n–ΔJ_t curves; in addition, stability criteria are established to help identify samples which are most likely to exhibit non-linear ΔJ_n–ΔJ_t curves.

3. Description of the magnetite powders

In order to obtain the broadest spectrum of particle-size distributions, both natural and synthetic magnetites were used. The physical descriptions and T_C values of the magnetite powders and the TRM properties of the corresponding samples are summarized in Table I. The samples and powders are numbered as in Levi (1974).

High-purity natural magnetite crystals whose saturation magnetization, $J_S(T_R)$, is 93 ± 1 e.m.u./g and whose Curie point, T_C, is 580°C were dry ground and sieved to obtain different size fractions (powders *2–4*). Grinding and ball-milling were done in repeated short intervals to avoid heating which might cause oxidation. The X-ray diffraction pattern of one of the ground powders exhibited only spinel lines associated with magnetite, yielding a cubic cell edge of 8.39 ± 0.01 Å.

Synthetic magnetite powders were generously supplied by several sources. Powder *11* (Toda Industries, Japan) is a synthetic magnetite powder whose particles are highly acicular (rod-shaped) with a mean axial ratio of 8 : 1. The expectation that powder *11* contains SD particles is supported by its bulk coercivity. H_c = 438 ± 3 Oe and by its ratio of saturation remanence to saturation magnetization, J_{RS}/J_S = 0.44 ± 0.01. This compares well with the theoretical value, J_{RS}/J_S = 0.50, for an assemblage of randomly oriented, magnetically uniaxial SD particles. Samples *5–9* contain equidimensional, synthetic magnetite powders, having H_C values near 100 Oe and J_{RS}/J_S values of about 0.11. Sample *5* contains magnetite powder supplied by Pfizer Co. (BK-5099); samples *6* and *7* contain identical magnetite powder supplied by the Columbian Carbon Co.; samples *8* and *9* contain identical magnetite powder prepared after a recipe by Elmore (1938).

Electron micrographs were used to determine the particle shapes and size distributions. Depending on the particular powder, between 64 and 249 particles were counted to arrive at the median values. The origins and shapes of the magnetite particles and their

TABLE I

Physical characteristics of the magnetites and TRM properties of the samples

Sample (powder) No.	Particle origin and shape	Particle size, d (μm)	T_C ($\pm 10°C$) (°C)	TRM (h_L = 0.46 Oe) (10^{-3} G)	$H_{1/2}$ (Oe)	$T_{1/2}$ (°C)	J/J_t liquid N_2 cycles in $h = 0$
2	natural crushed, sieved; irregular	$\bar{d} = 2.7$ $d < 150$	580	0.227	78 ± 4	475 ± 15	0.590 0.465 0.476
3	natural crushed, sieved; irregular	$\bar{d} = 1.5$ $d < 50$	580	2.06	138 ± 10	493 ± 10	0.593 0.521 0.497
4	natural ball-milled; regular polygons	$\bar{d} = 0.31$ $d < 2$	580	0.915	380 ± 8	444 ± 10	0.936 0.888 0.822
5	synthetic rgular polygons spheres to cubes	$\bar{d} = 0.24 \pm 0.1$ $d < 0.9$	565	2.87	347 ± 5	492 ± 10	0.945 0.935 0.929
6	synthetic regular polygons	$\bar{d} = 0.21 \pm 0.06$ $d < 0.5$	570	1.39	334 ± 5	507 ± 10	0.976 0.951 0.965
7	spheres to cubes			13.2	360 ± 15	508 ± 10	0.945 0.961 0.955
8	synthetic regular polygons	$\bar{d} = 0.12 \pm 0.04$ $d < 0.3$	575	1.08	292 ± 10	400 ± 15	0.990 0.970 0.986
9	spheres to cubes			0.97	295 ± 15	418 ± 10	0.965 0.910 0.907
11	synthetic acicular (needle shape)	mean axial ratio = 8 : 1 0.35 × 0.04	591	3.03	571 ± 20	519 ± 10	1.003 0.995 0.994

1Oe = 10^{-4} Wb/m^2 = 10^{-4} T.
1 G = 1 e.m.u./cm^3 = 10^3 A/m.

median and maximum diameters are listed, respectively, in columns 2 and 3 of Table I.

Synthetic magnetites which are prepared by precipitation from an aqueous solution are usually partly oxidized (Gallagher et al., 1968). In addition, the grinding of the natural magnetite introduces strains into the magnetic particles which substantially influence their magnetic properties. For these reasons and because the Thellier method deals with magnetic behaviour at elevated temperatures, the data of Table I and the bulk magnetic properties discussed above were obtained after heating the magnetite powders to 650°C for 6 h in a slightly reducing environment, using carbon and a residual N_2 atmosphere at pressures of about 10^{-1} torr. No higher temperatures were attained in the subsequent experiments. This heat treatment reduced the synthetic powders to stoichiometric magnetite (from X-ray diffraction) and stabilized the powders' magnetic properties through annealing and grain growth (from hysteresis parameters). It is interesting to note that heating to 650°C caused no significant grain growth for particles whose unheated diameters are greater than 0.2 μm (Levi, 1974).

High-field magnetization vs. temperature, $J-T$, curves were done for the heated powders; these heatings were also carried out in a similar reducing environment as described above. The curves of all the magnetite powders are reversible within 5%, each exhibiting a single Curie point, listed in column 4 of Table I.

4. Sample preparation and magnetic properties

Samples for the Thellier experiments were prepared by dilutely dispersing a particular magnetite powder in a matrix of high-purity alumina (Alcoa's A-16) and calcium-aluminate cement (Alcoa's CA-25). This matrix has excellent high-temperature characteristics and is non-magnetic for the purposes of the present study (Levi, 1974). The magnetite powder concentration is of the order of 1% by weight, the maximum concentration being less than 4% for sample *3* (due to its low J_{RS}/J_S value). The sample mixtures were sieved through a 250-μm sieve to break down clumps of the matrix and of the magnetite powder and improve sample homogeneity. The samples were molded into cylinders about 24 mm in diameter whose height is about 22 mm. Sample volume is usually between 9 and 10 cm^3, and the samples weigh between 15 and 19 g. The samples were slowly heated to 650°C for 6 h in a slightly reducing environment (identical to the method described in Section 3) to stabilize the chemical and magnetic properties of the samples. The samples were given repeated TRM's, using an identical heating procedure, until the TRM's were reproducible to within 2–3%. All samples spent at least 20 h above 600°C prior to the Thellier experiments of this study.

Some of the samples' pertinent TRM parameters are listed in the last four columns of Table I. Column 5 lists the samples' TRM (1 Gauss = 1 e.m.u./cm^3) acquired in a laboratory field of 0.46 Oe. These magnetization values are typical of the natural remanence of many igneous rocks. The large difference in the TRM's of samples *6* and *7* is due to approximately an order of magnitude difference in the concentration of their magnetite particles. Differences in the TRM's of other samples are due to both differences in the concentration as well as to intrinsic differences in the magnetites. Column 6 lists the samples' median demagnetizing field, MDF $\equiv H_{1/2}$: that peak alternating field required to reduce the sample magnetization to half its initial value. Excluding sample *11*, there is a maximum in the MDF data occurring near sample *4*, whose mean particle diameter is about 0.31 μm; samples with smaller equidimensional particles have lesser MDF values. The uncertainties associated with the MDF values are deviations from the mean of two independent determinations. Column 7 lists the samples' mean blocking temperatures, $T_{1/2}$: that temperature to which the sample must be heated in zero field to demagnetize half its remanence. The remanence is always measured at room temperature. Column 8 gives the samples' TRM-decay after cooling cycles to liquid N_2 temperature and reheating to T_R in zero field. Temperature cycles to below the isotropic point, which for stoichiometric magnetite is near 130°K (Bickford et al., 1956; Syono and Ishikawa, 1963), were first studied by Ozima et al. (1964). Subsequent studies by Kobayashi et al. (1965) and Merril (1970) have shown that the relative low-temperature decay of the magnetization decreases with decreasing grain size and is essentially absent for SD particles. It is now known that such low-temperature cycling reduces the remanence in MD particles whose rema-

nence is primarily controlled by magnetocrystalline anisotropy. The data of column 8 is consistent with these findings, showing that the low-temperature decay decreases with grain size from MD to SD particles. The data for each sample represent the fraction of TRM remaining after each of three successive low-temperature cycles. Because the total remanence in magnetite decreases further with each low-temperature cycle, three low-temperature cycles were used to obtain these data. However, the amount of remanence lost in an *individual* cycle usually decreases with each successive cycle such that it is not particularly useful to do more than about three such cycles. It is interesting to note that the pattern of magnetization decay after low-temperature cycles is the one magnetic property which most closely resembles the pattern of the samples' mean particle sizes.

5. Experiments and results

In this study of the Thellier method, the sample remanences are always laboratory TRM's (total or partial TRM's) acquired in a constant field of 0.460 Oe. Therefore, assumptions (2)–(5) of the Thellier method (see p. 247), are immediately satisfied. To satisfy assumption (6), to minimize irreversible changes of the samples' TRM properties, the samples' magnetic and chemical properties were first stabilized by heating to 650°C in a slightly reducing chemical environment, as described previously, and an identical procedure was followed for all subsequent heatings of the Thellier experiments. In addition, Levi (in press, 1976) has shown experimentally that the additivity of PTRM's in small external fields, $h < 0.5$ Oe, is obeyed to the same degree by these samples regardless of their magnetite particle sizes, satisfying assumption (1). Thus the present experiments are designed to test the effect of the magnetite particle size on the Thellier method.

In actual paleointensity determination many parameters which may affect the results are either poorly known or not known at all, such that accuracies of better than 10% are rarely expected or claimed — unless, of course, one is dealing with a sample which acquired remanence in a known field. In the present experiments, however, most of the sample and field parameters are known such that deviations of even a few percent might be significant.

Modified Thellier experiments were executed following Coe (1967a,b) and Coe and Grommé (1973):

(a) The NRM is measured at T_R.

(b) The sample is heated to $T_1 > T_R$ and cooled back to T_R in zero field; the magnetization is measured at T_R to obtain the PNRM lost between T_R and T_1.

(c) The sample is reheated to $T_1 > T_R$ and cooled back to T_R in h_L. *The field h_L is continuously present throughout the entire heating and cooling cycle.* The magnetization is measured at T_R to obtain the PTRM acquired between T_1 and T_R.

Steps (b) and (c) are repeated at successively higher temperatures until all the blocking temperatures are exceeded. The temperature is maintained at the particular elevated temperature to allow thermal equilibrium to be established. Depending on the temperature, the time at T_1 varies from 30 to 75 min. The laboratory field, h_L, in these experiments is known to better than ±0.5% and is reproducible to within ±0.5%. The field during step (b) is nulled to within ±50 γ in the region of the experiment. The absolute temperature is known to ±10°C, and the reproducibility of the temperature during a particular step of the paired heatings is determined by an automatic temperature controller and is thought to be better than ±3°C. The main difficulty encountered in reproducing the temperature is in reproducing the samples' positions in the oven.

The data is represented in Figs. 1 and 2. The magnetization is always normalized with respect to the NRM (laboratory TRM). The remanences are always along the axes of the sample cylinders. The numbers associated with the (PNRM, PTRM) points correspond to the temperature steps in °C. The lines are drawn to connect the initial and final points. The initial point is defined as (1.000, 0.000), and the small deviations of the final points from (0.00, 1.00) are attributed to small changes in the samples' TRM upon heating. The lines represent "ideal" behaviour in the Thellier sense.

The points of the $\Delta J_n - \Delta J_t$ plots for samples *2–4* (Fig. 1) systematically sag below the "ideal" line, and the sag (curvature) decreases from sample *2* to sample *4*. A linear approximation to the lower temperature points of samples *2* and *3* results in apparent paleointensities which are systematically high by as much as 35%, depending on the particular number of points used to define the line (Table II). If the linear

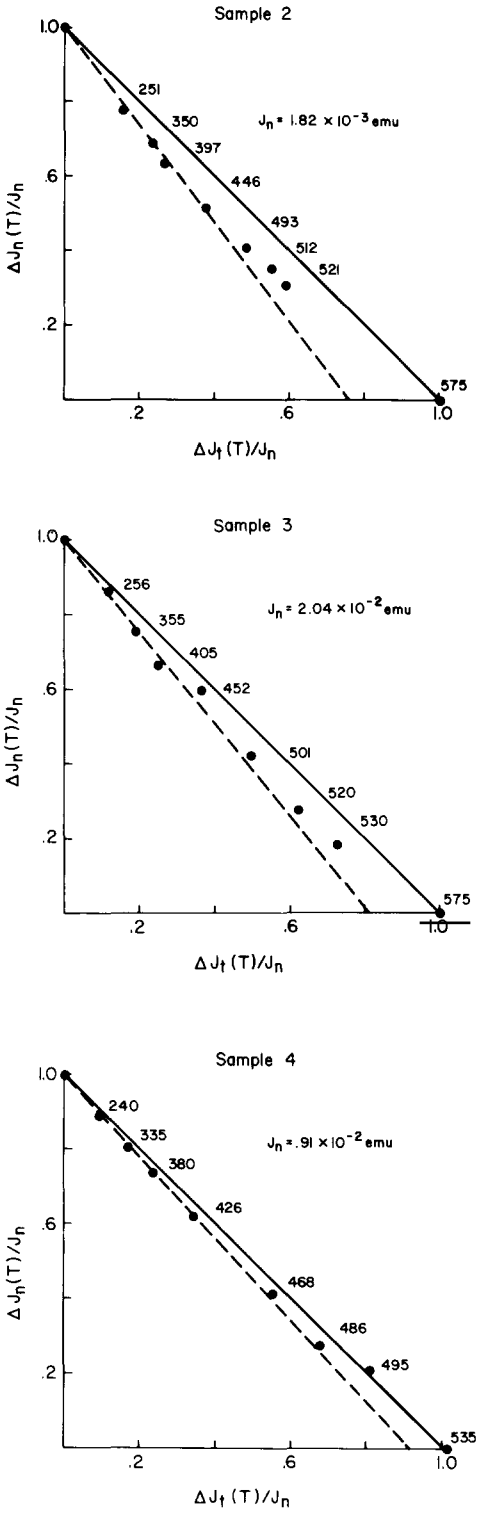

Fig. 1. Normalized $\Delta J_n - \Delta J_t$ curves for samples *2–4*. *Solid lines* represent ideal behaviour in the Thellier sense. *Broken lines* are linear approximations of the lower-temperature data. The numbers associated with the points are the temperatures in °C of the heating steps.

approximation is required to include data covering at least half of the sample's magnetization, including data through 493°C for sample *2*, 501°C for sample *3* and 486°C for sample *4*, the apparent paleointensities, using a least-squares fit, would be systematically high by 22% for sample *2*, 14% for sample *3*, and 5% for sample *4*. These data are in sharp contrast with the ratios of the initial to final points of all three samples which are 0.99 ± 0.01. The uncertainty represents the deviation from the mean for two determinations for each sample. ΔJ_t was always parallel to the NRM for samples *2* and *4*, and ΔJ_t was always induced antiparallel to the NRM for sample *3*.

It is noteworthy that the *deviation from ideal behaviour increases with increasing mean magnetite particle sizes*, and with *decreasing median demagnetizing-field* (values for samples *2*, *3* and *4* are 78, 138 and 380 Oe, respectively). Both in terms of particle sizes (Table I) and in terms of their stability the magnetic particles of samples *2–4* are typical of those found in many igneous rocks.

The $\Delta J_n - \Delta J_t$ plots for samples *5–9* and *11* (Fig. 2) are essentially linear for all their blocking temperatures. The reason for the deviation of the 522°C point of sample *6* is not known but may be due to a temperature discrepancy in steps (b) and (c) of the 522°C step of the Thellier experiment. In addition other factors may be involved as some slight reduction is observed for all samples, which is exhibited by the fact that the NRM/TRM $\leqslant 1$. In Table III, the slopes of the linear least-squares fits are shown for the $\Delta J_n - \Delta J_t$ data of samples *5–9* and *11*. Although the value for sample *6* is –0.89, by excluding the 522°C point the least-squares slopes becomes indistinguishable (–0.96) from the ratios of the initial to final points. Samples *8* and *9* contain the same magnetite powder and their TRM properties are quite similar. In the Thellier experiments sample *8* was always given PTRM's antiparallel to the NRM, and for sample *9* the PTRM's were given parallel to the original NRM; despite these differences in procedure, both samples are seen to have nearly identical

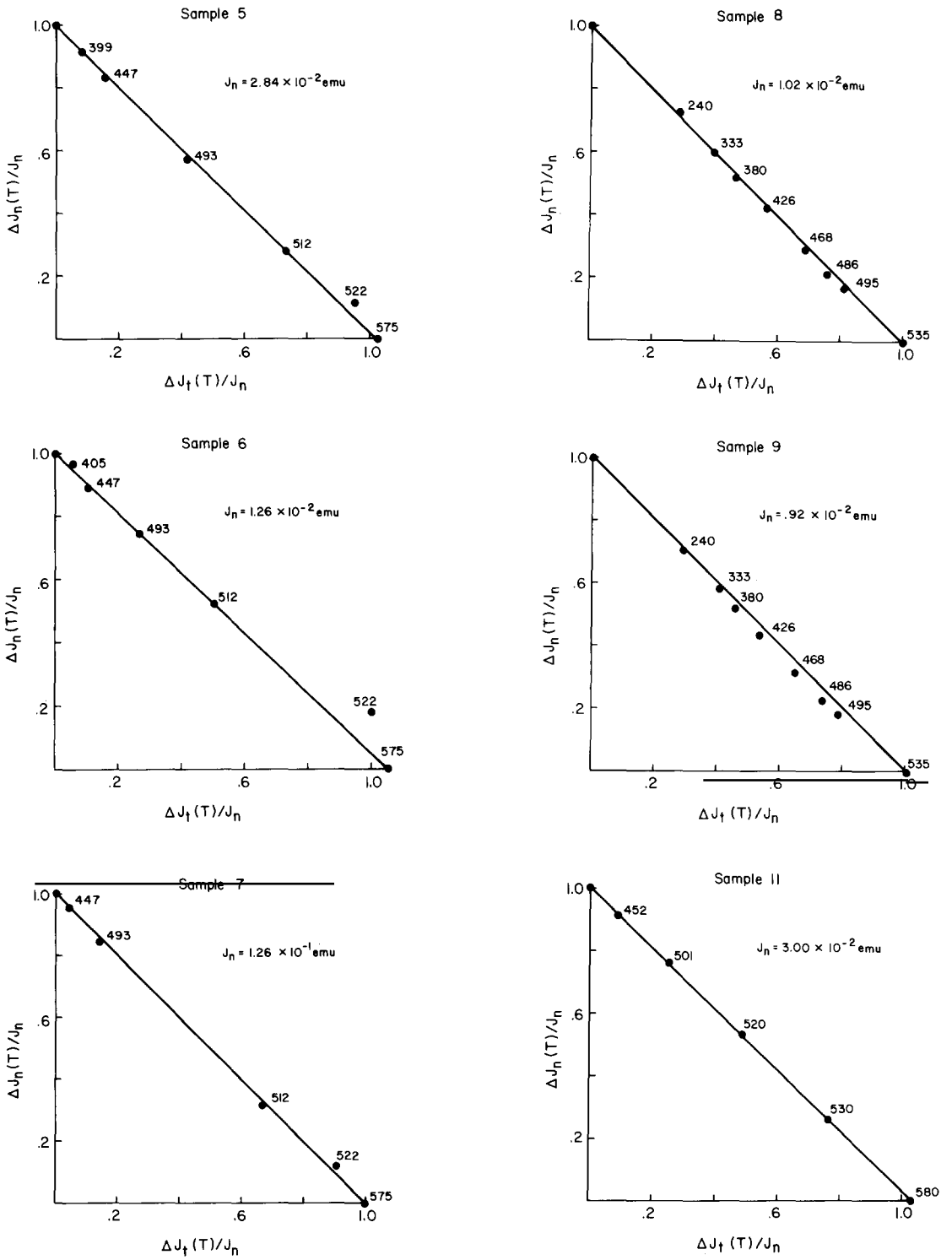

Fig. 2. Normalized $\Delta J_n - \Delta J_t$ curves for samples *5–9* and *11*. *Solid lines* join the initial and final points. The numbers associated with the points are the temperatures in °C of the heating steps.

TABLE II

Linear least-squares fit of $\Delta J_n - \Delta J_t$ data for MD samples

Sample *2*			Sample *3*			Sample *4*		
T (°C)	J/J_n	slope of line	T (°C)	J/J_n	slope of line	T (°C)	J/J_n	slope of line
397	0.63	−1.36	405	0.67	−1.34	380	0.74	−1.10
446	0.57	−1.30	452	0.60	−1.15	426	0.62	−1.09
493	0.41	−1.22	501	0.42	−1.14	468	0.41	−1.05
521	0.31	−1.14	530	0.18	−1.12	486	0.28	−1.05
Ratio of end-points		−0.99 ± 0.01			−0.99 ± 0.01			−0.99 ± 0.01

$\Delta J_n - \Delta J_t$ plots. The data for sample 11 indicate very linear behaviour, which is comforting, since sample *11* contains needle-shaped single-domain particles.

For completeness it should be stated that samples *1* and *10* do exist but were not included in this article. Sample *1* is a chip (3.569 g) from a single crystal of stoichiometric magnetite, which has such unstable remanence that no meaningful $\Delta J_n - \Delta J_t$ curve can be constructed. In contrast, sample *10* is very stable and the corresponding $\Delta J_n - \Delta J_t$ curve is linear throughout the entire spectrum of blocking temperatures; the data for sample *10* are omitted, because, due to the very dilute concentration of the magnetite particles, their sizes and shapes are not known.

In the Thellier experiments described thus far the procedure of Coe (1967a,b) was followed; this method is different from that described by Thellier and Thellier (1959). To see whether the experimental results depend on the particular procedure, the experiments were repeated following the procedure of Thellier and Thellier, where the samples are always heated in presence of the laboratory field, as outlined below.

(a) The NRM is measured at T_R.

(b) The sample is heated to $T_1 > T_R$ and cooled back to T_R in the continuous presence of $\boldsymbol{h}_L$; the magnetization is measured at T_R.

(c) The sample is rotated 180° about a horizontal axis normal to the laboratory geomagnetic meridian.

(d) The sample is reheated to the same $T_1 > T_R$ and cooled back to T_R in the continuous presence of $\boldsymbol{h}_L$. The magnetization is measured at T_R.

Half the vector sum of the remanences measured after steps (b) and (d) represents the PNRM that would remain after heating to temperature T_1 in zero field. Half the vector difference of the remanences obtained in steps (b) and (d) represents the PTRM acquired between T_1 and T_R. Steps (b), (c) and (d) are repeated at successively higher temperatures until all the blocking temperatures are exceeded. The data obtained using the Thellier procedure (Levi, 1974) has the same features as the data obtained using Coe's procedure of Figs. 1 and 2:

(i) The $\Delta J_n - \Delta J_t$ plots of samples *2–4* sag below the line connecting the initial and final points and are concave up with respect to it.

(ii) The $\Delta J_n - \Delta J_t$ plots of samples *5–9* and *11* are essentially linear, and as in the previous runs the $\Delta J_n - \Delta J_t$ plots of samples *8* and *9* sag somewhat below the line connecting the initial and final points.

TABLE III

Linear least-squares fit of $\Delta J_n - \Delta J_t$ data for SD and PSD samples (all points)

Sample	Slope of linear least-squares fit (all points)	Ratio of initial to final points
5	−0.95	−0.98 ± 0.01
6	−0.89	−0.96 ± 0.01
7	−0.98	−1.00
8	−1.02	−1.00
9	−1.01	−1.00
11	−0.96	−0.96

6. Explanation of the non-linear $\Delta J_n - \Delta J_t$ curves

Since the non-linear $\Delta J_n - \Delta J_t$ curves are observed only for samples containing MD particles and because the non-linearlity increases with an increasing fraction of MD particles, it is concluded that the observed non-linear $\Delta J_n - \Delta J_t$ curves are indeed due to the presence of MD remanence carrying particles. To explain the non-linear behaviour the following observations must be explained: (1) The non-linear $\Delta J_n - \Delta J_t$ curves are always concave-up; (2) the same concave-up non-linear behaviour is observed when the PTRM is produced both parallel and antiparallel to the original remanence; and (3) the same type of non-linear curves is observed for both the Thelliers' (1959) and Coe's (1967a,b) executions of the Thellier experiment.

Only a very simplified model for MD remanence is considered, which is essentially identical to the one discussed by Schmidt (1973) consisting of rectangular particles of width a and length $2a$, whose two domains are separated by a single 180° domain wall. It is assumed that the same domain configuration is maintained for all temperatures $T < T_C$. Temperature variations of the domain-wall width (δ) are neglected, and it is assumed that $\delta/a \ll 1$. Any external field (h) is applied in the plane of the domain wall, whose area $S = a^2$. In their demagnetized state each particle consists of two oppositely magnetized domains of equal size. The coordinate x is defined to measure the displacement of the wall from its demagnetized position such that the particle magnetization (J) is given by:

$$J = (x/a)J_S$$

where J_S is the saturation magnetization. To discuss the remanence of such particles an energy function is constructed, assuming that the particles do not interact. Following Schmidt (1973), the following magnetic interactions are considered:

(a) The magnetostatic energy due to the interaction of the particle magnetization ($\boldsymbol{J}$) and the external field ($\boldsymbol{h}$) is:

$$U_M = -\boldsymbol{h} \cdot \boldsymbol{J}V = -2AJ_S hx$$

(b) The magnetostatic self-energy of the interaction of the particle magnetization and the demagnetizing field ($\boldsymbol{H}_d$) due to the surface poles is:

$$U_D = -\tfrac{1}{2}\boldsymbol{H}_d \cdot \boldsymbol{J}V = (DJ_S^2 A/a)x^2$$

D is the particle demagnetizing factor, which is dependent on the particle geometry and domain configuration, and, although it is a gross oversimplification, D is assumed to be a constant.

(c) The third energy term is due to the interaction of the domain wall with stress accumulations in the particle caused by crystal imperfections and the presence of impurities. The distribution of stress concentrations is given by $F(r)$ which is assumed to be temperature independent. The interaction is strongly affected by J_S, according to the relation J_S^P, where P is an exponent >2. An additional temperature dependence is present in the value for the stress (σ) which usually decreases with increasing T:

$$U_W = -CJ_S^P \sigma(T)F(r)$$

where C is a measure of the interaction at $T = 0°K$.

The energy equation becomes:

$$U = -2AJ_S hx + (DAJ_S^2/a)x^2 - CJ_S^P \sigma(T)F(r) \qquad (3)$$

The temperature dependence of the energy function is contained in J_S and in σ, and because of the varying temperature dependence of the different energy factors, the effects on the remanence of the different energy terms become dominant at different temperatures. Just below T_C, U_M is dominant, and it exerts pressure on the domain wall:

$$p_M = \frac{-\partial U}{A\partial x} = 2J_S h$$

favouring homogeneous particle magnetization, thus tending to force the wall out of the particle. At lower temperatures, as J_S increases, the wall experiences increasing pressure due to the grain self-demagnetizing energy trying to displace the wall to a more demagnetized position in the interior of the particle. U_W also increases with decreasing temperature, expressing the increase in the interaction of the domain wall with the particle's stress field, which produces barriers to the domain-wall movement. TRM is blocked at temperature T_B, when the wall can no longer overcome such an energy barrier. Although at T_B the wall may have barely been blocked (i.e., wall movement at T_B might have been blocked near the top of a particular energy barrier) as the temperature decreases below T_B, the energy barriers increase faster than the other energy terms, because of the greater temperature dependence of U_W such that near room temperature (T_R) the wall

finds itself blocked by a formidable barrier.

With decreasing temperature U_D increases more rapidly than U_M; at $T < T_B$ there is net demagnetizing pressure on the wall, favouring a new wall position, which should yield a more demagnetized particle. This is equivalent to saying that for $T < T_B$ the wall climbs part way up the potential-energy barrier, but since U_W increases more rapidly than both U_M and U_D the wall remains blocked. When the field is removed at T_R, as for measuring the remanence, the net negative pressure on the domain wall is greater yet, so that in the absence of stress accumulations, $J = 0$ would be the equilibrium state for the particle's magnetization. However, the wall is blocked and there is no change in the remanence.

As the particle is reheated to T_B in zero field, J_S decreases affecting a decrease of the energy barriers. The absence of an external field during the thermal demagnetization step, places the particle in a higher energy configuration than during the blocking of the original TRM. Equivalently, the absence of an external field produces a net negative pressure acting on the domain wall. The presence of thermal fluctuations implies that there is a finite probability that sufficient energy will be available for the domain wall to overcome its potential-energy barrier. The mechanism by which this energy becomes available is not known, but it is probably related to the probability of generation of spin waves with the required energy. When sufficient energy is available for the domain wall to overcome the energy barrier, the self-demagnetizing pressure:

$$p_D = -2[DSJ_S^2/a]x$$

will drive the wall toward the particle's demagnetized configuration. (During the acquisition of the original TRM the availability of sufficient energy to overcome the barrier will result in no net demagnetization, because at T_B and in the presence of h there is no net pressure on the domain wall.)

During the PTRM step the particle is reheated to T_B in the presence of an external field. The domain wall is subjected to a magnetizing pressure:

$$p = 2J_S h - 2[DJ_S^2]x$$

which drives the wall to the demagnetized side of the "blocking" potential barrier. Due to the presence of the external field during the PTRM step, the input of slightly more energy than during the thermal demagnetization is required for the wall to overcome the barrier. In addition, the magnitude of the outward (magnetizing) pressure on the wall during the PTRM step is less than the demagnetizing pressure during the thermal demagnetization step. Thus a two-domain particle which is thermally demagnetized by heating to a particular temperature T_1 is likely to be remagnetized with less remanence when reheated to T_1 in an external field of equal intensity to the original TRM-producing field. This model requires higher temperature or more intense field during the PTRM step to produce $\Delta J_t = \Delta J_n$. In terms of viscous remanence, the above model predicts that at a given temperature the spontaneous decay of TRM is greater than the viscous acquisition in an external field equal to the TRM field. This conclusion is identical to that of Dunlop (1973b, pp. 873–879), regarding the viscous magnetization of two-domain particles.

For the MD model discussed above the PNRM lost during thermal demagnetization of a total TRM between T_R and some temperature $T_1 < T_C$ exceeds the PTRM acquired by cooling from T_1 to T_R in an external field of equal intensity to the field which imparted the original TRM. For an ensemble of MD particles with distributed blocking temperatures, this would lead to the concave-up ΔJ_n–ΔJ_t curves that are observed for samples containing MD particles. Since the particles which are critical in the discussion of the above model are statistically demagnetized after the thermal demagnetization step, the same behaviour is expected whether the PTRM is induced parallel to antiparallel to the original remanence. Concave-up ΔJ_n–ΔJ_t curves are predicted for both the Thelliers' (1959) and Coe's (1967a,b) executions of the Thellier method. It is predicted that the degree of curvature of the ΔJ_n–ΔJ_t curves will increase for increasing fractions of MD remanence. Generalizing the above model to include more complex MD particles would seem to explain the observed concave-up ΔJ_n–ΔJ_t curves of samples *2–4*, and it should apply equally well to MD particles of all ferri- and ferromagnetic substances. Clearly, this mechanism is valid only for MD particles. Therefore, the linear ΔJ_n–ΔJ_t curves of samples *5–9* suggest that for equidimensional magnetite particles with diameters less than 0.25 μm the acquisition of TRM and its thermal demagnetization are not through domain-wall movements.

7. Discussion

We have seen that samples containing SD magnetite particles (sample *11*) and samples containing small particles, which are entirely in the submicron size range (samples *5–9*) behave ideally in the Thellier sense. In addition, linear $\Delta J_n - \Delta J_t$ plots of the magnetite samples correlate with high stabilities with respect to alternating fields, AF ($H_{1/2} \gtrsim 300$ Oe). This has also been observed by Kono (1974) for volcanic rocks. On the other hand, there is no apparent relationship between blocking temperatures, $T_{1/2}$, and the degree of linearity of the PNRM–PTRM curves. There is high correlation between linear PNRM–PTRM curves and high magnetization resistance to temperature cycles in zero field to below magnetite's isotropic temperature. Such low-temperature cycles in magnetites provide a measure for the fraction of the remanence residing in non-SD sized particles. Comparison of columns 8 and 3 of Table I shows that the low-temperature cycles provide a better measure than AF or thermal stability for the relative magnetite grain sizes of the samples. More than 50% of the TRM of samples *2* and *3* decays after three successive low-temperature cycles, but there is less than 10% decay of the TRM of samples whose magnetite particles are wholly submicron. The behaviour of sample *4* is particularly interesting because of its high AF stability, $H_{1/2} = 380$ Oe (second only to sample *11*), although 18% of its remanence decays after three low-temperature cycles. The concave-up $\Delta J_n - \Delta J_t$ curve for sample *4* suggests that for magnetites the low-temperature decay character is more reliable than AF stability as a predictor for ideal behaviour in a Thellier experiment.

Whenever non-linearities in the $\Delta J_n - \Delta J_t$ curves are observed during a Thellier experiment, it is common to calculate the ancient field intensity from a linear approximation to the lower-temperature data, the rationale being that physical and chemical changes that irreversibly alter the sample's TRM properties are much more likely at elevated temperatures. This has been recently demonstrated by Coe and Grommé (1973). The experiments discussed here show that whenever multidomain particles contribute to a sample's TRM, non-linear PNRM–PTRM curves may result, which are concave-up with respect to the "ideal" line, and this behaviour is not associated with irreversible changes of the sample. Rather, it is due to intrinsic, reproducible differences between the remanence of MD particles on the one hand and SD and submicron magnetite particles on the other, and to the lack of symmetry of the domain-wall movements during the two heatings of the Thellier experiment.

A linear approximation to the lower-temperature data of samples *2–4* would lead to substantial errors in the paleointensity, which would always lead to paleointensities which are higher than the actual field, although the ratio of the end-points gives the correct results. On the other hand, if only the higher blocking-temperature data are used, the analysis would lead to apparent paleointensities lower than the actual field. Similar behaviour was observed by Coe (1967a,b) for the 1915 A.D. Mount Lassen dacite. Coe speculated at that time that the curious behaviour was due to the presence of multidomain particles.

It has been amply demonstrated that high temperatures can and often do cause irreversible changes in a sample's TRM properties, thus it is *not* advocated that the NRM/TRM ratio be used for paleointensity determinations. Such a procedure would discard the consistency checks for which the Thellier method was originally developed. Conversely, the experiments discussed here show that non-linear PNRM–PTRM diagrams cannot be assumed to be caused by irreversible changes of the TRM properties of the sample. If the geomagnetic intensity is to be determined using non-linear PNRM–PTRM diagrams, further experiments must be conducted to determine the cause of the non-linearity. For example, the PTRM test proposed by Thellier and Thellier (1959) can be used to redetermine PTRM acquisition at lower temperatures. Changes in the PTRM show that irreversible changes have taken place. However, Coe (1967b) pointed out that the Thelliers' PTRM test cannot detect irreversible changes of magnetic regions with blocking temperatures higher than the PTRM intervals; thus reproducibility of PTRM is a necessary but not sufficient condition to prove that no irreversible changes have occurred in the sample's TRM properties. A further test to check whether observed non-linearities are intrinsic to the sample's magnetic properties or whether they are due to irreversible changes of the sample is to repeat the Thellier experiment, using as "NRM" a laboratory TRM. If the same or similar non-linear features are observed in both Thellier experiments,

and if the end-points of the P'NRM'–PTRM curve reproduce the laboratory field, then the linear approximation to the lower temperature data might lead to an erroneous paleointensity. The NRM/TRM ratio should not be used by itself for paleointensity determinations, unless further tests justify its use.

If tests show that a sample's TRM properties undergo irreversible changes at higher temperatures, then an intensity determination, using a linear approximation to the lower-temperature data might yield a reliable result, provided the samples' NRM's are characterized by high AF stabilities, $H_{1/2} \gtrsim 300$ Oe. The last statement is very subjective and depends on the accuracy desired for the paleointensity determination and on the fraction of the NRM used to obtain the linear approximation. For a particular accuracy, lesser stabilities would require that a relatively greater fraction of the NRM be used and conversely; see Table II. Sample *4* couples non-linear behaviour with high AF stability of its TRM. However, using 60% of the NRM for a linear approximation, the resulting error in the intensity is only 5%, which is an acceptable error for most experiments. For magnetites and titanomagnetites that exhibit a low-temperature magnetocrystalline anisotropy transition [less than 10% ulvöspinel, according to Syono (1965)] a better stability test to assess the potential linearity of the PNRM–PTRM curves is the stability of the magnetization subject to temperature cycles to below the isotropic point. In magnetites, TRM decay of less than 10% is an indication for linear PNRM–PTRM curves.

As a consequence of the above discussion, it might be prudent to re-assess existing paleointensity data with particular emphasis on cases where a linear approximation to the lower-temperature points is used without sufficient justification in determining paleointensities.

In the preceding discussion we have been preoccupied with linear $\Delta J_n - \Delta J_t$ curves. If the framework outlined by the assumptions of the Thellier method is satisfied and if the resulting Thellier experiment yields a linear $\Delta J_n - \Delta J_t$ curve for the sample's entire blocking-temperature spectrum, then the geomagnetic intensity is obtained directly from the slope of the line. However, a linear $\Delta J_n - \Delta J_t$ plot in itself, is a necessary but not sufficient condition for a reliable and accurate intensity determination. It is easy to visualize a post-igneous process whereby assumption (2) (p. 247) is violated through recrystallization or oxidation and unmixing of the magnetic minerals. Such a change might be subtle and difficult to detect and the resulting magnetization (no longer the original TRM) might be stable, yielding $\Delta J_n - \Delta J_t$ curves that are linear, whose slope is totally unrelated to the paleofield.

8. Conclusions

The Thellier method for paleointensity determinations has been applied to prepared samples containing magnetite whose mean particle sizes range from SD to MD. The following are the principal findings.

(1) Linear (ideal) $\Delta J_n - \Delta J_t$ curves are obtained for samples containing SD and submicron magnetite particles.

(2) There is positive correlation between linear $\Delta J_n - \Delta J_t$ curves and high stability of the magnetization: (1) with respect to AF demagnetization, $H_{1/2} \gtrsim 300$ Oe; and (2) with respect to temperature cycles in zero field to below magnetite's isotropic temperature, $J/J_t > 0.90$.

(3) When a large fraction of the remanence resides in MD particles, non-linear (concave-up) $\Delta J_n - \Delta J_t$ curves are observed such that a linear approximation to the lower blocking-temperature data leads to apparent paleointensities that are higher than the actual paleofield; however, the ratio of the end-points, NRM/TRM, yields the correct (laboratory) intensity.

(4) The non-linear (non-ideal) $\Delta J_n - \Delta J_t$ curves, associated with MD particles, are explained in terms of the lack of symmetry of the domain-wall movements during the two heatings of the Thellier experiment.

(5) Paleointensity determinations should be based on data spanning the sample's entire blocking-temperature spectrum, and, whenever non-ideal behaviour is observed, further tests should be conducted to determine whether the non-linear behaviour is caused by irreversible physical or chemical changes of the sample or whether the non-linear behaviour is intrinsic to the magnetic particles.

(6) If non-linearities are caused by irreversible changes of a magnetite containing sample, an accurate paleointensity might be obtained from a linear approximation of the unaltered lower-temperature data, provided the sample is characterized by high AF sta-

bility, $H_{1/2} \gtrsim 300$ Oe, and high stability with respect to temperature cycles in zero field to below the isotropic point, $J/J_t > 0.90$.

(7) Paleointensities should not be obtained solely from the ratio NRM/TRM, because such a procedure would forfeit the built-in consistency checks for which the Thellier method was so painstakingly developed.

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