Preliminary Rock Magnetic Study of Archaeomagnetic Samples from Bulgarian Prehistoric Sites

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(Received January 5, 1996; Revised October 1, 1996; Accepted October 11, 1996)

Rock magnetic properties of archaeomagnetic samples taken from ovens are studied. Thermal demagnetization of saturation remanences and other studies reveal the presence of: (titano)magnetite, iron oxyhydroxides, and maghemite with \( T_b \sim 650°C \) which is stable with respect to inversion. During thermal demagnetization the soft IRM component (0.06 T) is always the strongest one, indicating the importance of the (titano)magnetite contribution. A break-up in the values of coercivity \( H_{c0} \) with respect to initial mass-specific magnetic susceptibility (\( \chi \)) occurs at \( \chi \sim 1.5 \times 10^{-6} \) m³/kg and separates poorer from better quality samples in the palaeointensity experiment. Separation of bad and good Thellier experiments is also observed in the relation between the coercivities and the concentration-independent parameter SIRM/\( \chi \). Thus, the poor quality of the palaeointensity experiments for some samples can probably be ascribed to the presence of weathering products and MD magnetite grains while the good quality of these experiments is related to "soft" hysteresis properties and a broad unblocking temperature spectrum.

1. Introduction

Archaeological materials made of burnt clay and volcanic rocks both carry a TRM, and they have been used extensively in the last few decades to obtain the palaeointensity of the geomagnetic field. Recently, however, questions have been raised about the suitability of archaeological materials for palaeointensity determination. It has been proved theoretically (Shcherbakov et al., 1993; Dunlop and Xu, 1994) that the additivity law of pTRM’s, which is a necessary condition for the Thellier-Thellier method (Thellier and Thellier, 1959) holds only for single domain (SD) grains, as predicted by the classic Neel theory (Neel, 1949; 1955). The same holds for pseudo-single domain (PSD) grains while the thermal demagnetization of multidomain (MD) grains exhibits "trails", extending up to \( T_b \) of the mineral which carries the TRM (Bolshakov and Shcherbakova, 1979; Xu and Dunlop, 1994). Most of the papers dealing with this problem have considered volcanic rocks (Thomas, 1993; Haag et al., 1995) with only few studies on archaeological samples (Walton, 1984, 1987; Aitken et al., 1986, 1988; Cui and Verosub, 1995; Cui et al., 1997). A first attempt to examine the results of rock magnetic studies in conjunction with the success or failure of the Thellier intensity experiment was recently carried out in the laboratory of the Geophysical Institute, Sofia (Kovacheva and Toshkov, 1994). The rock magnetic studies used in that work were limited, and the samples studied are only from the AD period. In the work presented here, the number of rock magnetic parameters is considerably enlarged, and the samples studied are from the older BC period.
2. Samples and Methods

The present study includes samples from ovens from 6 archaeological sites of the BC period in Bulgaria: 1) Djadovo (samples D144–D200)—multilevelled hill of the Bronze age, ca 2700 BC; 2) Isperih (samples 2117–2137)—ca 300 BC; 3) Sarovka (samples CA1–CA46) of the Early Bronze Age, ca 2800 BC, (Kovacheva et al., 1995); 4) Durankulak (samples Dk31–Dk90), ca 4200 BC; 5) Madrec (samples M3–M31), ca 3000 BC and 6) Kamenska chuka (samples 2141–2155)—ca 1200 BC (samples taken from archaeological features destroyed by an ancient fire). The corresponding sites locations are shown in Fig. 1.

![Location map showing the six archaeological sites studied. They are numbered 1 to 6 according to the legend, shown in the inset.](image)

Fig. 1. Location map showing the six archaeological sites studied. They are numbered 1 to 6 according to the legend, shown in the inset.

These collections were studied in order to evaluate the ancient direction and intensity of the geomagnetic field. 150 samples were studied for palaeointensity, of these 118 gave successful results according to the stringent acceptance criteria, established in the Sofia palaeomagnetic laboratory (Kovacheva and Kanarchev, 1986; Kovacheva and Toshkov, 1994). They include the following requirements: 1) the stability of the NRM direction; 2) not less than 6 experimental points on the Arai diagram used for determination of the ancient palaeointensity value; 3) pTRM checks showing less than 10% changes in TRM capacity; 4) less than 10% changes in the room temperature volume magnetic susceptibility $K$ into the temperature interval used for obtaining palaeointensity value. The rock magnetic studies were carried out on intact sister specimens to those used for palaeointensity determinations (Thellier and Thellier, 1959).
The methods applied are: 1) Thermal demagnetisation of saturation remanence \( J_{rs} \) in a field-free space was carried out on 1 cm\(^3\) cubic samples using a non-standard spinner thermomagnetometer with continuous registration (Burakov, 1977). Sensitivity of the device is 10 pT. 2) In order to obtain more precise information about the ferromagnetic minerals present in the samples, stepwise thermal demagnetization of 3-component isothermal remanent magnetization IRM (Lowrie, 1990) was also performed. 3) AF-demagnetization of natural remanent magnetization (NRM) and isothermal remanent magnetization (IRM) was also investigated and used for the Lowrie-Fuller test (Lowrie and Fuller, 1971). The determined median destructive field \( H_{1/2} \) relates to the laboratory induced IRM. 4) Hysteresis measurements on 27 cylindrical samples, as well as IRM-acquisition and DC-demagnetization studies were performed at the Geophysical Institute in Prague. 5) 12 specimens were subjected to the following procedure: i) inducing IRM in 2 T, measuring both IRM and \( K \) —the initial values; ii) heating to the temperature \( T_i \) and measuring the remained part of IRM; iii) reinducing IRM (2 T) and measuring it and \( K \); iv) repeating the steps ii) and iii) for each successive temperature. A sister specimen of each of these, subjected to the above procedure, was given an IRM in a field of 2 T and was only subjected to stepwise thermal demagnetization. The behaviour of the decay curves of IRM of the sister specimens and the part of IRM, remained after each heating step were used to detect whether a new magnetic mineral, which carries remanent magnetisation has originated during heating. The described procedure is similar to the method, proposed by Van Velzen and Zijderveld (1992) for detecting chemical changes, but does not include determination of the AF coercivity spectrum of the reinduced IRM.

3. Experimental Results and Discussion

3.1 Continuous thermal demagnetization of saturation remanence \( J_{rs} \) (2 T)

The continuous thermal demagnetization of \( J_{rs} \) permits a determination of the unblocking temperatures \( (T_b) \) of ferrimagnetic phases present in the specimens. The thermal demagnetization of \( J_{rs} \) was carried out twice for each specimen: first, after magnetic saturation of an unheated specimen \( (J_{rs1} \) curve) and second, after saturation of the previously heated specimen \( (J_{rs2} \) curve). The final heating temperature for different samples is that one at which a complete demagnetization of \( J_{rs1} \) was obtained. Usually it is in the range of \((400-600)\degree C\) depending on the mineralogy of the material. It should be noted the relatively high heating rate (about \(30\degree C/min\)) used in this experiment. The ratio of saturation remanence before the second heating \( J_{rs2} \) to saturation remanence of the unheated sample \( J_{rs1} \) was also calculated in order to check for chemical changes during the first heating. Three types of thermal demagnetization curves of \( J_{rs1} \) can be distinguished:

1) Specimens, showing low \( T_b \) of \((80-150)\degree C\) in addition to high \( T_b \) \((400-500)\degree C\) (Fig. 2a).
2) Specimens with \( T_b \sim(250-300)\degree C\), as well as one high \( T_b \) \((>400)\degree C\) (Fig. 2b).
3) Samples, showing one high \( T_b \) \((>400)\degree C\) only. In this case, a concave curve was frequently observed, suggesting a broad unblocking temperature spectrum (Fig. 2c).

The discontinuities in slope of the \( J_{rs1}(T) \) curves can be due to either reaching the unblocking temperatures of different ferriminerial phases or discrete grain-size fractions, belonging to one ferrimagnetic phase. The low unblocking temperatures \((80-150)\degree C\) in principle point to the presence of goethite, if we assume that it has been saturated in the field of 2 T, which we used. On the other side, this implies that the relative amount of \(\alpha-FeOOH\) should be significant, in order to contribute to the \( J_{rs} \) (Dekkers, 1989; Roberts et al., 1995). Having in mind the results from the thermal demagnetization of 3-axis IRM, discussed below, which all show a minor contribution of a hard IRM-component (acquired in a field of 2 T) (Fig. 4), as well as the AF-demagnetization (Fig. 3) and IRM-acquisition curves (Fig. 6), the possibility of a presence of significant amount of goethite can be excluded. Thus, the more probable explanation of the observed low \( T_b \)s
in the interval (80–150)°C is connected with unblocking of a particular grain-size fraction of magnetically soft mineral. Weathering processes acting during the burial time of archaeological remains can lead to a development of maghemite shell around the original titanomagnetite grains which carry thermoremanence (Cui et al., 1994; Van Velzen and Zijderveld, 1995). It brings about hardening of isothermal magnetic properties. As shown by Burov et al. (1986), the presence of such surface oxidised grains is reflected on the $J_{rs}(T)$ curves by low unblocking temperature together with a high $T_b$, more characteristic for maghemite which is stable with respect to inversion than for magnetite. Also, according to Van Velzen and Zijderveld (1995), breaking down of a maghemite shell occurs most effectively at about 150°C. Since 48% of the samples studied...
show low unblocking temperature, we conclude that the weathering processes often influence the magnetic properties of archaeological materials and complicate the archaeomagnetic intensity investigations.

Samples from the site Kamenska chuka (Nos 2147–2155) and sample Dk90 from the site Durankulak (Fig. 2d) show $T_b$'s of about 200°C clearly detected on both heating curves. We suppose that this $T_b$ is due to the presence of hemoilmenite which remains unaltered during repeated heatings (Pecherskij et al., 1975). The high stability of NRM upon AF-demagnetization supports this conclusion as well. In all other cases the ferrimagnetic phase with $T_b \sim (250–300)^\circ C$ disappears upon heating (Fig. 2b). The main ferromagnetic carrier, which is connected with the highest $T_b$, seems to be titanomagnetite. AF-demagnetizations of NRM (Fig. 3) show a magnetically soft behaviour, typical of titanomagnetite as well. In the case of sample M3a which also have a low $T_b$, the relative contribution of the hard component is greater.

![AF-demagnetization of NRM](image)

Fig. 3. AF-demagnetization of NRM.

Concave thermal demagnetization curves are obviously due to ferromagnetic particles of very different grain sizes, which progressively unblock at a wide range of temperatures. Thus, only the last “magnetite” or “hematite” $T_b$ can be determined. For this reason the hysteresis properties of these samples vary over a broad range.

For almost all samples, the second heating curve is usually concave and the low $T_b$ of (80–150)$^\circ C$ has disappeared. The final $T_b$ remains unchanged or is shifted towards higher temperatures.
3.2 Stepwise thermal demagnetization of composite IRM

Stepwise thermal demagnetization of 3-component IRM (Lowrie, 1990) is a useful tool for determining unblocking temperatures of ferromagnetic phases with different coercivities. In the present study, according to technical possibilities in the laboratory, the following magnetizing fields were used: for the hard component—2 T; for the intermediate—0.27 T and for the soft—0.06 T. In all cases, the soft component is of the greatest intensity compared with the hard and intermediate components (Fig. 4). Low unblocking temperature of ~ 150–200°C, detectable for the soft component, could be due to the presence of some MD magnetite grains (Fig. 4a, sample M4a). Because of very low magnetizing field used for this soft component, it is not very probable that the higher coercivity maghemitized grains are involved into it, or Ti-rich titanomagnetcites which presumably show much harder magnetic properties (O’Reilly, 1984; Nishitani and Kono, 1989). Most of the (titano)magnetite grains responsible for the NRM should be involved in the
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intermediate IRM component because of the higher coercivities of stable SD particles. Therefore, when the soft component is predominant (for example No CA3a, Fig. 4b), it may indicate the presence of some amount of MD or unstable SD particles. In this case, the reliability of the intensity experiment would be questionable if those coarse grains carry a part of TRM. The final unblocking temperature of this low coercivity component of the IRM is usually ~ 580–600°C which may be ascribed to magnetite. A $T_b > 600^\circ$C observed on the soft and intermediate IRM components (Fig. 4d, sample Dk59), is probably due to maghemite which is stable with respect to inversion (Osipov, 1978; Özdemir and Banerjee, 1984; Özdemir, 1990; Eyre and Shaw, 1994). If the stable maghemite is of secondary origin (i.e. it has appeared as a result of low temperature oxidation after the TRM acquisition) its persistence during the entire heating cycle could be a serious problem for the palaeointensity experiment. A convex demagnetization curve of the soft component (Fig. 4b, sample CA3a) implies a narrower unblocking temperature spectrum of low coercivity grains, while a concave curve (Figs. 4c, d, sample CA45 and Dk59b) suggests broader grain size distribution.

The relative contribution of the intermediate component varies for different samples. It can be as much as 50% of the soft component intensity (Fig. 4d, sample Dk59) or as little as 10% (Fig. 4b, sample CA3a). Presumably SD or PSD (titano)magnetite grains should saturate in the applied field strength (0.27 T) (Dankers, 1981; O’Reilly, 1984; Roberts et al., 1995).

The hard component (acquired with a magnetizing field of 2 T) is in most cases relatively weak, reaching at room temperature only 10–20% of the soft component (Figs. 4b, d). This component provides only in few cases an evidence for iron oxyhydroxides (for example in the case of sample M4a—Fig. 4a, a $T_b$ of ~ 120°C can be detected). In many samples a high $T_b$ ~ 600°C is also observed. This $T_b$ is probably connected with a slight oxidation of magnetite during the heating experiments carried out in air. $T_b$ characteristic of hematite is rarely observed, which suggests that this mineral is not present or is very fine grained and hence, not saturated in a field of 2 T. For sample CA45 (Fig. 4c) the hard component is stronger than the intermediate one, but the all three components have the same unblocking temperature—about 580°C. Thus, there is probably a wide range in the grain size distribution of the (titano)magnetite constituent.

The stepwise thermal demagnetization of the 3-component IRM allows us to discriminate more precisely among the ferrimagnetic phases of different coercivities and/or grain sizes than the thermal demagnetization of total IRM, where the contributions coming from different fractions are superimposed.

3.3 IRM-acquisition and DC-demagnetization experiments

These experiments were carried out on cylindrical natural samples, without destroying their texture, using a vibrating sample magnetometer, constructed in the Geophysical Institute in Prague (Zelinka et al., 1984).

IRM-acquisition curves differ from each other only in weak fields, that is up to about 110 mT (Fig. 5a). The initial remanence is not zero due to the relatively high residual field of the electromagnet poles. This has no effect on remanence measurements after magnetization at fields higher than the residual field, which is not high enough to reach $H_{1/2}$. The values of the acquisition remanence coercive force ($H_{cr}$) vary more significantly in comparison with the remanence coercivity ($H_{cr}$) and the coercive force ($H_c$). $H_{cr}$ ranges from 16 to 33 mT, $H_c$—from 10 to 17.5 mT. Most of the studied samples reach saturation at rather low fields—at about 120 mT (Tables 1, 2). We conclude that SIRM is carried mainly by magnetically soft carriers. To check if a true saturation is achieved in 200 mT, all samples were remagnetized in a field of 2 T. The $S$-ratio ($S = -b_{IRM}/S_{IRM}$, $b_{IRM}$ being oppositely directed weaker magnetic field of 0.2 T: Maher, 1986; Verosub and Roberts, 1995) was also calculated (Tables 1, 2). Most of the samples show $S$ values between 0.8–0.9, indicating a minor contribution from high coercivity minerals, like hematite and goethite (Dankers, 1981; O’Reilly, 1984; Dekkers, 1989). Only a few
Fig. 5. a) Acquisition and DC-demagnetization of IRM; b) differential remanence ($\Delta M(H) = I_{d.c.}(H) - (1 - 2IRM(H))$, Petrovsky et al., 1993), pointing to a negative type of interactions.
Table 1. Rock magnetic parameters for samples with \( \chi < 1.5 \mu m^3/kg \). The shape of the hysteresis loop is marked by \( R \) for regular "magnetite" type and by WWL for the "wasp-waisted" one. The last column includes the relative estimates of palaeointensity experiments.

| Sample No | \( \chi \) (\( \mu m^3/kg \)) | \( H_c \) (mT) | \( H_{ir} \) (mT) | \( H_{cr} \) (mT) | \( J_{cr}/J_s \) | \( H_{cr}/H_c \) | SIRM (\( x10^{-2} Am^2/kg \)) | SIRM/\( \chi \) (kA/m) | \( \chi_{ps} \) (\( x10^{-6} m^3/kg \)) | S | Hysteresis loop | Lowrie-Fuller test | TH |
|-----------|-----------------|--------------|--------------|--------------|--------------|--------------|-------------------------------|-----------------|--------------------------------|---|----------------|------------------|-----|
| D 148     | 0.27            | 9.2          | 15           | 17.6         | 33.0         | 0.17         | 1.92                          | 0.090           | R                             |   | WWL            | MD                | 4   |
| Dk 87     | 0.30            | 3.8          | 12           | 13.0         | 22.0         | 0.09         | 3.39                          | 9.9             | 0.200                          |   | WWL            | MD                | 1   |
| D 144     | 0.39            | 9.0          | 20           | 15.8         | 33.0         | 0.19         | 1.75                          | 8.2             | 21.3                           | 0.100          | R              | SD/MD             | 2   |
| D 150     | 0.38            | 8.7          | 14           | 15.2         | 30.0         | 0.14         | 1.74                          | 6.4             | 16.8                           | 0.100          | R              |                    | 1   |
| D 200     | 0.43            | 5.5          | 18           | 15.5         | 27.0         | 0.09         | 2.82                          | 5.4             | 12.4                           | 0.100          | WWL            | MD                | 3   |
| 2120      | 0.45            | 5.0          | 16           | 14.5         | 23.0         | 0.11         | 2.92                          | 4.1             | 9.0                            | 0.076          | R              | MD                | 1   |
| M 3       | 0.47            | 7.1          | 10           | 12.1         | 17.5         | 0.21         | 1.70                          | 10.8            | 23.0                           | 0.086          | R              | SD                | 2   |
| D 173     | 0.50            | 8.7          | 16           | 16.5         | 27.5         | 0.16         | 1.91                          | 8.8             | 17.7                           | 0.100          | R              | SD/MD             | 2   |
| CA 1      | 0.51            | 5.4          | 13           | 12.4         | 17.5         | 0.14         | 2.28                          | 0.100           | R                             |   | SD/MD           |                  | 5   |
| CA 46     | 0.52            | 2.5          | -            | 13.8         | 15.5         | 0.08         | 5.56                          | 2.4             | 4.6                            | 0.200          | R              |                   | 4   |
| CA 3      | 0.72            | 8.1          | 12           | 12.6         | 20.5         | 0.19         | 1.56                          | 9.6             | 13.5                           | 0.095          | R              | SD                | 3   |
| D 196     | 0.77            | 6.6          | -            | 15.2         | 27.0         | 0.12         | 2.31                          | 11.1            | 14.4                           | 0.100          | R              |                   | 3+  |
| D 160     | 0.82            | 7.5          | -            | 16.0         | 27.5         | 0.14         | 2.14                          | 12.1            | 14.8                           | 0.100          | R              |                   | 3   |
| D 162     | 0.83            | 6.9          | -            | 16.3         | 26.5         | 0.14         | 2.36                          | 10.4            | 12.5                           | 0.100          | WWL            |                   | 3   |
| D 191     | 0.84            | 5.9          | 12           | 12.8         | 23.0         | 0.11         | 2.19                          | 12.4            | 14.7                           | 0.071          | R              | SD/MD             | 4+  |
| D 180     | 1.40            | 6.7          | 18           | 16.3         | 27.0         | 0.14         | 2.44                          | 16.9            | 12.0                           | 0.087          | R              | MD                | 1   |
| M 30      | 1.46            | 7.0          | 16           | 14.1         | 27.0         | 0.16         | 2.00                          | 17.3            | 11.8                           | 0.056          | R              | SD                | 3   |
| 2141      | 1.50            | 4.9          | 12           | 12.2         | 15.0         | 0.15         | 2.47                          | 21.4            | 14.3                           | 0.006          | 0.86           |                   | 3   |
Table 2. Rock magnetic parameters for samples with high $\chi$ ($\chi > 1.5 \mu m^3/kg$). The remain as in Table 1.

| Sample No | $\chi$ ($\mu m^3/kg$) | $H_e$ (mT) | $H_{1/2}$ (mT) | $H_{cr}$ (mT) | $H_{cr}'$ (mT) | $J_r/J_s$ | $H_e/H_e$ | SIRM ($x10^{-2}$ A$m^2/kg$) | SIRM/$\chi$ ($x10^{-6}$ m$^3$/kg) | $\chi_{pa}$ (kA/m) | S | Hysteresis loop | Lowrie Fuller test | TH |
|------------|------------------------|------------|----------------|---------------|---------------|-----------|------------|-----------------------------|---------------------------------|----------------|---|----------------|-----------------|---|
| CA45       | 1.84                   | 3.4        | 10             | 13.5          | 18.0          | 0.10      | 2.92       | 13.0                        | 7.0                             | 0.091          | 0.54 | WWL           | SD               | 5 |
| 2134       | 2.29                   | -          | 12             | 10.8          | 20.0          | -         | -          | 38.0                        | 13.4                            | SD             | 4  |               |                 |    |
| Dk 52      | 3.47                   | 1.9        | 14             | 13.8          | 22.0          | 0.05      | 7.40       | 24.4                        | 7.0                             | 0.082          | 0.73 | WWL           | SD               | 4 |
| Dk 31      | 3.50                   | 3.2        | 16             | -             | -             | -         | -          | 20.8                        | 5.9                             | 0.90           | 0.90 | WWL           | SD               | 3 |
| 2117       | 3.60                   | 4.2        | 12             | 13.5          | 21.0          | 0.11      | 3.21       | 0.088                       | 0.088                           | SD             | 3  |               | R                |    |
| 2127       | 3.65                   | 3.5        | -              | 14.5          | 23.0          | 0.11      | 2.92       | 64.6                        | 17.7                            | 0.010          | 0.86 | WWL           | 4                |    |
| Dk 90      | 4.55                   | 1.9        | 15             | 16.6          | 16.0          | 0.05      | 8.91       | 34.7                        | 7.6                             | 0.100          | 0.65 | WWL           | SD               | 5 |
| 2154       | 7.00                   | 4.6        | -              | 13.7          | 21.0          | 0.14      | 2.95       | 86.7                        | 12.4                            | 0.057          | 0.65 | WWL           | 1                |    |
| Dk 62      | 7.80                   | 3.5        | 13             | 14.0          | 21.0          | 0.10      | 4.04       | 59.9                        | 7.7                             | 0.087          | 0.91 | WWL           | SD               | 5 |
specimens show a significant contribution from ferrimagnetic particles which are not saturated in a field of 200 mT, and they display other unusual properties compared to the rest of the collection. On the other hand, the domain state of the ferrimagnetic grains determines, to a great extent, the values of the hysteresis parameters. For non-interacting SD grains the ratio $J_{rs}/J_s$ should be 0.5, but this value is rarely achieved because of magnetostatic interactions among grains (Davis and Evans, 1976; Dunlop, 1981). Thus as a result of interactions $J_{rs}/J_s$ and $H_{1/2}$ may be lowered, while $H_{cr}$ and $H_{cr'}$ may become higher (Dankers, 1981). However, these considerations only apply to the positive type of interactions, where the sample tends to maintain its remanent record and requires rather high back fields to be erased. To evaluate magnetostatic interactions, we used differential remanence (Petrovsky et al., 1993). All the samples except for one (Dk90) show the so-called negative type of interactions (Fig. 5b). This behaviour can be explained in terms of mixtures of different domain states, with the remanence acquisition dominated mainly by multidomain (titano)magnetite grains. This conclusion is also supported by the plot of Day et al. (1977) (Fig. 6), where the majority of the data points plot in the PSD field. A mixture of (SD + MD) and (SD + SP) grains should plot in this field as well.

![Fig. 6. Day plot (Day et al., 1977) including data points for all samples. An average PSD state is revealed.](image)

A tumble alternating field demagnetization of the IRM was performed using a Molspin AF-demagnetizer. The median destructive field of the IRM ($H_{1/2}$) varied between 10 and 20 mT (Tables 1, 2). $H_{1/2}$ does not depend on concentration (Hartstra, 1982a, 1982b) and should reflect grain-size changes. However, for the studied archaeomagnetic samples, $H_{1/2}$ does not show any systematic change related to hysteresis parameters (Tables 1, 2). As noted above, the negative
type of interactions takes place in these samples (Fig. 5b). Perhaps the lowering of H_{1/2} caused by this does not allow us to see any relationship to the actual grain-size distribution.

3.4 Hysteresis measurements

\( J_{rs}/J_{s} \) and \( H_{cr}/H_{c} \) ratios are widely used to discriminate between different domain states (Day et al., 1977). In the case of mixture of grain sizes, coercivity and magnetization parameters are influenced in different ways by the presence of fine and coarse grains. In particular, \( H_{c} \) is controlled by the proportion of coarse particles while \( H_{cr} \) and \( J_{rs} \) values are determined by the presence of fine SD grains (Day et al., 1977; Parry, 1980, 1982). Thus, on the diagram of Day et al. (1977) points often plot in PSD range, as is the case for the archaeomagnetic samples in this study (Fig. 6). A few data points even show typical MD characteristics. When a mixture of particles with contrasting grain sizes (SD + SP, SD + MD) or coercivities (i.e. magnetite + hematite or goethite) are present in a sample, constricted hysteresis loops are obtained (Kapicka and Sjoberg, 1993; Roberts et al., 1995). Thus, the commonly used hysteresis parameters alone do not give unambiguous information about the domain state of the ferromagnetic particles. In our collection of archaeological samples, a number of hysteresis loops display constricted shapes (Fig. 7b—sample Dk62; Table 2).

Values of initial mass-specific magnetic susceptibility \( \chi \) encompass a relatively wide range—from 0.27 to 7.8 \( \times 10^{-6} \) \( m^3/kg \). The coercive force \( H_{c} \) and remanence coercivities \( H_{cr} \) and \( H_{cr'} \) are plotted as a function of \( \chi \) in Fig. 8. There is a relatively sharp decrease in \( H_{cr} \) as \( \chi \) increases from 0 to \( \sim 1.5 \times 10^{-6} \) \( m^3/kg \). The same trend in \( H_{cr} \) and \( H_{c} \) values is not pronounced. In general, the coercive force gradually decreases up to \( \sim 1.5 \times 10^{-6} \) \( m^3/kg \). The break-up in the coercivity parameter \( H_{cr} \) occurs at \( \chi \sim 1.5 \times 10^{-6} \) \( m^3/kg \). Because of this specific relation between \( \chi \) and remanence coercivities, the rock magnetic parameters are summarized in two tables—Table 1 for \( \chi < 1.5 \times 10^{-6} \) \( m^3/kg \) (Group A) and Table 2 for \( \chi > 1.5 \times 10^{-6} \) \( m^3/kg \) (Group B). The samples in group A possess the highest values of \( H_{c}, H_{cr} \) and \( H_{cr'} \) (Fig. 8, Table 1). Group B includes samples with \( \chi \)-values covering a much wider interval. In this group \( H_{cr}, H_{cr'} \) tend to increase as \( \chi \) increases from 1.5 to \( 4 \times 10^{-6} \) \( m^3/kg \).

Most of the samples having \( \chi < 1.5 \times 10^{-6} \) \( m^3/kg \) show low unblocking temperature, probably due to the presence of weathering products so that the harder magnetic properties (Table 1) probably do not reflect the predominance of SD particles. In a contrast Roberts et al. (1995) stated that the hysteresis properties will be influenced by the hard fraction (presented by goethite) only if it is present in a significant amount. This is clearly not the case in the present study, because the hard component of the three component IRM always has the lowest intensity (Fig. 4). Remanence coercivities \( H_{cr} \) and \( H_{cr'} \) are higher for samples exhibiting \( \chi < 1.5 \times 10^{-6} \) \( m^3/kg \). The coercivity ratio \( H_{cr}/H_{c} \) as well as \( J_{rs}/J_{s} \) show values typical for SD-PSD grains. An exception in this group is sample CA46, which shows much softer characteristics (Table 1). Samples belonging to this group often show mixed (SD/MD) behaviour from the Lowrie-Fuller test (Lowrie and Fuller, 1971) (Table 1) but pure SD and MD behaviour is obtained also. For sample Dk87 MD-hysteresis characteristics agree with the MD-results from the Lowrie-Fuller test, but in other cases (samples 2120, D180, D200) they are contradictory (i.e. PSD-type from hysteresis measurements and MD—according to the Lowrie-Fuller test). The reliability of the MD-behaviour obtained by the Lowrie-Fuller test is proved theoretically only in case of magnetite as a ferrimineral carrier and the influence of high coercivity minerals is not considered (Xu and Dunlop, 1995). For the contradictory examples mentioned above, the high coercivity contribution is observed and it might be a reason for the obtained results.

The higher \( \chi \) values may be due to the enhanced content of SP and/or MD grains or a higher concentration (i.e. higher packing density) of (titano)magnetite grains. An enhanced concentration of ferromagnetic grains will raise the \( \chi \) values, but it can hardly influence the remanence coercivity parameters. According to Day et al. (1977), concentrations above 5 weight
percent lead to a significant decrease in $H_c$, $H_{cr}$ and $J_{rs}/J_s$. The remanence coercivities $H_{cr}$ and $H_{cr}'$ have also been found to vary considerably, depending on the relative content of fine SD particles (Parry, 1980, 1982). The subdivision of original titanomagnetite grains by ilmenite lamellae (Hartstra, 1982b) also increases $H_{cr}$ and $H_{cr}'$. If we assume that an effective decrease in grain sizes occurs for values of $\chi$ between 2–3.5 $\times 10^{-6}$ m$^3$/kg, then the rise in $H_{cr}'$ and $H_{cr}$ can be explained. A small admixture of fine near-SD particles will affect $H_{cr}$ and $H_{cr}'$ without significant $\chi$ changes. According to Hartstra (1982b) the grain size dependence of remanence coercivities $H_{cr}'$ and $H_{cr}$ are significant and are more pronounced for $H_{cr}'$. Such a trend can be seen on the graph of $H_{cr}$ and $H_{cr}'$ versus $\chi$. Thus it appears that concentration or grain size controls the $\chi$-variations in these archaeological samples.
3.5 Monitoring the chemical alterations of magnetic minerals during thermal demagnetization

Chemical alterations that occur in samples during laboratory heatings cause irreversible changes in composition and grain-size distribution in the material. As a result, the magnetic capacity is also changed, so that the additivity law of partial TRMs (pTRM) is not fulfilled.

In the method used in this study magnetization of the samples after each temperature step produces remanent magnetization with the contribution both from the newly formed magnetic phases with $T_t$ higher than the next temperature and the ferrimagnetic phases initially present. It means that the curve of the IRM remained (full curve in Fig. 9) would reflect a creation of new magnetic grains which succeeded to grow up to stable SD sizes. When comparing this curve with the thermal IRM-decay curve (dashed line in Fig. 9) (IRM, induced only once before heating steps on a sister specimen), changes in magnetic fraction, capable of carrying stable remanence, are easily detected. An origination of a new magnetic phase would be first reflected on the $K$-variations, since SP grains cannot carry remanence.

The most significant changes are evidenced for sample 2125 (Fig. 9a). The strong $K$-decrease, accompanied by proportional but opposite change in IRM (2 T), induced after each temperature step, points to a process of increasing quantity of stable SD grains. Since the finest SP particles show the highest $K$-values (Maher, 1988; Thompson and Oldfield, 1986) their growth up to SD sizes leads to a susceptibility decrease. At the same time stable SD grains acquire remanent magnetization much more effectively. Probably the volume fraction of unstable SP/SD grains...
Fig. 9. Results from the method applied to detect mineralogical changes during laboratory heatings. Full diamonds—IRM (2 T), acquired after each temperature step; open diamonds—room temperature magnetic susceptibility $K$; full circles—IRM remained after heating; open squares—thermal demagnetization of IRM (2 T) induced only once before heatings in a sister specimen.
is crucial, since the two IRM-demagnetization curves (dashed and full lines in Fig. 9a) differ, beginning from 130°C up to the final temperature of 620°C. It can be concluded that the product of chemical alteration is magnetite (the final $T_b$ is close to $T_b$ of magnetite).

Different type of behaviour of mineral magnetic changes is evident for the sample M3 (Fig. 9b). In contrast to the previous example, magnetic susceptibility $K$ and IRM (2 T), induced after each temperature do not change very much (about 10–12%). However, on the curve of IRM
remained after each heating step, a significant contribution of a new magnetic mineral appears, beginning at \( \sim 100^\circ \text{C} \). It can be supposed that this new phase is maghemite which converts to hematite above \( \sim 300^\circ \text{C} \) (Fig. 9b). The reason for the weak changes in \( K \) and IRM (2 T), induced after each heating, could be the process of simultaneous oxidation of primary titanomagnetite grains together with an appearance and transformation of maghemite. The appearance of thermally unstable maghemite maybe due to the presence of lepidocrocite (\( \gamma \)-FeOOH) in samples as a weathering product (Barbetti et al., 1977).

Chemical changes occurring during heating in a sample M30 (Fig. 9c) are relatively weaker. Magnetic susceptibility and IRM, induced after each heating remains almost constant up to \( T = 550^\circ \text{C} \). The only indication, pointing to some alteration, is the deviation of the curve of IRM, remained after heating from the IRM decay curve in the interval (200–320)\(^\circ \text{C} \) (Fig. 9c). Such a behaviour could be due to an origination of a small amount of unstable maghemite which subsequently converts to hematite at about 300\(^\circ \text{C} \), as it was the case for the previous sample.

Another example of significant chemical changes during heating, is shown in Fig. 9d—sample Dk31. Among the magnetic parameters monitored, IRM (2 T), induced after each heating shows the most pronounced changes. The alteration begins above \( T = 170^\circ \text{C} \) when \( K \) decreases and IRM-increases. It can be seen, that in this case the quantitative changes in \( K \) and IRM (2 T), induced after each heating, are not comparable, as it was for sample 2125 (Fig. 9a). This means that different process is responsible for the observed behaviour. The opposite \( K \)- and IRM (2 T)-changes at low temperatures (up to 400\(^\circ \text{C} \)) could be due to lamella subdivision of original titanomagnetite grains (Holm and Verosub, 1988), leading to an effective decrease in grain size. Such a supposition is also supported by the slight increase in IRM, remained after heating (Fig. 9d). Above 420\(^\circ \text{C} \) exsolution of titanomagnetite grains probably occurs. As a result, a new stronger magnetic phase appears—titanomagnetite of composition, close to that of magnetite.

Samples, showing minor or no chemical changes during heating, are characterized by identical relations among the parameters monitored during the experiment. Some examples are shown in Fig. 10. In contrast to the previous case (Fig. 9), the IRM-demagnetization curve and the curve of IRM, remained after each temperature step, are almost identical. This reveals that no significant changes in the composition or grain sizes of the ferromagnetic fraction that contributes to remanent magnetizations, occur. Variations in \( K \)- and IRM, induced after each temperature step are restricted up to about 10% (No D191 in Fig. 10), or they lack any changes (No2134, CA45).

From the above considered method for revealing changes during laboratory heatings, it could be concluded that studying simultaneously a number of magnetic parameters (including \( K \) and isothermal remanence) during the thermal demagnetization gives much better and unambiguous information about the chemical alteration.

4. Rock Magnetic Properties of the Archaeological Samples and the Palaeointensity Experiment

It is well known that the Thellier method (Thellier and Thellier, 1959) can be used for a palaeointensity determination only if SD or PSD particles carry the TRM. If MD grains are present or if chemical alteration of ferromagnetic minerals occurs during heating, the experiment fails or gives incorrect values for the ancient intensity of the geomagnetic field (e.g. Bolshakov and Shcherbakova, 1979; Dunlop and Xu, 1994; Haag et al., 1995). The question of the influence of chemical alteration on the reliability of the palaeointensity determination has been widely discussed (Coe, 1967; Shaw, 1974). Obviously, the primary or secondary nature of the ferromagnetic minerals in samples should be considered to determine if the initial material, acquired a TRM during cooling from high temperatures through the \( T_b \) of the ferromagnetic minerals is remained unchanged.
Products of low temperature changes are frequently present in archaeological materials, as already has been shown. They are considered to be a source of error in the palaeointensity experiment. The only ferrimagnetic oxyhydroxide that forms at room temperature is goethite (O’Reilly, 1984). Since goethite is unstable upon heating, its transformation will affect NRM and TRM behaviour during the Thellier experiments. Unblocking temperatures are typically found to be between 70–120°C, but its dehydration occurs in the temperature interval 250–400°C (Dekkers, 1990). As the remanent magnetization carried by goethite is weak, its concentration must be considerable to have a significant influence on the total NRM (considered as a TRM). In the samples we studied, the hardest IRM component is always the weakest one (Fig. 4, see also high values of S-ratio in Tables 1, 2), so that eventual goethite contribution to the NRM should lead to only minor alteration during heating.

The iron oxyhydroxide lepidocrocite (γ-FeOOH) is also a mineral present in natural clays. If it was initially existing in clays which were burnt in antiquity, it can transform to maghemite (Özdemir and Dunlop, 1993) and carry a TRM. It has been shown (Özdemir and Banerjee, 1984; Özdemir, 1990) that when microstructural defects are present fine grained acicular maghemite is stable with respect to inversion to hematite at temperatures up to 750°C. Its TRM intensity is found to be a stable and linear function of the magnetizing field in the range (10–100) × 10^{-6} T. If such a stable maghemite acquires a TRM during an initial burning of the clay in an archaeological material, it would be a primary mineral and might even be an ideal material for palaeointensity study as a mineral possessing higher spontaneous magnetization compared to that of titanomagnetites (Hartstra, 1982a).

Maghemite (γ-Fe$_2$O$_3$) which is unstable upon heating is a mineral, which is regarded as a problem for the palaeointensity experiment (Thomas, 1993). Such maghemite is an oxidation product of magnetite, that is, an indication of low temperature oxidation and weathering (Lowrie and Heller, 1982; O’Reilly, 1984). Metastable maghemite transforms to stable hematite upon heating to temperatures above 250°C (Özdemir, 1990). This process causes a significant decrease in $J_{rs}$ and K and an increase in $H_c$, $H_{cr}$ and $H_{cr'}$. Maghemite is a strongly magnetic mineral while hematite—a weakly magnetic. Therefore, γ-α conversion should be accompanied by a significant K- and $J_{rs}$-decrease. However, if together with γ-Fe$_2$O$_3$, titanomagnetites are present, γ-α transition will be obscured by the oppositely directed changes in titanomagnetites. For the samples from Djadovo (D141–D173) and Isperih (2116–2140) the ferrimagnetic phase with $T_b \sim 300°C$ dominates in $J_{rs1}$ (Fig. 2a, b) and probably reflects the presence of both Ti-magnetite and Ti-maghemite.

Titanomagnetites of different composition are the most common ferromagnetic constituents that carry TRM in archaeological samples (and specially samples taken from ovens and bricks) (Kovacheva and Toshkov, 1994; this study). We found that most of the specimens show unblocking temperatures, characteristic for titanomagnetite in a relatively high oxidation state (Fig. 2).

The obtained palaeointensity values from samples which were studied were evaluated from 1 to 5 (1—rejected; 2—bad; 3—intermediate; 4—good; 5—excellent) (Tables 1, 2). The relative distribution of a “bad” and “good” quality samples between the two $\chi$-groups (group A—$\chi < 1.5 \times 10^{-6}$ m$^3$/kg; group B—$\chi > 1.5 \times 10^{-6}$ m$^3$/kg) is rather interesting. Only 20% of the intensity results from the samples with low $\chi$ were of a good quality, the remainder were rejected (category 1) or were of bad quality (category 2 and 3). Samples from group B ($\chi > 1.5 \times 10^{-6}$ m$^3$/kg) generally show much better results (category 4 and 5) except for No 2154 (discarded) and two others of intermediate quality. In comparison, if samples are grouped according to their $T_s$, successful and unsuccessful Thellier experiments are not so clearly separated although the greatest number of discarded samples have low $T_s$ (80–150°C).

In Tables 1 and 2 and Fig. 11, it is obvious that $\chi$ and SIRM values change simultaneously. Since the two parameters are strongly concentration dependent, the question arises of whether the separation between good and bad Thellier experiments results only from the stronger NRM values
In order to reveal the influence of grain-size changes on the distribution of samples ("bad" and "good"), a ratio SIRM/\chi was used as an indicator of the presence of SP or MD fraction, paramagnetic component as well as high coercivity minerals (Maher, 1988; Thompson and Oldfield, 1986). As it is seen in Tables 1 and 2, there is a higher paramagnetic contribution in samples showing low \chi-values. Particular case is observed for the sample No M3 where high SIRM/\chi probably is due to the presence of significant high-coercivity fraction. This supposition agrees with the relatively low S-value (S = 0.69) for this sample. It is obvious from Fig. 12 that coercivity parameters of samples, exhibiting high quality of the Thellier experiment (full symbols), show almost one and the same H_{cr'}, H_{cr}, and H_{c}, independently of the value of SIRM/\chi ratio. In contrast, H_{cr'} for samples, showing low quality of palaeointensity experiment (open symbols in Fig. 12), increases as SIRM/\chi increases. H_{c} and H_{cr} do not vary significantly for

(i.e. more precise measurements during the Thellier experiment). This seems not to be the case, or at least not the only reason, because H_{cr'} and H_{cr} values do not depend on concentration up to 5 weight percent (Day et al., 1977). These and higher magnetic concentrations are not observed in most natural rocks. Therefore, the behaviour of H_{cr'} and H_{cr} with respect to \chi should be due mostly to compositional or grain size changes. If bad palaeointensity determination is due to the presence of MD grains, the high coercivity and low \chi-values for samples from Table 1 must be explained. One possible answer could be found in analytical and numerical models, developed by Xu and Merrill (1990) and Xu and Dunlop (1993). These authors show that due to screening by soft walls in MD grains, the AF-stability of saturation remanence is usually higher than the expected maximum microcoercivity associated with the domain wall pinning. Thus, the higher H_c, H_{cr} and H_{cr'} values could be the result of the large number of soft domain walls in MD grains. The coercivity values in our study were obtained from specimens previously AF-demagnetized in a field of 100 mT, so that we do not contradict to the study of McClelland and Shcherbakov (1995).
all samples. Such a behaviour of coercivity parameters could be due to a greater contribution of high-coercivity fraction in samples, showing low quality of Thellier experiment. On the other hand, a relatively constant $H_{cr}$ values, accompanied by an increase in $H_{cr}$ as SIRM/χ increases, may point also to an increasing strength of negative interactions among the ferromagnetic grains.

Almost identical coercivity values $H_c$ through the whole SIRM/χ range are likely to be due to the presence of stable SD particles, which contribute to SIRM, but have less influence on χ values. Low SIRM/χ could reflect the presence of an SP fraction, which raises the χ values. Constricted hysteresis loops (Table 2) for most of these samples also support the idea of a significant SP contribution. At this point our results contradict the conclusion of Cui et al. (1997) that samples exhibiting wasp waisted loops are not suitable for the palaeointensity determination. Furthermore, Pick and Tauxe (1993) report successful Thellier experiments of samples, showing constricted hysteresis loops.

As it was shown earlier, chemical changes in sample 2125 (Isperih) (Fig. 9a) are attributed to the growth of SP grains up to stable SD sizes, causing changes in initial magnetic capacity. As a result, the number of magnetic grains carrying laboratory induced TRM will be greater than those carrying NRM before this heating step. This means that NRM-demagnetization curve will decay more slowly than the increase of TRM, which is exactly the case for samples of this locality (graphs not shown here). In spite of the chemical changes evidenced (Fig. 9a), the linearity of the Arai diagram, obtained for a sister specimen, in the interval (130-550)°C is very good. Therefore, a growth of SP grains up to SSD sizes does not cause strong deviations of data points on the
Arai diagram. Not withstanding, the existence of chemical alterations, causing an increase in the quantity of SSD grains suppose that the obtained value for palaeointensity is lower than the real one. In this sense, the above described processes may not be detected by usual checks, intended to denote chemical changes occurring during Thellier experiment (pTRM checks and K-behaviour). It should be noted that for all samples, which have been subjected to the Thellier experiment (150 samples—N. Jordanova, Ph.D. thesis) pTRM checks do not exceed 5–7% and usually show 2–3% changes in magnetic capacity.

Next example with significant chemical changes (sample M3—Fig. 9b) is attributed to an origination of a new ferrimagnetic phase—maghemite. The quality of the Thellier experiment for this sample is low (Table 2). In contrast to the previous example (No 2125), in this case chemical alterations strongly affect the linearity of the Arai diagram.

The third sample—No M30 (Fig. 9c) shows weaker chemical changes and again they are reflected on the behaviour of K- and IRM, induced after each temperature. Such a behaviour is in agreement with the better quality of the Thellier experiment. Exactly in the temperature interval, where chemical changes take place, data points on the Arai diagram deviate from the straight line (for the sake of place not shown here).

Chemical alteration is also apparent for the sample Dk31 (Fig. 9d). It was supposed that above $T \sim 400^\circ$C significant changes in primary titanomagnetite grains occur. Thus, the appropriate temperature interval for deriving palaeointensity value should be restricted to 400°C, which has been taken into account.

Results for samples, shown in Fig. 10 allow us to exclude significant chemical changes in primary minerals during heating. The Thellier experiment for all these samples is highly successful and the palaeointensity value is determined from a wide temperature interval.

Thus, preliminary experiments for detection eventual chemical alteration of primary minerals in the archaeomagnetic samples provide valuable information about the degree of deterioration of the quality or obtaining non-real palaeointensity values using the Thellier method.

5. Conclusions

Our experimental results can be summarized as follows:

1. All analyses used show that a low coercivity ferromagnetic phase dominates in samples studied. The most successful Thellier experiments are associated with samples showing broad unblocking and coercivity spectra.

2. Since hysteresis parameters of natural samples reflect the response of all ferromagnetic phases and domain states present, there is no direct correlation between their values and the success of the palaeointensity experiment.

3. Coercivities $H_c$, $H_{cr}$ and $H_{cr'}$ show notable dependence on the $\chi$-values with decreases in the range $\chi < 1.5 \times 10^{-6}$ m³/kg and increases for $\chi > 1.5 \times 10^{-6}$ m³/kg. The Thellier experiments for most of the samples falling in the group with low $\chi$ are unsuccessful while those from the group with high $\chi$ are successful.

4. The magnetic susceptibility of archaeological samples studied is controlled not only by the concentration of ferromagnetic minerals. The failure or success of the palaeointensity experiment is dependent on $\chi$-values through the remanence coercivities.

5. Successful Thellier experiments are obtained for the sister specimens of these showing minor (up to 10%) or no changes in magnetic susceptibility $K$ and IRM, induced after each temperature step, combined with a coincidence of the curves of IRM, induced only once before heating and the IRM, remained after each temperature.

As a preliminary rock magnetic investigation, this work was not designed to give definite rules for acceptance or rejection of samples for the palaeointensity determination. Future studies on more archaeological samples will provide better conclusions on the problems discussed above.
One of the authors (N.J.) highly acknowledges the financial support from the Geophysical Institute in Prague during her stay there. We are very grateful to Didi Jordanova for many useful suggestions and help during the whole preparation of the manuscript.

The constructive comments and suggestions made by the two reviewers are highly appreciated.

This work is supported by Grants NZ-405/94 and MU-IS 4/94 of the Bulgarian Ministry of Education, Science and Technology.

REFERENCES

Aitken, M., A. Allsop, G. Bussell, and M. Winter, Palaeointensity Determination Using the Thellier Technique: Reliability Criteria, J. Geomag. Geoelectr., 38, 1353–1363, 1986.

Aitken, M., A. Allsop, G. Bussell, and M. Winter, Determination of the intensity of the Earth's magnetic field during archaeological times. Reliability of the Thellier technique, Rev. Geophys., 26, 3–12, 1988.

Barbetti, M. F., M. W. McElhinny, D. J. Edwards, and P. W. Schmidt, Weathering processes in baked sediments and their effects on archaeomagnetic field-intensity measurements, Phys. Earth Planet. Int., 13, 346–356, 1977.

Bolshakov, A. S. and V. V. Shcherbakova, Thermomagnetic criteria for determination of domain structure of ferrimagnetics, Fizika Zemli, 2, 38–47, 1979 (in Russian).

Burakov, K. S., Thermomagnitometer, Fizika Zemli, 5, 92–96, 1977 (in Russian).

Burov, B., D. Nurgaliev, and P. Yasonov, Palaeomagnetic analysis, Kazan Univ., 36–42, 1986.

Coe, R. S., The determination of paleo-intensities of the Earth's magnetic field with emphasis on mechanisms which could cause non-ideal behaviour in Thellier's method, J. Geomag. Geoelectr., 19, 157–179, 1967.

Cui, Y. and K. L. Verosub, A mineral magnetic study of some pottery samples: possible implications for sample selection in archaeointensity studies, Phys. Earth Planet. Int., 91, 261–271, 1995.

Cui, Y., K. Verosub, and A. Roberts, The effect of low temperature oxidation on large multidomain magnetite, Geophys. Res. Lett., 21, 757–760, 1994.

Cui, Y., K. L. Verosub, A. P. Roberts, and M. Kovacheva, Mineral magnetic studies of archaeological samples: implications for sample selection for paleointensity determinations, J. Geomag. Geoelectr., 49, this issue, 567–585, 1997.

Dankers, P., Relationship between median destructive field and remanent coercive forces for dispersed natural magnetite, titanomagnetite and hematite, Geophys. J. R. astr. Soc., 64, 447–461, 1981.

Davis, P. M. and M. E. Evans, Interacting single-domain properties of magnetite intergrowths, J. Geophys. Res., 81, 989–994, 1976.

Day, R., M. Fuller, and V. A. Schmidt, Hysteresis properties of titanomagnetites: grain-size and compositional dependence, Phys. Earth Planet. Int., 13, 260–267, 1977.

Dekkers, M. J., Magnetic properties of natural goethite—II. TRM behaviour during thermal and alternating field demagnetization and low temperature treatment, Geophys. J., 97, 341–355, 1989.

Dekkers, M. J., Magnetic properties of natural goethite—III. Magnetic behaviour and properties of minerals, originating from goethite dehydration during thermal demagnetization, Geophys. J. Int., 103, 233–250, 1990.

Dunlop, D., The rock magnetism of fine particles, Phys. Earth Planet. Int., 26, 1–26, 1981.

Dunlop, D. and S. Xu, Theory of partial thermoremanent magnetization in multidomain grains. 1. Repeated identical barriers to wall motion (single microm coercivity), J. Geophys. Res., 99, 9005–9023, 1994.

Eyre, J. K. and J. Shaw, Magnetic enhancement of Chinese loess—the role of γ-Fe2O3?, Geophys. J. Int., 117, 265–271, 1994.

Haag, M., J. R. Dunn, and M. Fuller, A new quality check for absolute palaeointensities of the Earth magnetic field, Geophys. Res. Lett., 22, 3549–3552, 1995.

Hartstra, R. L., A comparative study of the ARM and Isr of some natural magnetites of MD and PSD grain size, Geophys. J. R. astr. Soc., 71, 497–518, 1982a.

Hartstra, R. L., Grain-size dependence of initial susceptibility and saturation magnetization—related parameters of four natural magnetites in the PSD-MD range, Geophys. J. R. astr. Soc., 71, 477–495, 1982b.

Holm, E. J. and K. Verosub, An analysis of the effects of thermal demagnetization on magnetic carriers, Geophys. Res. Lett., 15, 487–490, 1988.

Jordanova, N., Rock magnetic studies in archaeomagnetism and their contribution to the problem of reliable determination of the ancient geomagnetic field intensity, Ph.D., Sofia, 1996.

Kapica, A. and B. A. Sjoberg, Hysteresis effects of varying concentration of magnetite, hematite, pyrrhotite and greigite grains in a diamagnetic matrix, Studia Geophys. et Geodaetica, 37, 423–432, 1993.
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Kovacheva, M. and M. Kanarchev, Revised archaeointensity data from Bulgaria, *J. Geomag. Geoelectr.*, 38, 1297–1310, 1986.

Kovacheva, M. and A. Toshkov, Geomagnetic field variations as determined from Bulgarian archaeomagnetic data. Part I: The last 2000 years AD, *Surveys in Geophysics*, 15, 673–701, 1994.

Kovacheva, M., N. Jordanova, and D. Jordanova, Archaeomagnetic study of the Early Bronze Age settlement Sarovka near Dubene, Karlovo district, *Reports of Prehistoric Res. Projects*, 1, 32–43, 1995.

Lowe, W., Identification of ferromagnetic minerals in a rock by coercivity and unblocking temperature properties, *Geophys. Res. Lett.*, 17, 159–162, 1990.

Lowe, W. and M. Fuller, On the alternating field demagnetization characteristics of multidomain thermoremanent magnetization in magnetite, *J. Geophys. Res.*, 76, 6339–6349, 1971.

Lowe, W. and F. Heller, Magnetic properties of marine limestones, *Rev. Geophys. Space Phys.*, 20, 171–192, 1982.

Maher, B., Characterization of soils by mineral magnetic measurements, *Phys. Earth Planet. Int.*, 42, 76–92, 1986.

Maher, B., Magnetic properties of some synthetic sub-micron magnetites, *Geophys. J.*, 94, 83–96, 1988.

McClelland, E. and V. P. Scherbakov, Metastability of domain state in multidomain magnetite: Consequences for remanence acquisition, *J. Geophys. Res.*, 101, 3841–3857, 1995.

Neel, L., Théorie du trainage magnétique des ferromagnétiques en grans fins avec application aux terres cuites, *Ann. Geophys.*, 5, 99–136, 1949.

Neel, L., Some theoretical aspects of rock-magnetism, *Phil. Mag. Sup.*, 4, 191–242, 1955.

Nishitani, T. and M. Kono, Effect of low-temperature oxidation on the remanence properties of titanomagnetites, *J. Geomag. Geoelectr.*, 41, 19–38, 1989.

O'Reilly, W., *Rock and Mineral Magnetism*, 220 pp., Blackie, Glasgow and London, 1984.

Osipov, J. B., *Magnetism of Soils*, 199 pp., Nedra, Moscow, 1978 (in Russian).

Özdemir, O., High-temperature hysteresis and thermoremanence of single-domain maghemite, *Phys. Earth Planet. Int.*, 65, 125–136, 1990.

Özdemir, O. and S. K. Banerjee, High temperature stability of maghemite (γ-Fe₂O₃), *Geophys. Res. Lett.*, 11, 161–164, 1984.

Özdemir, O. and D. Dunlop, Chemical remanent magnetization during γ FeOOH phase transformations, *J. Geophys. Res.*, 98, 4191–4198, 1993.

Parry, L. G., Shape-related factors in the magnetization of immobilized magnetite particles, *Phys. Earth Planet. Int.*, 22, 144–154, 1980.

Parry, L. G., Magnetization of immobilized particle dispersions with two distinct particle sizes, *Phys. Earth Planet. Int.*, 28, 230–241, 1982.

Pecherskij, D. M., V. I. Bagin, S. J. Brodskaja, and Z. V. Sharonova, *Magnetism and Conditions during Origination of Magmatic Rocks*, pp. 106–107, Nauka, Moscow, 1975 (in Russian).

Petrovsky, E., P. Hejda, T. Zelinka, V. Kropacek, and J. Subrt, Experimental determination of magnetic interactions within a system of synthetic haematite particles, *Phys. Earth Planet. Int.*, 76, 123–130, 1993.

Pick, T. and L. Tauxe, Holocene paleointensities: Thellier experiments on submarine basaltic glass from the East Pacific Rise, *J. Geophys. Res.*, 98, 17,949–17,964, 1993.

Roberts, A. P., Y. Cui, and K. L. Verosub, Wasp-waisted hysteresis loops: Mineral magnetic characteristics and discrimination of components in mixed magnetic systems, *J. Geophys. Res.*, 100, 17,909–17,924, 1995.

Shaw, J., A new method of determining the magnitude of the palaeomagnetic field. Application to five historic lavas and five archaeological samples, *Geophys. J. R. astr. Soc.*, 39, 133–141, 1974.

Scherbakov, V. P., E. McClelland, and V. V. Scherbakova, A model of multidomain thermoremanent magnetization incorporating temperature-variable domain structure, *J. Geophys. Res.*, 98, 6201–6216, 1993.

Thellier, E. and O. Thellier, Sur l'intensite du champ magnetique terrestre dans le passe historique et geologique, *Ann. Geophys.*, 15, 285–376, 1959.

Thomas, N., An integrated rock magnetic approach to the selection or rejection of ancient basalt samples for paleointensity experiments, *Phys. Earth Planet. Int.*, 75, 329–342, 1993.

Thompson, R. and F. Oldfield, *Environmental Magnetism*, 227 pp., Allen and Unwin, Winchester, Mass., 1986

Van Velzen, A. J. and D. A. Zijderveld, A method to study alterations of magnetic minerals during thermal demagnetization applied to a fine-grained marine marl (Trubi formation, Sicily), *Geophys. J. Int.*, 110, 79–90, 1992.

Van Velzen, A. J. and D. Zijderveld, Effects of weathering on single-domain magnetite in Early Pliocene marine marls, *Geophys. J. Int.*, 121, 267–278, 1995.

Verosub, K. L. and A. P. Roberts, Environmental magnetism: Past, present and future, *J. Geophys. Res.*, 100, 2175–2192, 1995.

Walton, D., Re-evaluation of Greek archaeomagnitudes, *Nature*, 310, 740–743, 1984.

Walton, D., Improving the accuracy of geomagnetic intensity measurements, *Nature*, 328, 789–791, 1987.
Xu, S. and D. Dunlop, Theory of alternating field demagnetization of multidomain grains and implications for the origin of pseudo-single-domain remanence, *J. Geophys. Res.*, 98, 4183–4190, 1993.

Xu, S. and D. Dunlop, Theory of partial thermoremanent magnetization in multidomain grains. 2. Effect of microcoercivity distribution and comparison with experiment, *J. Geophys. Res.*, 99, 9025–9033, 1994.

Xu, S. and D. Dunlop, Toward a better understanding of the Lowrie-Fuller test, *J. Geophys. Res.*, 100, 22,533–22,542, 1995.

Xu, S. and R. T. Merrill, Toward a better understanding of magnetic screening in multidomain grains, *J. Geomag. Geoelectr.*, 42, 637–653, 1990.

Zelinka, T., P. Hejda, and V. Kropacek, Vibrating-sample magnetometer for measuring magnetically weak materials, *Tesla Electron.*, 17, 35–43, 1984.