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Abstract

Nonlinearities observed in Thellier's plots are explained in terms of a weathering model. This model is based on the reduction in size of the originaly present iron oxide particles, due to leaching. In the general case, the slope of the Thellier's plot is a function of the particle size destributions of the magnetic particles, both newly formed and leached ones.

In the special case in which the newly formed magnetic particles are superparamagnetic, the limiting value of the slope of the Thellier's plot towards the magnetic ordering temperature is equal to the ratio of the ancient field intensity to the modern one.

1. Introduction

Clays and other types of soil, as well as rocks, fired in ancient times have been investigated by various branches of scientifiv research in order to obtain a multitude of information, related mainly to problems concerning archeology and paleomagnetism (Aitken, 1972 and Banerjee, 1976). The data obtained have given a variety of clues concerning e.g. provenance, manufacturing technology or trade routes of ancient pottery, or the magnitude and the direction of the earth's magnetic field in ancient times.

Although these materials have been at the focus of extensive studies during the last few decades, little attention has been given to the alterations these samples could have suffered during the interval elapsed between the time they were fired and today. In fact one should expect some alterations to take place in a material that has been produced at least 1000 years ago and has since been exposed to various environmental conditions. In this paper we would like: (i) to briefly review the evidence for the existence of such "weathering" effects as obtained from Mössbauer spectroscopy and bulk magnetization measurements and (ii) to present a quantitative model explaining these effects as they are manifested in paleomagnetic field intensity measurements.

2. Evidence for weathering

Mössbauer measurements in ancient ceramic samples (Kostikas et al, 1976) show iron to be present there mainly as haematite in the form of small particles with an average diameter ranging down to several tens of Angstroms. These data show also that most of the iron oxide present in ancient ceramics belongs to particles which are superparamagnetic for Mössbauer spectroscopy at room temperature. Therefore only a small percentage of particles is responsible for the thermoremanence in these samples. Furthermore, evidence (Kostikas at al, 1976) has been presented pointing to the possible existence of a correlation between the iron oxide particle's size and the "age" of the pottery wares. This correlation indicates a decrease of the iron oxide particle's size with the age of the wares. The possibility of the existence of such a correlation has been further supported by the results on a group of Brazilian pottery (Danon, 1976).

In an investigation of the weathering effects in ancient pottery, Gangas et al (1976) suggested the operation of a mechanism based on the disruption of the ceramic network by water followed by leaching of the iron oxide particles to smaller sizes.

On the basis of differential thermal analysis and X-ray diffraction studies a mechanism for the aging phenomena has been proposed by Danon et al (1977) according to which the rehydration of mineral species in the pottery is the determinant process. The decrease in particle size with the age of the ware is attributed to the diffusion and growth of the interlayer water shell in clay silicates and iron oxides.

Finally, in a recent paper Barbetti et al (1977) pointed to the non-linearities observed in Thellier's plots obtained for the determination of ancient magnetic fields from baked sediments. They proposed also an explanation according to which weathering of the samples transformed part of the haematite to lepidochrosite or goethite. When the samples were fired in the laboratory, the transformation of the weathering products back to haematite gave rise to non-linearities in the Thellier's plots. However, this explanation is only qualitative and does not reproduce satisfactorily the trend of the observed non-linearities.

In the next section we present a quantitative model for these non-linearities, which is based on the reduction of the size of the iron oxide particles present in the ancient sample.

3. Effect of weathering on the Thellier's plot.

For simplicity we model the decrease of the size of the iron oxide particles with time and environment in fired clay samples according to a "leaching" mechanism, i.e. each oxide particle of the sample has been leached with time to a smaller size. The material that has been leached away from the "parent" particles will form "daughter" ones, which may grow with time. If their volume becomes large enough, their magnetic moment will be blocked at ambient temperature and will remain so as their volume increases further.

Originally, the sample contained a distribution of oxide "parent" particles. Let N(T)dT be the mumber of these particles having blocking temperatures between T and T + dT. After the sample has been heated up above the Néel or Curie temperature T_N of the oxide material, it acquired during its cooling in the ancient magnetic field H_{AN} a thermoremanence. Each "parent" particle of volume V(T), where T is its blocking temperature, contributed to the room temperature value of this ancient thermoremanence an amount equal on the average to

$$J(T_R)V(T)\,\mathrm{th}\,\left\{\frac{J(T)V(T)H_{AN}}{kT}\right\} \simeq J(T_R)V(T)\,\frac{J(T)V(T)H_{AN}}{kT}$$

Where T_R stands for room temperature and

$J(T)$ is the magnetization of the bulk oxide material at temperature T.

Subsequently, leaching reduced the particle's volume from $V(T)$ to its present value $V(T')$, where T' is the new blocking temperature and $T'<T$. Each particle contributes now along the direction of the ancient magnetic field a magnetic moment equal on the average to

$$J(T_R)V(T')\,\frac{J(T)V(T)H_{AN}}{kT},$$

since leaching does not affect the direction of magnetization as long as the particle remains large enough to stay blocked at ambient temperature.

Assuming for the moment that the "daughter" particles are so small that they are superparamagnetic at room temperature, leaves only the remnants of the "parent" particles as the origin of the ancient thermoremanence(TRM_{AN}) observed today.

Thus, the loss of TRM_{AN} of the sample due to its heating up from T' to $T'+dT'$ and to its subsequent cooling in zero external field amounts to

$$d(TRM_{AN}) = -J(T_R)V(T')N(T')\,\frac{J(T)V(T)H_{AN}}{kT}\,dT' \qquad (1)$$

Furthermore, the increase of the thermoremanence when the sample is cooled from $T'+dT'$ down to T' in an externaly applied magnetic field H_{MOD} after the second laboratory firing up to the temperature $T'+dT'$, is

$$d(TRM_{MOD}) = J(T_R)V(T')N(T')\,\frac{J(T')V(T')H_{MOD}}{kT'}\,dT' \qquad (2)$$

From (1) and (2) we obtain the following expression for the slope of the Thellier's plot at T':

$$\left|\frac{d(TRM_{AN})}{d(TRM_{MOD})}\right|_{T'} = \frac{J(T)V(T)T^{-1}}{J(T')V(T')T'^{-1}}\cdot\frac{H_{AN}}{H_{MOD}}$$

While for an ideal Thellier's plot the value of the slope is temperature independent and equal to the ratio H_{AN}/H_{MOD}, here we obtain a temperature dependent multiplicative factor before H_{AN}/H_{MOD}. Noting that the expression $J(T)V(T)T^{-1}$ is an increasing function of T (Néel 1949) and that $T'<T$, we

observe that the factor while larger than unity tends to unity at the limit $T^- \rightarrow T_N$. Therefore, the slope of the Thellier's plot is in this case a decreasing function of temperature and the "true" value of the ancient field can be obtained rather from an extrapolation of the values of the slope towards T_N, than from a straight line fit of the low temperature part of the plot (Barbetti et al 1977).

Turning now our attention to the newly formed particles, let us assume that leaching of the "parent" particles took place to such an extend so that now all of them are superparamagnetic at room temperature, while on the other hand the "daughter" particles grew in size to such an extend that a significant number of them is blocked at ambient temperatures. Evidently, their magnetic moment became blocked when the particle's blocking temperature reached that of their surroundings T_R. So a particle belonging to that category, contributed at that time and along the direction of the ancient field a magnetic moment which on the average is

$$J(T_R)V(T_R)\,\frac{V(T_R)J(T_R)H^{*}_{AN}}{kT_R}$$

where H^{*}_{AN} is the earth's magnetic field at that time.

Subsequently, the particles kept on growing in size as new material was deposited on them and today a particle of this category will have a blocking temperature T^- and a volume $V(T^-)$, where

$$T^- > T_R \quad \text{and} \quad V(T^-) > V(T_R)$$

This particle's magnetic moment will now have a component along the direction of the magnetic field H^{*}_{AN} equal on the average to

$$J(T_R)\;V(T^-)\;\frac{V(T_R)J(T_R)\;H^{*}_{AN}}{kT_R} \tag{3}$$

Thus in this case the decrease in TRM_{AN} in the temperature interval T^- , $T^- + dT^-$ will be according to (3)

$$d(TRM_{AN}) = -J(T_R)V(T^-)M(T^-)\,\frac{V(T_R)J(T_R)H^{*}_{AN}}{kT_R}\,dT^- \tag{4}$$

In this expression $M(T^-)dT^-$ presents the number of "daughter" particles with blocking temperature between T^- and $T^- + dT^-$. On the other hand the increase of the sample's thermoremanence in the same temperature interval as above will be

$$d(TRM_{MOD}) = J(T_R)V(T^-)M(T^-)\ \frac{J(T^-)V(T^-)H_{MOD}}{kT^-} \qquad (5)$$

Therefore, from (4) and (5) we obtain the following expression for the slope of the Thellier's plot:

$$\left|\frac{d(TRM_{AN})}{d(TRM_{MOD})}\right|_{T^-} = \frac{V(T_R)J(T_R)T_R^{-1}}{V(T^-)J(T^-)T^{-\,-1}} \cdot \frac{H^*_{AN}}{H_{MOD}}$$

This expression is also a decreasing function of temperature, tending however to zero for $T^- \to T_N$. Thus, again the sample will show a nonlinear Thellier's plot and the "true" value of the ratio H^*_{AN}/ H_{MOD} can be estimated from an extrapolation of the values of the slope towards T_R. These results apply also to the chemical remanence of sediments and rocks.

A combination of the two cases exposed above separately leads to the following expression for the slope of the Thellier's plot:

$$\left|\frac{d(TRM_{AN})}{d(TRM_{MOD})}\right|_{T^-} = \frac{N(T^-)}{N(T^-)+M(T^-)} \cdot \frac{T^{-1}V(T)J(T)}{T^{-\,-1}V(T)J(T^-)} \cdot \frac{H_{AN}}{H_{MOD}} + \frac{M(T^-)}{N(T^-)+M(T^-)} \cdot \frac{T_R^{-1}V(T_R)J(T_R)}{T^{-\,-1}V(T^-)J(T^-)}\ \frac{H_{AN}}{H_{MOD}} \qquad (6)$$

Thus, in the general case we observe that the slope is not a simple and monotonic function of the temperature only, but it depends also on the distributions and the nature of the "parent" and "daughter" particles, i.e it critically depends on the extend and mechanism of the "weathering" of the sample. In particular, it follows from this expression that the true value of H_{AN}/ H_{MOD} cannot be simply deduced in this case.

4. An application of the weathering model

In figure 1 we present an application of expression (6) for two nonlinear Thellier's plots measured by M. Barbetti et al (1977). The "parent" and "daughter" particles are taken to be haematite. The value of H_{AN}/H_{MOD} has been kept constant and equal to 0.86, as given by Barbetti et al (1977) for samples obtained from the same area and showing linear Thellier's plots. Taking $H^*_{AN} = H_{AN}$ and making the crude assumption that the ratio $\frac{N(T^-)}{N(T^-) + M(T^-)}$ does not vary much with temperature, we obtained that the data can be reproduced with the set of parameters shown in Table I.

In this table δ represents the thickness of a shell leached away from the "parent" haematite particles, which have been assummed to be spherical. The parameter δ connects the present value of the blocking volume $V(T^{-})$ of a "parent" particle to its ancient value $V(T)$ and thus establishes a relation between T and T^{-} for the evaluation of the first term in the right hand side of equation (6). The value of the ratio $\frac{N(T^{-})}{N(T^{-}) + M(T^{-})}$ has been determined for each of the samples of figure 1 in the following way: The slope given by expression (6) at $T^{-} = T_N$ has been obtained from a straight line extrapolation towards T_N of the values of the slope at temperatures larger than 450°C.

We note that the results given in Table I for the two samples are compatible to each other in the sense that a larger value for thickness δ corresponds to a smaller percentage of "parent" particles still present in the samples.

5. Concluding Remarks

The model presented above offers a quantitative basis for the study of weathering effects in ancient materials studied via bulk magnetization measurements. Moreover, it points out procedures for the deduction of the correct value of the ancient field intensity from non-linear Thellier's plots.

Throughout the above exposition we have tacitly assummed that the oxide particles are non-interacting single domains. The consequences of the relaxation of these assumptions go further than the phenomenological scope of this work would allow.

Concluding we would like to emphasize the need for systematic studies of the extend and the effects of alterations in the structure of materials such as rocks, fired clays and sediments on their physical and chemical properties because of the "life" of these materials in various environments.

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Figure Caption

FIGURE 1. Slope of Thellier's plot versus firing temperature for sample MR9-A_1 and MR9-D_1 from Barbetti et al (1977). The lines drawn result from expression 6 and for two different values of the thickness δ of a shell leached away from the "parent" oxide particles. (See text).

Table I

Results from the application of the leaching model.

Sample	δ (Å)	$\frac{N(T^-)}{N(T^-) + M(T^-)}$ (%)
$MR9\text{-}A_2$	200-400	10
$MR9\text{-}D_1$	10-200	40

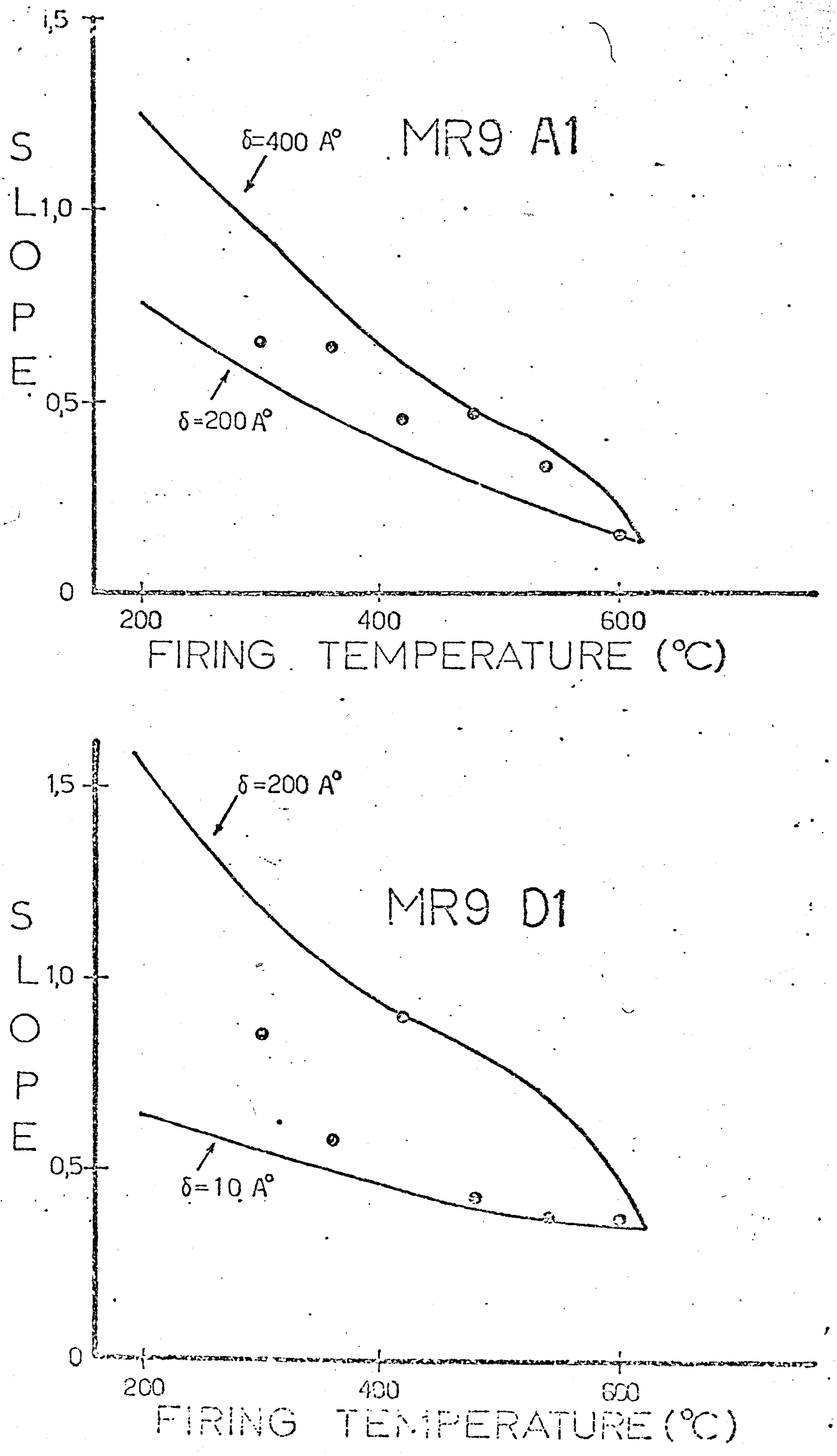

Figure 1, Sigalas and Gangas