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Key Points:
- Paleofields from single crystals have small additional errors due to their small number of particles
- Nanomagnetic imaging of cloudy zones of meteorites does not allow conclusions about the paleofield
- Average intensity centimeter-size samples usually contain enough magnetic particles to be accurate recorders

Supporting Information:
- Data S1

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Does size matter? Statistical limits of paleomagnetic field reconstruction from small rock specimens

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Abstract As samples of ever decreasing sizes are being studied paleomagnetically, care has to be taken that the underlying assumptions of statistical thermodynamics (Maxwell-Boltzmann statistics) are being met. Here we determine how many grains and how large a magnetic moment a sample needs to have to be able to accurately record an ambient field. It is found that for samples with a thermoremanent magnetic moment larger than 10^{-11} Am^2 the assumption of a sufficiently large number of grains is usually given. Standard 25 mm diameter paleomagnetic samples usually contain enough magnetic grains such that statistical errors are negligible, but “single silicate crystal” works on, for example, zircon, plagioclase, and olivine crystals are approaching the limits of what is physically possible, leading to statistic errors in both the angular deviation and paleointensity that are comparable to other sources of error. The reliability of nanopaleomagnetic imaging techniques capable of resolving individual grains (used, for example, to study the cloudy zone in meteorites), however, is questionable due to the limited area of the material covered.

1. Introduction

A recent trend in paleomagnetism is the study of samples of ever decreasing sizes, going down even to microscopic scales (“nanopaleomagnetism”). These include recent works on meteorites using Superconducting Quantum Interference Device (SQUID) microscopy on olivine-bearing chondrules of submillimeter size [*Fu et al.*, 2014] and X-ray photoemission electron microscopy (XPEEM) on the cloudy zones in iron meteorites of 400 nm width [*Bryson et al.*, 2014a], as well as works on single millimeter-sized plagioclase crystals with magnetic inclusions [*Cottrell and Tarduno*, 1999; *Tarduno et al.*, 2001, 2006], quartz crystals with magnetic inclusions [*Tarduno et al.*, 2010], olivine with magnetic inclusions from pallasite meteorites [*Tarduno et al.*, 2012], and recently on zircon crystals [*Tarduno et al.*, 2015] using three-component SQUID magnetometers. These methods have a variety of advantages over conventional paleomagnetic methods, in particular the study of ideal magnetic recorders enclosed in protecting minerals like plagioclase [*Tarduno et al.*, 2006]. Despite the great potential of these techniques, care has to be taken regarding one of the fundamental assumptions of paleomagnetism: that samples contain a sufficiently large number of magnetic grains that the laws of statistical thermodynamics (Maxwell-Boltzmann statistics) can be applied at the time of acquisition of a remanent magnetization. If a sample does not contain a sufficiently large number of particles in a Maxwell-Boltzmann statistical sense, then it will not record the ambient field accurately at the time of magnetic acquisition (i.e., blocking). Hence, even in the hypothetical case of a perfect measurement of the remanent magnetization of a sample, paleofield could not be accurately reconstructed from the remanence data. However, until now, this “large” number has not been quantified. Here we derive an expression to calculate the number N of particles that a sample needs to contain such that the remanent magnetization accurately represents the ambient field at the time of recording according to Maxwell-Boltzmann statistics that current theories of rock magnetism and paleointensity are based on.

2. Statistical Error of Paleointensities

The aim is to calculate the statistical error of the total recorded magnetization for an ensemble of N magnetic particles at the time when a rock is acquiring a remanent magnetization (note that ensemble here can refer to the magnetic grains in a single sample or in various samples that recorded the same event). The energy of a single spheroidal single-domain (SD) grain whose easy axis is at angle ϕ to an external field H_0 is approximately given by [see, e.g., *Dunlop and Özdemir*, 1997, equation (8.5)]

$$E_1(\phi) = -E\cos\phi = -\mu_0 V_B M_s\left(T_B\right) H_0 \cos\phi\,, \tag{1}$$

for the magnetization aligned along the easy axis in field direction, where μ_0 is the vacuum permeability, V_B is the volume of the grain at the time of blocking, and $M_s\left(T_B\right)$ is its spontaneous magnetization at the blocking temperature. If the magnetization vector is in the opposite direction, the energy is

$$E_2(\phi) = -E\cos\phi = \mu_0 V_B M_s\left(T_B\right) H_0 \cos\phi\,. \tag{2}$$

Let us suppose that the external field H_0 is along the x axis. For randomly oriented grains, the probability that a grain is at an angle between ϕ and $\phi + d\phi$ to the x axis is found by integrating the probability distribution

$$f(\phi)\; d\phi = \sin\phi\, d\phi\,, \tag{3}$$

where ϕ goes from 0 to $\pi/2$, over a semisphere. The particle can only be magnetized in two possible directions: the direction that is closest to the applied field direction (let us call this the positive direction) and the direction that is farther away. If the ensemble of particles is in thermodynamic equilibrium with the ambient field at the time of blocking, then the probability that one particular grain is magnetized in the positive direction is given by a Maxwell-Boltzmann distribution

$$p(\phi) = \frac{e^{x_B\cos\phi}}{e^{x_B\cos\phi} + e^{-x_B\cos\phi}} = \frac{1}{2}\left[1 + \tanh\left(x_B\cos\phi\right)\right]\,, \tag{4}$$

where

$$x_B = \frac{\mu_0 V_B M_s\left(T_B\right) H_0}{kT_B}\,. \tag{5}$$

For small external fields (small here means significantly smaller than the microscopic coercivity H_c of the grain: as blocking occurs over timescales between seconds and thousands of years, the ratio $\mu_0 V M_s H_C/kT$, which by the blocking condition equals $\ln(t/\tau_0)$, is of the order of approximately 25 to 40. Hence, if the external field H_0 is a few hundred times smaller than H_C, then x_B can be considered small), this is approximately

$$p(\phi) \approx \frac{1}{2}\left(1 + x_B\cos\phi\right)\,. \tag{6}$$

Once the ensemble has become magnetized (blocked), the remanent magnetization can be measured in the laboratory. The results, however, will only be meaningful if the error introduced to the measured magnetization by the statistical thermodynamical variation is small. We therefore have to calculate (1) the expected (mean) measured remanent magnetization and (2) the standard deviation of the measured remanent magnetization. To calculate the mean remanent magnetization that is measured after the grains are blocked, we first note that the component of the magnetic moment along the x axis of one particular grain is

$$m_x = \pm M_s(T) V \cos\phi\,, \tag{7}$$

where T is the temperature at which the sample is measured and V is the grain volume at the time of measuring (which may have changed since blocking due to grain growth). The mean value of the magnetic moment $\bar{m}_x$ along the x axis is found by integrating the magnetization over the probabilities for their orientations $f(\phi)$, equation (3), and remanent magnetizations $p(\phi)$, equation (6):

$$\bar{m}_x = \int_0^{\pi/2} \left[m_x f p - m_x f(1-p)\right]\, \mathrm{d}\phi\,. \tag{8}$$

Substituting for m_x, $f(\phi)$, and $p(\phi)$, one gets

$$\bar{m}_x = \int_0^{\pi/2} M_s(T) V x_B \sin\phi \cos^2\phi\, \mathrm{d}\phi = \frac{1}{3} M_s(T) V x_B\,. \tag{9}$$

Similarly, the standard variation is given by

$$\sigma_x^2 = \int_0^{\pi/2} \left[m_x^2 fp + (-m_x)^2 f(1-p) \right] \, \mathrm{d}\phi - \bar{m}_x^2 \, .$$

Substituting and integrating, one gets

$$\sigma_x = M_s(T) V \sqrt{\frac{1}{3} - \left(\frac{x_B}{3} \right)^2} \, . \tag{10}$$

As x_B is small, this is

$$\sigma_x = \frac{1}{\sqrt{3}} M_s(T) V \, .$$

For a sample that contains an ensemble of N grains the mean total magnetic moment $\bar{M}_x$ in the x_B direction is

$$\bar{M}_x = N \bar{m}_x = \frac{1}{3} N M_s(T) V x_B \, , \tag{11}$$

and the standard deviation is

$$\sigma_{x,N} = \sqrt{N} \sigma_x = \sqrt{\frac{N}{3}} M_s(T) V \, . \tag{12}$$

The number of grains needed to get a relative error of $\delta m_x = \sigma_{x,N} / \bar{M}_x$ can then be obtained by rearranging

$$N = \frac{3}{x_B^2 \left(\delta m_x \right)^2} = \frac{3 k^2 T_B^2}{\mu_0^2 V_B^2 M_s^2 \left(T_B \right) H_0^2 \left(\delta m_x \right)^2} \, , \tag{13}$$

which translates into a necessary total magnetic moment of

$$\bar{M}_x(T) = \frac{V M_s(T) k T_B}{V_B M_s(T_B) \mu_0 H_0 (\delta m_x)^2} \, . \tag{14}$$

If the remanence was acquired by a thermoremanent magnetization (TRM), then the volume of the grains does not change and $V = V_B$, such that

$$\bar{M}_x(T) = \frac{M_s(T) k T_B}{M_s \left(T_B \right) \mu_0 H_0 (\delta m_x)^2} \, . \tag{15}$$

This equation provides an easy way to decide whether or not a sample has a sufficiently strong magnetic moment to obtain accurate paleointensity data. In a thermal demagnetization experiment one can get an approximate value by taking a single temperature T_B where most unblocking occurs. The change in magnetization around this temperature should be at least the value given by equation (15). If it is less, the inferred paleointensity value is not reliable. For example, if a paleointensity value is obtained using demagnetization data between 200°C and 300°C, then the change in the magnetic moment of the sample between these two temperatures should be greater than the value given by the equation for $T \approx 250$°C. In the following, when quoting natural remanent/thermoremanent magnetization (NRM/TRM) intensities, it is understood that these values refer to the change in NRM/TRM intensity at the temperatures where most blocking occurs. In paleointensity experiments this may often be only a small percentage of the initial NRM, and in paleodirection experiments, this intensity is limited by the possible presence of any magnetic overprints.

The equations are still valid when the sample is an alternating field (AF) demagnetized at room temperature or when its magnetization is measured using microscopic techniques, provided one can make an estimate of the blocking temperature. We can use the blocking condition

$$V_B = \frac{k T_B \ln \left(t / \tau_0 \right)}{\mu_0 H_K \left(T_B \right) M_s \left(T_B \right)} \, , \tag{16}$$

to solve equations (13) and (14) to

$$N = \frac{3H_K^2\left(T_B\right)}{H_0^2 \ln^2\left(t/\tau_0\right)\left(\delta m_x\right)^2} \tag{17}$$

and

$$\bar{M}_x(T) = \frac{V M_s(T) H_K\left(T_B\right)}{\ln\left(t/\tau_0\right) H_0 \left(\delta m_x\right)^2} . \tag{18}$$

3. Statistical Error of Paleodirections

In an analogous way to equation (7), the component $m_\perp$ of the magnetization along an axis perpendicular to the field is given by

$$m_\perp = \pm M_s(T) V \sin\phi \sin\theta , \tag{19}$$

where θ is the azimuth of the particle's easy axis. The mean value of the magnetization $\bar{m}_\perp$ along the perpendicular axis is found in the same way as in equation (8), however, integrating over the azimuth as well:

$$\bar{m}_\perp = \int_0^{\pi/2} \mathrm{d}\phi \int_0^{2\pi} \mathrm{d}\theta \left[m_\perp f p - m_\perp f (1-p)\right] , \tag{20}$$

which after substituting and solving equals 0, which is expected as the magnetization should on average align with the field and have no perpendicular component. The standard deviation, however, is nonzero and is given by

$$\sigma_\perp^2 = \int_0^{\pi/2} \mathrm{d}\phi \int_0^{2\pi} \mathrm{d}\theta \left[m_\perp^2 f p + \left(-m_\perp\right)^2 f (1-p)\right] , \tag{21}$$

which after solving is found to be

$$\sigma_\perp = M_s(T) V \sqrt{\frac{2\pi}{3}} \tag{22}$$

and

$$\sigma_{N,\perp} = M_s(T) V \sqrt{\frac{2\pi N}{3}} .$$

The angle α of the magnetization vector **m** to the x axis is given by

$$\alpha = \tan^{-1}\left(\frac{\sigma_\perp}{\bar{m}_x}\right) = \tan^{-1}\left(\frac{\sqrt{6\pi}}{x_B}\right) .$$

The angle α_{95} of the magnetization vector to the x axis for the 95% confidence limit (which corresponds to two standard deviations) for an ensemble of N particles is similarly

$$\alpha_{95} = \tan^{-1}\left(\frac{2\sigma_{N,\perp}}{\bar{M}_x}\right) = \tan^{-1}\left(\frac{1}{x_B}\sqrt{\frac{8\pi}{3N}}\right) , \tag{23}$$

which solving for N gives

$$N = \frac{8\pi k^2 T_B^2}{3\mu_0^2 V_B^2 M_s^2\left(T_B\right) H_0^2 \tan^2\alpha_{95}} .$$

For the blocking condition (16) this is

$$N = \frac{8\pi H_K^2\left(T_B\right)}{3H_0^2 \ln^2\left(t/\tau_0\right)\tan^2\alpha_{95}} . \tag{24}$$

Again, this can be rewritten in terms of total magnetic moment using equation (11)

$$\bar{M}_x(T) = \frac{8\pi k T_B V M_s(T)}{9 V_B M_s\left(T_B\right) \mu_0 H_0 \tan^2 \alpha_{95}}. \tag{25}$$

These equations are formally equivalent to equations (13) and (14), and in the same way they provide a minimum intensity and grain number estimates that are necessary to obtain a statistical directional error less than α_{95}. Numerically, α_{95} and δm_x are almost identical; for example, $\alpha_{95} = 1°$ corresponds to $\delta m_x = 1\%$, $\alpha_{95} = 10°$ corresponds to $\delta m_x = 10\%$, and $\alpha_{95} = 90°$ corresponds to $\delta m_x = 94\%$. Also, these statistical confidence limits can easily be converted one into the other: the $\alpha_{95} = 1°/\delta m_x = 1\%$ confidence limit requires 100 times the magnetic moment $\bar{M}_x$ and grain number N of the $\alpha_{95} = 10°/\delta m_x = 10\%$ confidence limit and 10,000 times the moment and number of the 90°94% confidence limit.

4. Pseudo-Single-Domain Grains

The above derivation assumed single-domain grains, but it can be extended to small pseudo-single-domain (PSD) grains using a simple model: Although the volume of PSD grains is larger than SD grains, their net magnetic moment is significantly smaller, as they contain nonuniform vortex states. From numerical simulations, *Muxworthy et al.* [2003] estimated that the remanent magnetization to saturation magnetization ratio M_{RS}/M_S of a 150 nm PSD magnetite grain is about 10% that of a 30 nm SD grain. The moment is contained within the vortex core. We can model this as a first approximation by adding a factor $w = 10\%$ to all occurrences of the volume V and blocking volume V_B in the above derivation. Equation (13) is amended by multiplying by w where $w = 0.1$ for grains larger than 100 nm for magnetite and tetrataenite and 20 nm for iron, and $w = 1$ for smaller volumes:

$$N = \frac{3k^2T^2}{\mu_0^2 w^2 V_B^2 M_s^2 H_0^2 \left(\delta m_x\right)^2} \tag{26}$$

and similarly for the other equations. In this simple model, the magnetic moment of a PSD grain is strongly reduced as compared to SD grains. Therefore, its likelihood of aligning with the applied field is smaller, leading to a larger number of grains required to obtain reliable statistics.

5. Estimates for Common Minerals

We can estimate the number of grains/magnitude of the total magnetic moment necessary to obtain accurate paleointensity and paleodirection estimates. We can calculate the required number of grains as a function of blocking temperature and blocking volume using equation (13). In practice, when trying to assess the statistical thermodynamical accuracy of a sample, one needs to determine M_s and estimate the blocking volume V_B of the sample, which is often difficult. One therefore needs to keep in mind that if, for example, one's estimate of V_B is off by a factor of 10 (i.e., off by a factor of 2 in each dimension), then the number of grains will change by a factor of 100. Nevertheless, in many cases, a rough order of magnitude estimate of the required number of grains is sufficient to determine either that the statistical thermodynamical error is negligible or that it is very large. For the spontaneous magnetization we will use the analytical approximation

$$M_s(T) = M_{s,0}\sqrt{1 - \frac{T}{T_C}},$$

where $M_{s,0}$ is the spontaneous magnetization at room temperature and T_C is the Curie temperature. Due to their importance in natural terrestrial and extraterrestrial rocks, we calculated the confidence limits for three materials: iron (αFe), magnetite, and tetrataenite (iron-nickel alloy). The values of $M_{s,0}$ and T_C that are used are given in Table 1. The resulting 1°/1% confidence limits are drawn in Figure 1 for an ambient field of $H_0 = 50\mu T$. This confidence limit can be considered sufficient for any paleomagnetic study. The contour lines show $\log_{10} N$ of the number of grains needed as a function of blocking temperature and grain volume at the time of blocking. The blocking volume and the blocking temperature are related to each other by equation (16), and this is indicated by the bold line in the figure.

The equations for the numbers of grains necessary are valid for both thermoremanent (TRM) and chemical remanent magnetizations (CRM). In the TRM case, a grain cools from a high temperature, on the right of the

Table 1. Spontaneous Magnetization at Room Temperature $M_{s,0}$ and Curie Temperature T_C for Common Magnetic Minerals, Together With the Results for the Number of Grains N and Magnetic Moment $\bar{M}_x$ Needed to Obtain a 1°/1% and 10°/10% Confidence Limit for Grains

Mineral	$M_{s,0}$ (kA/m)	T_C (°C)	N (-)	$\bar{M}_x$ (kA/m)	N (-)	$\bar{M}_x$ (kA/m)	N (-)	$\bar{M}_x$ (kA/m)	N (-)	$\bar{M}_x$ (kA/m)
Iron (αFe)	1715	765	10^{10}	10^{-12}	10^{8}	10^{-11}	10^{10}	10^{-12}	10^{8}	10^{-11}
Magnetite	480	580	10^{10}	10^{-12}	10^{7}	10^{-11}	10^{10}	10^{-12}	10^{7}	10^{-11}
Tetrataenite	1300	550	10^{9}	10^{-12}	10^{8}	10^{-11}	10^{9}	10^{-12}	10^{8}	10^{-11}
T_B (°C)			20	20	$T_C - 10$	$T_C - 10$	20	20	$T_C - 10$	$T_C - 10$
$\alpha_{95}/\delta m_x$ (°/%)			1	1	1	1	10	10	10	10

plot, to a cooler temperature, i.e., toward the left until it has reached the bold line (representing the blocking condition), at which time it blocks. This may often be the case for magnetite and iron. For a CRM, a small grain, on the bottom of the graph, grows and moves upward in the graph until it reaches the bold line and blocks. Note that the grain may continue to grow afterward, but for the treatment here it is the volume at which the grain becomes blocked that is of interest. Although the exact blocking mechanism of tetrataenite is not well understood, it is most likely a CRM or thermochemical remanent magnetization (TCRM) as it forms from slow cooling and ordering at 320°C and can therefore be approximately described by this simple model.

The dotted contours in Figure 1 represent the grain volumes of PSD grains. As these have smaller magnetic moments (hence a smaller tendency to align with the external field) despite their large volumes, they require larger numbers for the same confidence limit than SD grains. The discontinuity of the graph again corresponds to the grain size that starts to form vortex/PSD states.

As all blocking occurs on the bold line, we can plot the necessary number of grains along this line as a function of blocking temperature only by making use of equation (17). For simplicity, we are assuming that the magnetic properties of the grains are dominated by shape anisotropy

$$H_K = \left(N_b - N_a\right) M_s ,$$

where $\left(N_b - N_a\right)$ is the anisotropy factor. The exact value is not significant, so we assume 0.5, which is the value for needle-like grains. The result is plotted in Figure 2. As the blocking volume increases with blocking temperature, the number of grains decreases with blocking temperature. The number of grains needed for a given confidence limit follows the shape of the $M_s\left(T_B\right)$ curves: At low temperatures, the number is relatively constant, being of the order of billions of grains. Only very close to the Curie temperature are fewer grains necessary, reducing the numbers by about 2 orders of magnitude. The approximate numbers are summarized in Table 1.

Using equation (15), it is also possible to calculate a minimum magnetic moment that is required for a given confidence limit (Figure 3). As samples are usually measured at room temperature, we can assume $T = 20$°C. Although the required number of grains decreases with increasing blocking temperatures (Figure 2), the required magnetic moment increases, because high blocking temperatures imply large grains that have a large magnetic moment.

Figure 3 shows three confidence limits: a 1°/1% confidence limit, a 10°/10% confidence limit, and a 90°/94% confidence limit. In general, if the confidence limit is smaller than 1°/1%, we can assume that the error introduced due to the statistical thermodynamics nature of the remanence acquisition is negligible compared to other error sources commonly encountered in paleomagnetic studies (e.g., orientation and instrumental uncertainties). For 10°/10%, caution has to be taken, as this uncertainty is likely to be of the order of, or even larger than, other error sources. Nevertheless, a 10°/10% confidence limit is probably acceptable for novel techniques in nanopaleomagnetism. The confidence limit of 90°/94%, however, represents a lower limit below which paleomagnetic remanence data do not allow to make conclusions about the presence or absence of a paleofield (even less about its intensity or direction) because the (statistical thermodynamical) error of the magnetization is of the same order as the magnitude itself. Hence, we propose that caution should be taken when working with particle numbers such that the confidence limit is larger than 1°/1% and that now conclusions should be made about the paleofield when particle numbers are so low that the confidence limit is

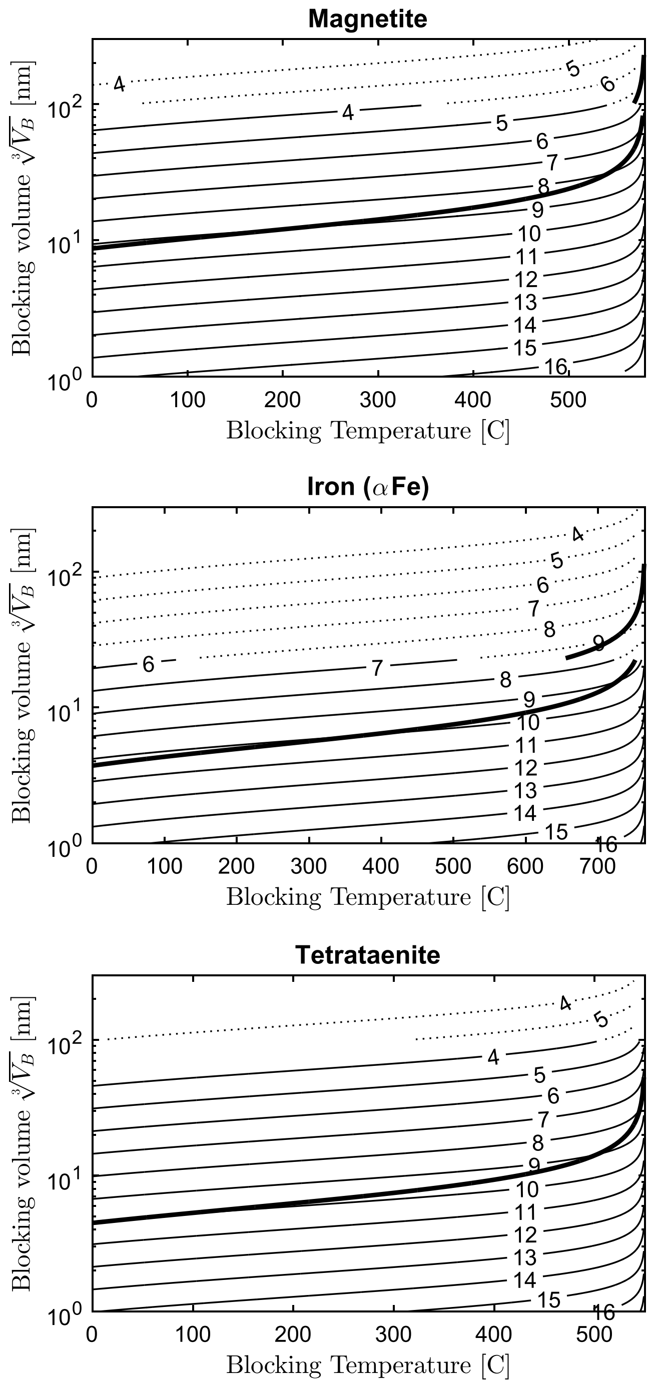

Figure 1. Contours indicate the number of grains $\log_{10}N$ that are required to obtain accurate paleointensity and paleodirection estimates with errors less than $\alpha_{95} = 1°$ for paleodirections and $\delta m_x = 1\%$ for paleointensity (1°/1% confidence limit). Bold line indicates blocking volume as a function of temperature according to equation (16). Dotted contours indicate PSD grains.

larger than 90°/94%. As can be seen, if blocking occurs significantly below the Curie temperature, a magnetic moment of 10^{-11} Am^2 is needed for the 1°/1% confidence limit, 10^{-13} Am^2 for the 10°/10% confidence limit, and 10^{-15} Am^2 for the 90°/94% confidence limit, for all the minerals.

Although the equations for the numbers of grains necessary are valid for both TRMs and CRMs, equation (15) for the required magnetic moment made the additional assumption that the grain volume is equal to the blocking volume. In the case of a CRM by grain growth/exsolution, this condition is not given, as the grain

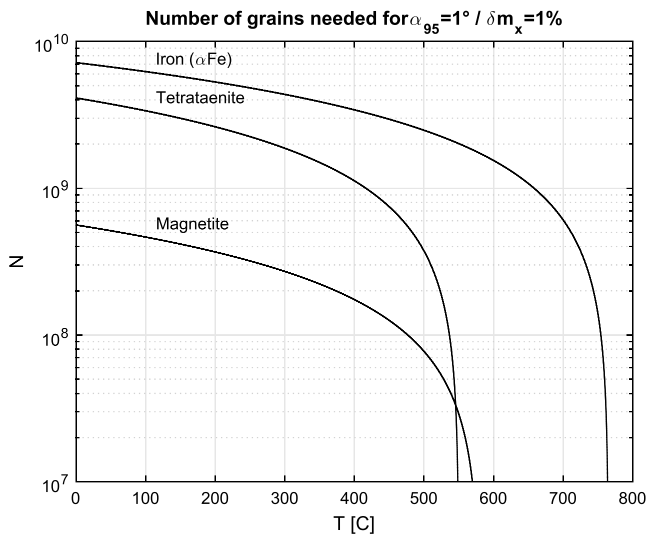

Figure 2. Number of grains necessary to obtain accurate paleointensity and paleodirection estimates versus temperature where most blocking occurs for common magnetic minerals. Confidence limits obtained from samples with these numbers of grains N have an $\alpha_{95} = 1°$ for paleodirections and a relative error of $\delta m_x = 1\%$ for paleointensity.

generally continues to grow after it is blocked. In this case, an initially small grain may block with a high level of uncertainty because of its weak magnetic moment but then continue to grow and contribute to the total magnetization with a much larger magnetic moment. In order to account for this effect, equation (18) has to be used and is shown in Figure 4. The bold line indicates the grain volume where blocking occurs, but the volume at the time of measurement can be above the line. In order to read off the required magnetic moment of the sample for a 1°/1% confidence limit, one needs to know both the grain size of the sample at the time of measuring and the blocking temperature (at the time of blocking; this translates into the grain size at the time of blocking). If a grain doubles in size after blocking (i.e., volume increases by a factor of 8), then also the required magnetic moment multiplies by 8. Large grains close to or above the SD/PSD threshold may therefore require a significantly higher magnetic moment up to 3 orders of magnitude larger than predicted by the TRM treatment above.

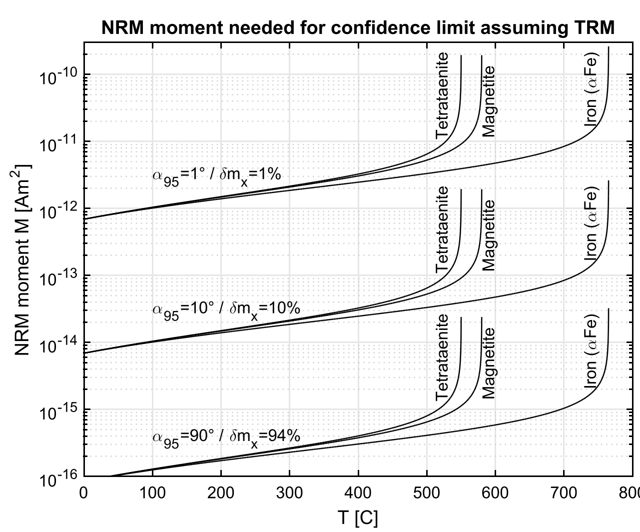

Figure 3. Total magnetic moment of the NRM to obtain accurate paleointensity and paleodirection estimates versus temperature where most blocking occurs. Confidence limits for paleodirections α_{95} and relative errors δm_x for paleointensities are indicated.

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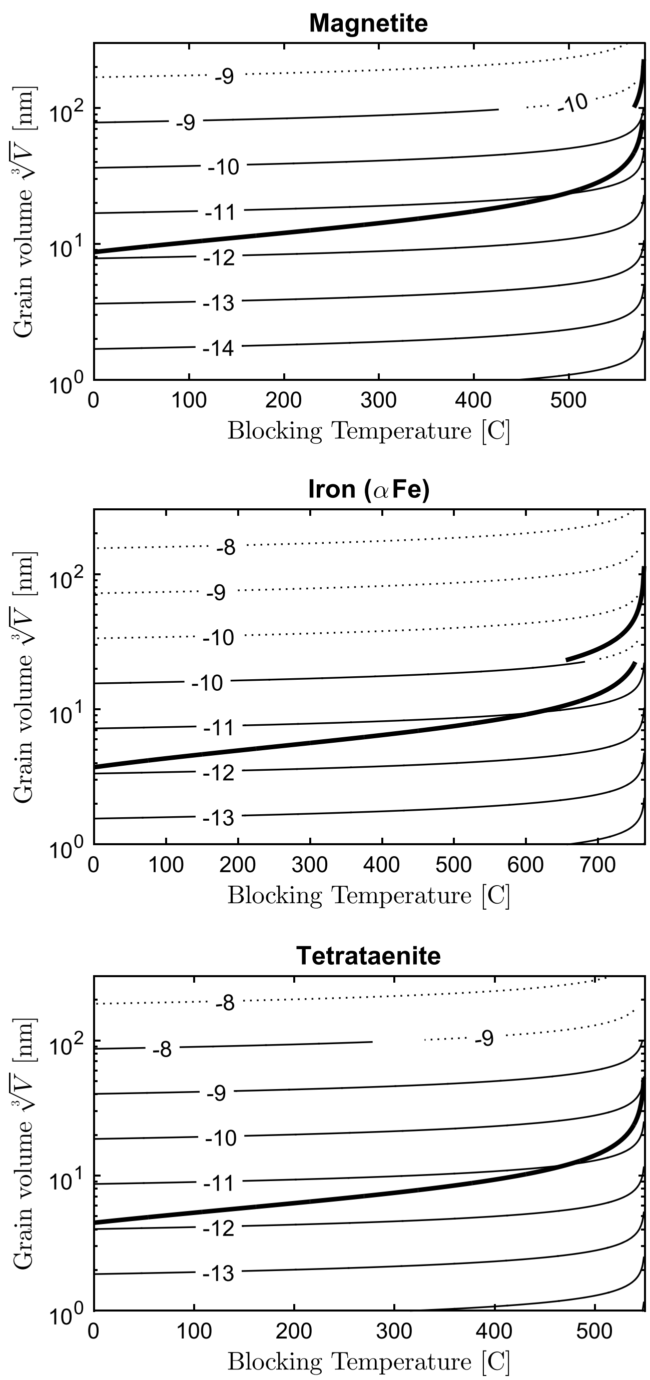

Figure 4. Contours indicate the magnetic moment $\log_{10} M$ (in Am^2) of the natural remanent magnetization necessary to obtain accurate paleointensity and paleodirection estimates with errors less than $\alpha_{95} = 1°$ for paleodirections and $\delta m_x = 1\%$ for paleointensity (1°/1% confidence limit). Bold line indicates blocking volume as a function of temperature according to equation (16). Dotted contours indicate PSD grains. The *y* axis indicates the grain size at the time of measuring the magnetization, which may be larger than the blocking volume in the case of a (thermo-)chemical remanence magnetization (TCRM/CRM).

Table 2. Summary of Typical Magnetic Moments for Samples Using Common Paleomagnetic Techniques and for Recent Nanopaleomagnetic Studies, and Comparison to Their Reliability as a Magnetic Recorder

Sample Size	Magnetic Moment (Am^2)	Technique/Example	Confidence Limit
25 mm core	10^{-8} to 10^{-4}	SQUID / spinner	<0.01°/0.01%
1 cm core	10^{-9} to 10^{-5}	SQUID / spinner	<0.03°/0.03%
Millimeter size	10^{-8} to 10^{-7}	SQUID / Microwave demagnetization	<0.01°/0.01%
10^{-5} m^2	1×10^{-11}	2-D array of nanodots	2°/2%
Millimeter size	$> 5 \times 10^{-11}$	Single plagioclase crystals	<0.3°/0.3%
Hundreds of micrometers	$> 3 \cdot 10^{-12}$	SQUID microscopy on olivine-bearing chondrules	2°/2%
3 μm × 400 nm	250 to 12,000 grains	XPEEM on cloudy zone	>90°/94%

6. Estimates of Common Sample Sizes

It is instructive to compare the results of this study to sample sizes that are commonly used, as well as samples that were used in recent nanopaleomagnetic works. Arguably the most common size is the 1 inch/25 mm core. As the derivation above is based on TRM and CRM acquisition, it only applies to igneous and metamorphic rocks and not to sedimentary rocks. If we suppose a total natural remanent magnetization (NRM) of 1A/m) for a typical igneous/metamorphic rock [*Butler*, 1992; *McElhinny and McFadden*, 2000], then a 25 mm specimen has a total magnetic moment of about 10^{-5} Am^2. Assuming a TRM with blocking temperature not close to the Curie temperature, the confidence limit will be smaller than 0.01°/0.01% (Table 2). Equally, if a 1 cm core is used, the magnetic moment would be about 10 times smaller but still be very accurate. Similarly, the millimeter-sized samples used in microwave demagnetization [*Suttie et al.*, 2010; *Böhnel et al.*, 2009] are strong enough: moments used in that study are around 10^{-8} – 10^{-7} Am^2.

Krása et al. [2009] produced two-dimensional arrays of magnetite particles of precisely controlled sizes and interparticle spacings over areas of 3×10^{-6} to 2×10^{-5} m^2. They and *Muxworthy et al.* [2014] analyzed the fidelity of the magnetic recording of these samples. One of the samples was in the SD range with oblated grains of 74 nm diameter times 39 nm height. From the interparticle separation of 300 nm (center to center) we can estimate the number of grains to be around 10^8. This implies a 2°/2% confidence limit (lower if blocking occurs close to T_C). On the other hand, the TRM/M_{rs} ratio is reported to be 1.3%, and the saturation remanence is $M_{rs} = 0.11 M_s$, which means that the TRM magnetization of the sample is 690 A/m. As the grain volume is 1.5×10^{-22} m^3, the total magnetic moment of a TRM is 1×10^{-11} Am^2. This value has a 0.3°/0.3% confidence limit. Although there is a discrepancy between these two values, which is probably due to imprecise measurements of M_s, M_{rs}, etc., both values agree in that the statistical thermodynamic error in this case is negligible. The experiments conducted by *Muxworthy et al.* [2014] support the conclusion that these samples are accurate recorders for both paleointensity and paleodirections.

Cottrell and Tarduno [1999] and *Tarduno et al.* [2006] used millimeter-sized single plagioclase grains that contained single-domain (SD) and pseudo-single-domain (PSD) magnetite and titanomagnetite particles of sizes about 50 to 350 nm. They selected only plagioclase grains, with a total magnetic moment larger than 5×10^{-11} Am^2. This value has a 0.3°/0.3% confidence limit assuming a TRM. On the other hand, we can estimate the number of grains in their samples: their hysteresis loops, although not originally measured to assess the number of grains and should be taken with caution, indicate spontaneous magnetizations M_S with moments around 10^{-8} Am^2, which translates to a total magnetic volume of around 10^{-14} m^3. Given the grain size ranges from 50 to 350 nm, this implies a number of grains between 10^6 and 10^8. Grains of these sizes would have blocking temperatures within about 10°C from the Curie temperature, in which case a number of the order of 10^7 grains would be needed for a 1°/1% confidence limit and statistical thermodynamical error would probably be negligible. However, the demagnetization plots in the paper show significantly lower unblocking temperatures, too. The authors conclude that these lower unblocking temperatures are due to a high titanium content, in which case they would still be accurate.

Recently, *Tarduno et al.* [2015] investigated Hadean and Paleoarchean single zircon crystals using the same method to find that the geodynamo was already running 4.2 billion years ago, obtaining paleointensity estimates between 1.0 and 0.12 times the present geomagnetic field for the time between 3.3 and 4.2 billion years ago. The zircon crystals had minimum initial NRMs of at least 10^{-12} Am^2, but paleointensity estimates were made using only demagnetization data between 550°C and 580°C. Estimating from the plots in the supporting information, these data account for around 50% of the initial NRM. Hence, we can use 5×10^{-13} Am^2 as a minimum intensity and a blocking temperature around 565°C. For the samples that recorded a strong geodynamic field of 1.0 times the present field, this means a statistical error of 5%; however, for the samples that recorded a weak early geodynamic field of 0.12 times the present field (around $5\mu T$), the error is around 15%. In the supplementary material of *Tarduno et al.* [2015] and in *Tarduno et al.* [2014], the authors calculate that even in the absence of a geodynamo, the solar winds would create a field of $0.6\mu T$. For such a weak field (that a zircon like those investigated by *Tarduno et al.* [2015] would hypothetically have recorded), the statistical error is 45%: This error, although very large, is still distinguishable from the weakest geodynamo-generated fields obtained by the authors, and thus we can conclude that although the paleointensity values in Hadean times have an additional statistical thermodynamic uncertainty, their main conclusion that the geodynamo was already running can be considered reliable.

Fu et al. [2014] used a SQUID microscope to measure olivine-bearing chondrules with magnetic moments between 10^{-10} and 10^{-12} Am^2 due to iron (kamacite) particles. They found magnetic particles of around 60 nm size and report unblocking temperatures between 350 and 750°C. Figure 4 shows that 60 nm grains should block very close to the Curie temperature, i.e., around 750°C, but the lower unblocking temperature would have to be due to smaller particles. For the case of thermoremanent blocking at 750°C, an NRM intensity of 2×10^{-11} Am^2 is required (1°/1% confidence limit). The weakest grains of their work would have a confidence limit of about 4°/4% (note that this is small compared to other error sources in this study). If smaller grains contribute significantly, however, also the weakest samples can be considered accurate with respect to errors arising from statistical thermodynamcis. In order to estimate the number of grains contained in the samples, we can (based on the study by *Muxworthy et al.* [2014]) again assume that the M_{rs}/M_s ratio is around 0.1 and the M_{TRM}/M_{rs} ratio is around 0.01. Then the NRM-quoted moments translate into M_s=10^{-6} to 10^{-8} Am^2, and if the typical grain size is 60 nm, the number of grains is 10^8 to 10^{10}. According to Figure 2, the samples can be considered accurate magnetic recorders from a statistical thermodynamics point of view under the assumption of very high blocking temperatures.

Bryson et al. [2014b, 2015] studied the capability of the cloudy zone in an iron-rich matrix of iron meteorites to record magnetic fields by using XPEEM, which can produce a magnetic map of the sample. It has a resolution of 10 nm over an area of 3 μm × 400 nm, although the map is blurred by a convolution function of about 120 nm. They used transmission electron microscopy and a numerical model to show that the resulting map is nevertheless accurate enough to detect a bias in the magnetization of the grains. In these images it can be seen that the cloudy zone consists of tetrataenite "islands" that gradually change in size along the zone, decreasing from 100 nm to 10 nm in diameter. Hence, for the largest grains (see their Figure A1), the area covered by the XPEEM contains only 250 grains, and the fine-grained cloudy zone may contain only up to 12,000 grains.

The authors argue that the samples are reliable magnetic recorders: In their appendix they do a simple calculation based on Maxwell-Boltzmann statistics similar to the one in this study but assuming three perpendicular easy axes, one of which is aligned with the external field. For 60 nm long grains and a blocking temperature of 320°C they obtain a 50% alignment to the field direction. They did not do an error analysis, but doing so would yield an unrealistically low error of 6% for a single grain (much smaller for hundreds of grains). This is due to the fact that they did not adequately capture the blocking mechanism in their calculation. The authors argue that the acquisition mechanism is a chemical transformation remanent magnetization by spinoidal decomposition. Assuming that this process can be modeled by grain growth, we can apply the theory developed in this work to obtain confidence limits. If blocking occurred at 320°C, then this implies that the grains blocked already when they were only 8 nm large. For a 1°/1% confidence limit, 10^{10} grains are needed in this case, and even for the 90°/94% confidence limit, 10^6 grains are required. We can therefore conclude that these samples are not large enough to obtain accurate paleomagnetic data.

7. Conclusions

As samples of ever decreasing sizes are being studied, care has to be taken that the underlying assumptions of statistical thermodynamics (Maxwell-Boltzmann statistics) are being met. The equations derived in this study provide an easy way to decide for a given sample if the magnetic signal is strong enough to consider it an accurate paleomagnetic recorder from a statistical thermodynamics perspective, by either checking the magnetic moment or the number of particles, the latter of which may be more suitable for microscopic techniques.

It was found that macroscopic samples are certain to have a sufficiently large number of magnetic grains to be considered accurate magnetic recorders, whereas "single-crystal" studies are approaching the limits of what is physically possible. Nanomagnetic imaging techniques investigating individual grains, however, are unlikely to be able to access a sufficiently large number of particles to be statistically significant.

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