Application of a New Technique to Greek Archaeomagnitudes

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An improved method for measuring the anomalous magnetic moment produced by mineral alteration during heating of archaeomagnetic samples is described. After subtraction of the anomalous moment the ancient geomagnetic field deduced from the data becomes reproducible to about $\pm 5\%$.

1. Introduction

In order to be useful, the reproducibility of experimental values for the ancient geomagnetic field needs to be better than about 10\%. However, in practice it is often worse than 50\%. The reason for this large error is that undetected mineral alteration which takes place during the heating required for laboratory processing compromises the results (WALTON, 1983, 1984, 1985, 1986, 1987). The alteration which occurs is not detected by conventional tests (see e.g., COE, 1967; AITKEN, 1983; AITKEN et al., 1986) because it is thermally activated. However, because it is thermally activated it is time dependent, and can be detected by a simple series of measurements of the moment as a function of time. This has been discussed at some length in a recent review article (WALTON, 1988) so what follows is an abbreviated outline.

The obvious way to measure the change in moment due to alteration is to hold the sample at the (elevated) temperature in question, in a field close to the ancient field, and monitor the moment. If the laboratory field is sufficiently close to the ancient field any viscous change in the moment is completely negligible, with the result that any changes are due to alteration. In effect, this was the method used in a first attempt to correct for alteration (WALTON, 1984). The moment cannot be measured as accurately at elevated temperatures, so it is better to cool the sample in order to measure the moment, as in the standard Thellier methods (COE, 1967). One way of implementing this is to heat for a short time, cool to the temperature at which the moment is measured, then heat again for a longer time and cool and measure again, any difference then being due to alteration. This method was used in a second attempt (WALTON, 1987), on modern bricks for which the original field was known precisely. Correction for alteration reduced the scatter in that data to $\pm 5\%$. This was considerably less than the scatter in the previous results (WALTON, 1984).

Unfortunately, both these methods require that the sample be at thermal
equilibrium, and because alteration proceeds faster initially, the change in moment
before equilibrium is achieved is considerable. In order to be able to monitor the
progress of alteration better, it is desirable for the first heating to be as short as
possible. If the least possible time at elevated temperature is desired it is necessary to
accept some thermal disequilibrium in the sample. In that case, however, it is
obviously impossible to perform the second heating for a longer time since
differences in thermal equilibrium can manifest themselves as differences in
magnetic moment. The progress of alteration must then be monitored by a series of
precisely identical short heatings, the corrected moment being obtained by extra-
polation to zero time. It should be emphasized that alteration is a cumulative
process, so that the extrapolated moment at a given temperature includes the
alteration which has occurred at all preceding temperatures, and this must be
subtracted in order to obtain the correct unaltered moment. Finally the natural
remanent moment (NRM) remaining will also be affected by the alteration, and
must be corrected. This is the method employed in obtaining the results to be
presented here.

While it can be anticipated that alteration can also occur during the original
firing and subsequent burial, we have found that this affects only a minor fraction of
the baked clay samples that we have investigated.

2. Experimental

Sample moments were measured with a second-order gradiometer which
employed a S.Q.U.I.D. as the sensitive element. The samples consisted of flat discs
4.5 mm in diameter by 1–2 mm thick. The sample geometry was chosen to be a thin
disc in order to minimize the time required for the sample to come to thermal
equilibrium. This time appeared to be less than one second. The magnetization
density of the samples was not large enough to require a correction for demagnet-
izing fields introduced by the sample shape. The samples were mounted in an oven
located below the cryostat containing the magnetometer in such a way that the
sample moment could be measured while the sample was held above the ambient
temperature. The oven in turn was mounted on a goniometer which was used to
align the sample moment with the axis of the magnetometer. Stepping motors were
used to move the sample-oven-goniometer assembly in and out of the sensitive
region of the magnetometer for the purpose of monitoring and then subtracting
uninteresting changes in the background level. The whole assembly was surrounded
by a mu-metal shield which reduced external magnetic fields by a factor of about 50.
The laboratory field, $H$, was provided by a coil wound on a form located inside the
shield. That field was set at 50 $\mu$T for all the measurements.

The measurement procedure consisted of three rapid heatings in the laboratory
field, $H$, to a temperature $T$, followed by cooling to the measurement temperature
$T_R$, which was 150°C. The sample took about 20 secs to reach $T$, was held at $T$ for 5
secs, and then cooled to $T_R$ in a time which depended on $T$, but was about two mins.
on average. The moment was measured at $T_R$ after each heating. Finally the sample
was heated to $T$ for a fourth time, this time in zero field, and the NRM remaining was measured. The procedure is illustrated schematically in Fig. 1.

It is better to perform the in-field heatings before the zero field heating because of the viscous delay in recovering the moment removed during the zero-field step; if some moment is removed during a zero field heating, and, in an attempt to replace the lost moment, the sample is then heated to the same temperature for the same time in a field close to the ancient field, it is found that all the moment removed is not replaced. This is because the rate at which the sample approaches equilibrium is proportional to the difference between its moment and the equilibrium value. This difference decreases as the rate of approach decreases, and it is necessary to wait for an infinite time to replace all the lost moment. To some extent this is still true if the temperature is increased, but the difference rapidly become negligible for quite moderate increases in temperature because of the very large temperature dependence of the relaxation rate.

The three values for the moment obtained from the in-field heatings monitor the progress of alteration in the sample. By extrapolating a curve fitted to these three points back to zero time, an approximation of the unaltered moment at $T$ was obtained. It would clearly have been preferable to be able to use more readings, but even with the very short heatings used the instrumental uncertainty made it impossible to detect any changes in moment after the third heating.

The samples employed were those still available from the set used for previous studies (WALTON, 1979; WALTON, 1984).

3. Results and Discussion

Let the moment at the end of the first heating and cooling in $H$ be $M_1$, that at the end of the second be $M_2$, that at the end of the third be $M_3$, and the NRM remaining after heating and cooling in zero field be $M_0$. The differences between $M_1$, $M_2$ and $M_3$ measure the alteration that has taken place. If the time dependence of the alteration is known, it is possible to extrapolate back to zero time in order to obtain the unaltered moment. Unfortunately, the information provided by just three

![Measurement Sequence for Ancient Material](image)

Fig. 1. Schematic representation of the multiple heating method: in the first three steps the sample is heated to a temperature $T$ in a laboratory field of 50 $\mu$T, and cooled to 150°C. When equilibrium is reached at the lower temperature the field is switched off and the moment measured. In the last step the sample is heated to $T$, and then cooled to 150°C in zero field.
values does not permit us to determine the functional dependence of alteration on time, so it was necessary to assume some function and fit the data to it. Two functions were used: the first is a simple linear function of $t$ which although clearly wrong was used simply to test the sensitivity of the correction procedure to the functional form assumed:

$$M(t) = M_i + At.$$  \tag{1}

The second was a $t^{1/2}$ law which is obeyed by oxidation reactions \cite{FROMHOLD, 1976}. This does not imply that oxidation of magnetite to hematite is assumed to be the mechanism of alteration. The square root law simply provides a convenient function whose first derivative decreases with time.

$$M(t) = M_i + Bt^{1/2},$$  \tag{2}

where $M_i$ is the unaltered value of the moment.

Obviously, if $\tau$ is the effective time at temperature during the first heating,

$$M_1 = M(\tau), \quad M_2 = M(2\tau), \quad M_3 = M(3\tau), \quad \text{and} \quad M_i = M(0),$$

whatever the function $M(t)$ may be.

The constants in Eqs. (1) and (2) can be obtained from a least squares fit to the three values of $M$. We are interested in the intercept, which is $M_i = M(0)$. Now the true moment, $M_t$, is obtained by subtracting the sum of all preceding corrections from $M_i$,

$$M_t = M_i - \sum_{k=1}^{i-1} 2B_k,$$

where the factor 2 arises from the square root of the time taken, in units of $\tau$, for the three in-field plus one zero-field measurements. A similar calculation was made for the linear case.

The NRM remaining, $N$, is obtained by correcting $M_0$ as follows:

$$N = M_0 - \left[ \sum_{k=1}^{j} 2B_k \right] M_0 / M_i.$$

The best straight line through the points in a plot of $M_i$ against $N$ then yields the corrected ancient field. A representative plot is displayed in Fig. 2.

Table 1 displays the values of the ancient field calculated from Eqs. (1) and (2), and the average value of the uncorrected field calculated from $[M_1 + M_2 + M_3]/3$ for the sherds. It can be seen that the correction made using the linear $t$ relationship is not very different from that using a $t^{1/2}$ law. This encourages us to believe that our correction procedure is robust, and not overly sensitive to the functional form assumed. This is probably because the amount of alteration is not very great, and the corrections are small.
Fig. 2. A typical series of results, for sample Corinth 6. The sample moment measured at the end of the three in-field heatings is plotted on the horizontal axis, and the NRM remaining after the zero field step is plotted on the vertical axis. In the absence of alteration all three values for each temperature would coincide. Had the laboratory field been equal to the ancient field the points would lie on a vertical straight line. The solid circles are the measurements at the end of the first, the open circles the second, and the crosses the third heating step. The corrected points are represented by the triangles.

The moments have all been corrected for a difference between the rapid laboratory cooling rate and the presumed much slower rate after the original firing in antiquity (WALTON, 1980; FOX and AITKEN, 1980; WALTON and WILLIAMS, 1988). Assuming a time to cool of roughly 24 hours in antiquity the correction is about 10%, so all the values of $M_t$ were multiplied by 0.9.

The results, after correction using the $t^{1/2}$ function, are plotted in Fig. 3. The two dashed lines are $5\mu T$ apart; it can be seen that with the exception of three points all the rest lie within or on these two lines. Thus 90% of the data lies in a band whose width is 10%.

Whether or not the true values of the ancient geomagnetic intensity also lie within that band can, of course, never be determined. However, confidence that it does must await measurements on material from other locations. In order to be confident that changes in the field arise from the earth's core, these should be separated from Athens and Corinth by distances less than the separation between the earth's surface and the core-mantle boundary.
Three things are clear from these results: the first is that the crude correction procedure being used here is capable of yielding data that is reproducible to about ±5%. The second is that each point in Fig. 3 is the result of a single determination on a different sherd. In order to determine the rough limits to the accuracy obtainable from thermal methods, no attempt was made to reduce the error by averaging. Thus the reproducibility can be expected to be improved further; four samples from each sherd, for instance, will reduce the statistical uncertainty by a factor of two. The third is that one Athens 6, and possibly two other, Corinth 5 and 7, points appear to be anomalous. This could possibly be due to alteration occurring prior to laboratory heating. Again, a number of determinations for each date will help to distinguish such outliers from the rest.
4. Conclusions

It is clear from the results we have presented that it is possible to correct for thermal alteration to some extent, thereby improving the reproducibility of the results. Past experience encourages caution, and the problem of alteration prior to laboratory processing exists. Our data indicates that this is not serious, but it is hardly conclusive at this stage.

Whether or not the improved reproducibility we have reported here will lead to reliable values for the geomagnetic intensity must await comparison between sequences obtained from separate geographical locations that are still close enough for the field intensities to be expected to be equal. Such a project is underway, and should be complete at the time of publication of this paper.

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