Error analysis of frequency-dependent magnetic susceptibility measurements: magnetic viscosity studies with the Bartington MS2 system


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Abstract

Magnetic viscosity of rocks associated with magnetic relaxation of ultrafine ferrimagnetic mineral grains (superparamagnetism) is employed in magnetic grain size measurements. Magnetic viscosity is most often estimated from dual frequency measurements of magnetic susceptibility. The measured susceptibility values bear uncertainty that comprises two components: an instrument error and a drift. The instrument error refers to the accuracy of the measurement system and shows how precise the data are in ideal operation conditions. This error affects especially the low susceptibilities of weak samples, which thus should be measured on a high sensitivity range. Drift is due to external factors, such as changes in the temperature of sensors and/or samples, as well as in the orientation of the samples relative to the sensor, vibration, electromagnetic noise, etc. Drift, more critical for measurements on strong samples, is manageable by the operator. To reduce drift, every effort should be made to maintain suitable ‘quiet’ operation conditions.

Keywords: magnetic viscosity; superparamagnetism; frequency-dependent magnetic susceptibility; measurements; errors

Introduction

Magnetic viscosity, or a magnetic after-effect, is a property of ferrimagnetic materials to respond with a lag to the applied external field because of magnetic relaxation. The lag in their magnetization, magnetic permeability, and other changes may range from fractions of a second to tens of thousand years (Trukhin, 1973). The magnetic after-effect shows up in almost all ferrimagnetics, including rocks where it results from magnetic relaxation of single domain ferrimagnetic mineral grains (Bolshakov, 1996).

Magnetic viscosity is most often treated as geological noise that interferes with paleomagnetic results (Gubbins and Herrero-Bervera, 2007) or with TEM responses to be interpreted in terms of “normal” electrical conductivity (Buselli, 1982; Dabas and Skinner, 1993; Lee, 1984a,b; Pasion et al., 2002; Zakharkin et al., 1988). However, these effects may bear useful information on the composition and structure of uppermost crust and manmade objects, and record shallow geological processes (Barsukov and Fainberg, 1997, 2002; Kazansky et al., 2012; Kozhevnikov and Antonov, 2008; Kozhevnikov and Snopkov, 1990, 1995; Kozhevnikov et al., 2001, 2003; Stognii et al., 2010).

Superparamagnetism of rocks is commonly studied by measuring frequency-dependent magnetic susceptibility. It may help to discriminate mineral grain sizes and enables estimating the amount of ultrafine superparamagnetic particles which are indicative, in turn, of climate or soil changes (Heller and Evans, 2003; Tompson and Oldfield, 1986). The Bartington Instruments MS2 Magnetic Susceptibility system is the most popular tool for these measurements (reported in a great number of publications impossible to cite in a small paper). However, the related accuracy issues have been discussed almost nowhere except the guide by Dearing (1994) and a recent paper by Hrouda and Pokorny (2011). Dearing (1994) gives some recommendations for operators in reducing errors and Hrouda and Pokorny (2011) postulate extremely high demands for accuracy in precise measurements of frequency-dependent magnetic susceptibility for magnetic viscosity implications.

We discuss parameters used in frequency-dependent magnetic viscosity studies and errors in their values measured with an MS2D dual-frequency sensor of the Bartington MS2 instrument.
Frequency-domain magnetic susceptibility measurements: Basic concepts, definitions, and parameters

Magnetic susceptibility is often defined as the constant of proportionality between the applied magnetic field $H$ and the induced magnetization $J$: $\kappa = J/H$ (Clark, 1997; Gubbins and Herrero-Bervera, 2007), and is assumed to be independent of the frequency of the applied field. However, in the general case, magnetic susceptibility of rocks is complex and frequency-dependent:

$$\kappa^*(\omega) = \text{Re}(\kappa^*(\omega)) + j \text{Im}(\kappa^*(\omega)),$$

where $\omega$ is the angular frequency, and the two terms $\text{Re}(\kappa^*(\omega))$ and $\text{Im}(\kappa^*(\omega))$ represent, respectively, the real (in-phase) and imaginary (out-of-phase or quadrature) components of magnetic susceptibility; $j = \sqrt{-1}$. The complex frequency-dependent magnetic susceptibility allows describing the magnetic viscosity effects in the frequency domain.

The measured frequency-dependent magnetic susceptibilities are often attributed to an assembly of single-domain (SD) grains. The magnetization of a single-domain particle has the relaxation time ($\tau_0$),

$$\tau = \tau_0 \exp(KV/kT),$$

where $K$ is the anisotropy energy, $V$ is the particle volume, $T$ is the absolute temperature, $k$ is Boltzmann’s constant, and $\tau_0 = 10^{-9}$ s. The complex frequency-dependent magnetic susceptibility of such a particle is (Emerson, 1980; Kozhevnikov and Snopkov, 1990; Worm et al., 1993)

$$\kappa^*(\omega) = \kappa_0 - \omega^2 \tau^2,$$

where $\kappa_0$ is the static (at $\omega = 0$) magnetic susceptibility of the particle.

Grains in rocks may be of different sizes, and their magnetic relaxation times differ correspondingly, in a range defined by the weight function $f(\tau)$, called the distribution function. The distribution of time constants in an assembly of SD particles with uniformly distributed energy barriers between stable magnetization states, especially important in magnetic viscosity studies, is described by the Froelich function (Fannin and Charles, 1995). The relaxation times $\tau$ in this function are in the range from $\tau_1$ to $\tau_2$: $\tau_1 \leq \tau \leq \tau_2$. Inside the range,

$$f(\tau) = \frac{1}{\tau \ln(\tau_2/\tau_1)},$$

and outside it $f(\tau) = 0$.

In the frequency domain, the contribution into susceptibility by SD grains with their time constants described by the Froelich function is given by (Das, 2006; Fannin and Charles, 1995; Lee, 1984a,b; Trukhin, 1973)

$$\kappa^*(\omega) = (\kappa_3 - \kappa_\infty) \left[ 1 - \frac{1}{\ln(\tau_2/\tau_1)} \cdot \ln\left(\frac{1 + j\omega\tau_2}{1 + j\omega\tau_1}\right) \right],$$

where $\kappa_3$ and $\kappa_\infty$ are, respectively, the susceptibilities measured at the frequencies $\omega \ll 1/\tau_1$ and $\omega \gg 1/\tau_2$.

The total magnetic susceptibility, produced by the particles magnetized synchronously with the applied field as well as the SD particles with magnetic relaxation, is

$$\kappa^*(\omega) = \kappa_\infty + (\kappa_3 - \kappa_\infty) \left[ 1 - \frac{1}{\ln(\tau_2/\tau_1)} \cdot \ln\left(\frac{1 + j\omega\tau_2}{1 + j\omega\tau_1}\right) \right]. \tag{1}$$

The general frequency-dependent behavior of magnetic susceptibility (Fig. 1) is illustrated by the curves of its real and imaginary components, and the absolute susceptibility calculated by (1) for rocks with $\kappa_3 = 0.02$ SI units, $\kappa_\infty = 0.01$ SI units, $\tau_1 = 10^{-6}$ s, and $\tau_2 = 1$ s.

The susceptibility $\kappa^*(\omega)$ approaches the static $\kappa(0) = \kappa_3$ at low frequencies and tends to $\kappa_\infty$ at high frequencies. At the frequencies $1/\tau_2 < \omega < 1/\tau_1$, the real component of $\kappa^*(\omega)$ decreases proportionally to logarithmic frequency while the imaginary component is frequency independent (Fannin and Charles, 1995).

The data shown in Fig. 1 have been obtained assuming $\kappa_\infty = \kappa_3 - \kappa_\infty$, in order to highlight the frequency-dependent behavior of magnetic susceptibility. However, usually $\kappa_3 - \kappa_\infty \ll \kappa_\infty$, $\kappa_3$.

The imaginary component of measured complex magnetic susceptibility is most often reported to be much lower than the real one, and $\text{Re}(\kappa^*(\omega)) = \kappa^*(\omega)$.

The frequencies at which magnetic susceptibility is usually measured are within $1/\tau_2 \ll \omega \ll 1/\tau_1$. In this case (Das, 2006; Mullins and Tite, 1973; Pasion et al., 2002),

$$\frac{\partial \text{Re}(\kappa)}{\partial \ln \omega} = \frac{2}{\pi} \frac{\text{Im}(\kappa)}{\ln(\tau_2/\tau_1)}. \tag{2}$$

According to (2), the quadrature susceptibility component, as well as the parameter $(\kappa_3 - \kappa_\infty)\ln(\tau_1/\tau_2)$, can be found knowing the slope of the real magnetic susceptibility ($y$-axis) vs. logarithmic frequency ($x$-axis) plot.

Fig. 1. Frequency-dependent real ($f$) and imaginary ($2$) components and absolute values ($3$) of magnetic susceptibility for rocks with $\kappa_3 = 0.02$ SI units, $\kappa_\infty = 0.01$ SI units, $\tau_1 = 10^{-6}$ s, and $\tau_2 = 1$ s. The dashed-line box indicates the frequency band (10 Hz–100 kHz) representative of TEM responses.
This slope is defined by two points. The dual-frequency Bartington MS2 instrument (Dearing, 1994) measures the absolute magnetic susceptibility at \( f_1 = 465 \text{ Hz} \) and \( f_2 = 4650 \text{ Hz} \) (low and high frequencies, respectively). Inasmuch as \( \text{Re}(\kappa'(\omega)) = \kappa'\text{'}(0) \), the slope is estimated using the absolute \( \kappa_f \) and \( \kappa_d \) instead of the real component.

In this case, obviously

\[
\frac{\partial \text{Re}(\kappa)}{\partial \ln \omega} \approx \frac{\kappa_f - \kappa_d}{\ln f_2 - \ln f_1},
\]

whence, with regard to (2), it follows that

\[
\kappa_s = \kappa_m = \frac{\kappa_f - \kappa_d}{\ln f_2 - \ln f_1} \cdot \ln (\tau_2/\tau_1).
\]

With the latter equation, one can estimate the difference between the static and dynamic susceptibilities (\( \kappa_s - \kappa_m \)) proceeding from the \( \tau_2/\tau_1 \) ratio. This difference allows comparing quantitatively the magnetic viscosity effects. If magnetic viscosity is associated with magnetization of superparamagnetic particles, it appears reasonable to assume the difference (\( \kappa_s - \kappa_m \)) to be proportional to their content. This difference can be known from independent measurements and used, in turn, to estimate the \( \tau_2/\tau_1 \) ratio that characterizes the relaxation time range for the assembly of superparamagnetic grains.

The relative contributions of superparamagnetic grains to the total susceptibility is usually characterized by percentage frequency dependent susceptibility \( \kappa_{fd} = 100(\kappa_f - \kappa_d)/\kappa_f \) (Dearing, 1994).

**Measurement errors in (\( \kappa_f - \kappa_d \)) and \( \kappa_{fd} \)**

The total uncertainty in magnetic susceptibilities measured by the Bartington MS2 instrument with an MS2D dual-frequency sensor comprises two components: an instrument error (\( \Delta \kappa \)) and a drift. The instrument error, or accuracy, refers to the ability of the equipment to measure very small values (Dearing, 1994), i.e., the accuracy \( \Delta \kappa \) means that it is impossible to measure susceptibility to an error less than \( \Delta \kappa \) and thus shows how precise are the measurements by an instrument used as recommended by the manufacturer, in ideal conditions and in the absence of noise. The accuracy of the Bartington MS2 meter (Dearing, 1994) is \( \Delta \kappa = 0.1 \times 10^{-5} \) and \( \Delta \kappa = 1.0 \times 10^{-5} \) SI units for samples with low and high susceptibilities (weak and strong samples, respectively).

However, the operating conditions are often not ideal in practice, and external factors can produce drift besides the instrument error. Measurement drift may result from temperature changes in the sensor and/or sample, misorientation of the sample relative to the sensor, vibration, external electromagnetic noise, etc. Note that we use the term drift in a broader sense than Dearing (1994) who rather assigns it to air readings with the sensor empty. The magnitude of drift is estimated by the product drift-\( \kappa \), where \( \kappa \) is the measured susceptibility and drift is relative error, which may exceed 1% (Dearing, 1994).

Analysis of relative errors in \( \kappa_f - \kappa_d \) and \( \kappa_{fd} \) is important to judge the quality of measurements. Let \( \delta \) be the relative error (% of the measured value). Then,

\[
\delta (\kappa_f - \kappa_d), \% = 100 \cdot \frac{\Delta(\kappa_f - \kappa_d)}{\kappa_f - \kappa_d},
\]

\[
\delta (\kappa_{fd}), \% = 100 \cdot \frac{\Delta(\kappa_{fd})}{\kappa_{fd}},
\]

where \( \Delta(\kappa_f - \kappa_d) \) and \( \Delta(\kappa_{fd}) \) are the absolute errors in the \( (\kappa_f - \kappa_d) \) and \( \kappa_{fd} \) values, respectively.

With the rule for estimating the absolute error in indirect measurements, as well as with equations for relative errors in the sum, difference, and quotient of two values (e.g., Squires, 1968), it is easy to show that

\[
\delta (\kappa_f - \kappa_d), \% = \sqrt{\left(2/\kappa_f\right)^2 + \left(\text{drift} \cdot \kappa_f\right)^2} \cdot \frac{\Delta(\kappa_f - \kappa_d)}{\kappa_f - \kappa_d},
\]

\[
\delta (\kappa_{fd}), \% = \sqrt{\left(2/\kappa_f\right)^2 + \left(\text{drift} \cdot \kappa_f\right)^2} \cdot \frac{\Delta(\kappa_{fd})}{\kappa_{fd}}.
\]

The difference between high- and low-frequency susceptibilities is known to be within 10–15% even in very magnetically viscous samples (Dearing, 1994; Dearing et al., 1996). Bearing this in mind, one may assume drift-\( \kappa_f \approx \text{drift} \cdot \kappa_f \), the more so as it is the relative uncertainty rather than the exact amount of error to be calculated. Then (3) becomes

\[
\delta (\kappa_f - \kappa_d), \% = 100 \cdot \sqrt{\left(\Delta \kappa\right)^2 + \left(\text{drift} \cdot \kappa_f\right)^2} \cdot \frac{1}{\kappa_f - \kappa_d}.
\]

Inasmuch as \( \kappa_f - \kappa_d \ll \kappa_f \), the second term in square brackets from (4) is far less than the first one, and can be neglected. Therefore, the equation for \( \delta (\kappa_{fd}) \) will be similar to (5):

\[
\delta (\kappa_{fd}), \% = 100 \cdot \sqrt[2]{\left(\Delta \kappa\right)^2 + \left(\text{drift} \cdot \kappa_f\right)^2} \cdot \frac{1}{\kappa_f - \kappa_d}.
\]

Given that \( \kappa_f - \kappa_d = \kappa_{fd} \cdot \kappa_f \), (6) may be rewritten as

\[
\delta (\kappa_{fd}), \% = 100 \cdot \sqrt[2]{\left(\Delta \kappa\right)^2 + \left(\text{drift} \cdot \kappa_f\right)^2} \cdot \frac{1}{\kappa_{fd} \cdot \kappa_f}.
\]

The use of equations (3) and (4) is illustrated by Figs. 2 and 3.

Figure 2 shows how \( \delta (\kappa_f - \kappa_d) \) changes as a function of \( (\kappa_f - \kappa_d) \) for samples with low and high susceptibility (weak
and strong samples), $\kappa_f$ being $10 \times 10^{-5}$ and $\kappa_f = 10^3 \times 10^{-5}$ SI units for the weak and strong samples, respectively. The curves in Fig. 2 have been obtained assuming that $\kappa_{fd}$ of each sample varies from 0.1% (a very low percentage of superparamagnetic grains) to 10% (a high percentage of superparamagnetic grains). Correspondingly, $\kappa_{lf} - \kappa_{hf}$ is in the range from $0.01 \times 10^{-5}$ to $1 \times 10^{-5}$ SI units in the weak sample and from $1 \times 10^{-5}$ to $10^2 \times 10^{-5}$ SI units for the strong one.

For curves in Fig. 2a, b, the effect of drift has been assumed negligible compared to the instrument error ($\text{drift} = 0$), and $\delta(\kappa_l - \kappa_f)$ is calculated assuming $\Delta \kappa = 1 \times 10^{-5}$ and $0.1 \times 10^{-5}$ SI units in the panels a and b, respectively. Thus, at negligible drift, $\delta(\kappa_l - \kappa_f)$ is directly proportional to instrument error and inversely proportional to the $(\kappa_l - \kappa_f)$ difference (compare the curves in panels a and b of Fig. 2). In weak samples with small $(\kappa_l - \kappa_f)$, the $\delta(\kappa_l - \kappa_f)$ error can be very large: It exceeds 100% at $\Delta \kappa = 10^{-5}$ SI units even when $\kappa_{id} = 10\%$ (corresponding to $\kappa_l - \kappa_{hf} = 10^{-5}$ SI units), but becomes ten times smaller at $\Delta \kappa = 0.1 \times 10^{-5}$ SI units, or 10% for the sample with $\kappa_{id} = 10\%$. For strong samples, $\delta(\kappa_l - \kappa_f)$ will be 10% at $\kappa_{id} = 1\%$ ($\kappa_l - \kappa_{hf} = 10 \times 10^{-5}$ SI units) and only 1% at $\kappa_{id} = 10\%$ ($\kappa_l - \kappa_{hf} = 100 \times 10^{-5}$ SI units).

The relationship of $\delta(\kappa_l - \kappa_f)$ with $\Delta \kappa$ and $(\kappa_l - \kappa_f)$ difference and on the instrument accuracy in the absence of drift.

The $\kappa_l - \kappa_{hf}$ difference, being in the denominator in (8), leads to a large error in weak samples (where it is small). The only way to reduce $\delta(\kappa_l - \kappa_f)$ in this case is to improve the instrument accuracy. The latter, however, is intrinsic to a given measurement system, and one can at best approach some improvement by repeated air readings with the sensor empty to make sure of getting the most accurate measurements. On the contrary, strong samples, with $(\kappa_l - \kappa_f)$ being large even at low $\kappa_{id}$, give good results in measurements at a vanishing drift.

The drift effect is illustrated in panels c and d of Fig. 2 that show the behavior of $\delta(\kappa_l - \kappa_f)$ as a function of $(\kappa_l - \kappa_f)$ at drift $= 0.01$, or 1% of the measured susceptibility. Drift causes only minor effect in weak samples but
becomes the main accuracy control of \( \delta(\kappa_{lf} - \kappa_{hf}) \) in measurements on rocks with high susceptibility, while the instrument error becomes insignificant. Compare the panels \( a \) and \( c \), and especially, \( b \) and \( d \) of Fig. 2: the total \( \delta(\kappa_{lf} - \kappa_{hf}) \) error remains almost the same at small drift = 0.01 in the case of a weak sample but becomes nearly ten and hundred times greater (at \( \Delta\kappa = 10^{-5} \) and \( \Delta\kappa = 0.1 \times 10^{-5} \) SI units, respectively) for the strong sample. The reason is quite clear. For instance, even minor warming or displacement will affect the \( (\kappa_{lf} - \kappa_{hf}) \) difference in a strong sample but will remain negligible (much below the instrument error) for a weak one.

This inference is consistent with equation (5). If the instrument error is negligible compared to drift \( (\Delta\kappa \ll \text{drift} \cdot \kappa_{lf}) \),

\[
\delta(\kappa_{lf} - \kappa_{hf}), \% = 100\sqrt{2} \cdot \frac{\text{drift} \cdot \kappa_{lf}}{\kappa_{lf} - \kappa_{hf}}. \tag{9}
\]

The product \( \text{drift} \cdot \kappa_{lf} \) being in the nominator, measurements on strong samples (with large \( \kappa_{lf} \)) will bear a large total error \( \delta(\kappa_{lf} - \kappa_{hf}) \) at large drift.

On the other hand, the user can manage drift by optimizing the operation conditions, unlike the instrument accuracy intrinsic to the system. One way of reducing drift—and, hence, the total \( \delta(\kappa_{lf} - \kappa_{hf}) \) error—consists in repeated susceptibility measurements with analysis of the data series and statistical estimation (Dearing, 1994; Squires, 1968). Another way is to minimize or totally avoid any warming of samples during measurements. One of us (Ya.K.) noted while studying basalts from the Vitim Plateau (Kazansky et al., 2012) that the readings became more stable when the operator avoided touching them by holding the samples placed into the sensor with a simple cardboard or plastic tool. The stability of results worsens from any minor change in heat (e.g., warming from a hand and subsequent cooling).

The behavior of the error \( \delta(\kappa_{fd}) \) as a function of \( \kappa_{fd} \) has the same implications as that of \( \delta(\kappa_{lf} - \kappa_{hf}) \) discussed above. In the absence of drift (Fig. 3a, b), \( \delta(\kappa_{fd}) \) is directly proportional to \( \Delta\kappa \) and inversely proportional to \( \kappa_{lf} \) and \( \kappa_{fd} \). Inasmuch as \( \kappa_{lf} \) and \( \kappa_{fd} \) are in the denominator of (7), \( \delta(\kappa_{fd}) \) will be unacceptably high even at \( \Delta\kappa = 0.1 \times 10^{-5} \) SI units, especially if the samples are weak. For a specific sample, with given \( \kappa_{lf} \) and \( \kappa_{fd} \) unmanageable by the user, \( \delta(\kappa_{fd}) \) can only decrease if the instrument error becomes smaller. On the other hand, strong samples measured within the practically relevant range \( (1% \leq \kappa_{fd} \leq 10%) \) show \( \delta(\kappa_{fd}) \leq 10\% \) even at \( \Delta\kappa = 10^{-5} \) SI units.

The effect of drift is to increase \( \delta(\kappa_{fd}) \), especially in strong samples (compare the panels \( a, c \) and \( b, d \) in Fig. 3). However,
the user can always reduce drift by maintaining the stable temperature and/or orientation of samples during measurements.

Conclusions

Equations (3)–(9) enable estimating relative errors in \( (\kappa_{lf} – \kappa_{hg}) \) and \( \kappa_{ld} \) data acquired with a dual-frequency magnetic susceptibility meter, for any combination of parameters for the measurement system and the samples \( (\Delta \kappa, \text{ drift, } \kappa_{lf}, \kappa_{hf}) \).

Uncertainty in measured frequency-dependent magnetic susceptibilities commonly comprises the instrument error \( (\Delta \kappa) \) and the drift. The former refers to the instrument accuracy and affects mostly the \( (\kappa_{lf} – \kappa_{hg}) \) and \( \kappa_{ld} \) relative error in weak samples. Therefore, these samples should be measured on the higher sensitivity range.

Drift may result from changes in the temperature of sensors or samples, in the sample orientation with respect to the sensor, vibration, external electromagnetic noise, etc., and is especially significant in susceptibility measurements of strong samples. The external effects, and thus the drift, are manageable by the user by maintaining the optimum operation conditions, especially when measuring strong samples.

We have shown with equations (3)–(9) that frequency-dependent magnetic susceptibilities measured with the broadly used Bartington MS2 dual-frequency system may bear very large error controlled mostly by instrument accuracy in the case of weak samples and by drift (operation conditions) for strong samples.

Magnetic viscosity effects show up in both frequency and time domains. Of special interest in this respect are TEM (TDEM) systems applicable to estimate magnetic viscosity of rocks either in laboratory (Dabas and Skinner, 1993; Kamnev et al., 2012) or in the field (Colani and Aitken, 1966; Kozhevnikov and Antonov, 2012; Kozhevnikov et al., 2012; Stognii et al., 2010; Thiesson et al., 2007). As far as we know from the literature, the accuracy of TDEM magnetic viscosity prospecting has never been specially analyzed. It is well known, however, that TEM data are advantageous over frequency induction measurements being free from the primary field effect (McNeill, 1980; Velikin, 1971). Another important advantage is that, unlike the dual-frequency susceptibility data, time-domain transient responses bear magnetic viscosity information in a broad frequency range (Fig. 1). Therefore, further development and application of TEM systems for time-domain magnetic viscosity studies appears to be a promising strategy, despite some technical and methodical problems (Kamnev et al., 2012).

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References


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