

MAGNETIZATION OF ANCIENT CERAMICS*

J. VAN KLINKEN

Kernfysisch Versneller Instituut, Universiteit Groningen,
Zernikelaan 25, 9747 AA Groningen, the Netherlands
and

Drents Prehistorische Vereniging, Geelbroek 1, 9455 TD Geelbroek, The Netherlands

The saturation magnetization σ of soft baked pottery appears to be determined during the firing process by transitions between the iron oxides magnetite, maghemite, hematite and perhaps goethite. The finding of large variations in σ motivated the design and construction of a 'magnetization-gravitation', or 'MG', balance for rapid non-destructive magnetization measurements. The first results with this MG balance are presented: iso- σ contours, typical histograms and correlations with colour features. Practical MG applications are summarized.

KEYWORDS: MAGNETIZATION, MG BALANCE, FERRIMAGNETISM, IRON OXIDES, MAGNETITE, MAGHEMITE, HEMATITE, GOETHITE, TERP POTTERY

INTRODUCTION

Recent surface clearings near the Kernfysisch Versneller Instituut (KVI) and near an archaeological site called Paddepoel-IV (van Es 1968) revealed early medieval potsherds. Using KVI expertise with modern permanent neodymium-iron magnets (NdFe; Hoogduin and van Klinken 1997), it appeared that the sherds were attracted by these magnets with forces varying from potsherd to potsherd, sometimes by more than two orders of magnitude. How could this large variation be explained and how could it be studied in more detail? These questions motivated the design of a device named hereafter a *magnetization-gravitation*, or *MG*, balance. It is an easy to construct tool, which requires only the use of a small NdFe magnet suspended on two thin wires.

In archaeometry, one aspect of magnetism is well known: the observable *remanence* as induced by the geomagnetic field in fired clays and bricks in the direction of the Earth's field (Reinders *et al.* 1999). This paper is, however, related to the *saturation magnetization* σ , which parameter is distinctive for magnetic materials. It can be observed in a convenient and non-destructive way with the MG balance, but to my knowledge, its potential archaeometric role has escaped general awareness. However, a search in the literature revealed a very interesting study on ancient pottery techniques by Coey, Bouchez and van Dang (1979). They sampled powders from ceramics and characterized them by performing laboratory measurements of the magnetic hysteresis loops characterized by remanence, coercivity and saturation magnetism.

The magnetic features of common pottery are due to iron, which occurs in North Sea clays at roughly the 2.5% level. Other magnetic elements such as nickel, cobalt or rare-earth elements are rare; analysis¹ of some KVI sherds with X-ray and proton activation showed only Ni traces less than $5 \times 10^{-3}\%$ and none of the rare-earth elements. A large fraction of the iron is at substitutional sites in silicate-sheet structures; for example, Fe^{++} replacing a Mg^{++} , or Fe^{+++} replacing an Al^{+++} cation (Velde 1995). During complex firing processes at temperatures up to

* Received 25 January 2000, accepted 28 June 2000.

¹ X-ray fluorescence, X-ray diffraction, proton activation analysis, carbon determination, ¹⁴C dating and prehistoric classification were performed at various RUG laboratories.

about 750°C this fraction of silicate-bound Fe ions remains immobile. Embedded in the crystal structure, these ‘bound’ Fe ions are not in contact with each other and cannot create ferro- or ferrimagnetism. These forms of magnetism occur with ‘free’ particles of iron oxides, which can find a place between the silicate-sheet layers with a sufficient distance between the layers (≥ 0.35 nm as in smectides and illinite; kaolinite offers no space). The firing processes do not change the total iron content of the original clay, but they do redistribute the Fe over the ‘free’ iron oxides and over (at higher temperatures) silicate–Fe.

Three iron oxides—magnetite, maghemite and hematite—are the main agents in the magnetization of potsherds, while a fourth—goethite, or α -FeOOH, being a precursor of hematite—may play a role in very soft-baked pottery in which it has not yet fully dehydrated.

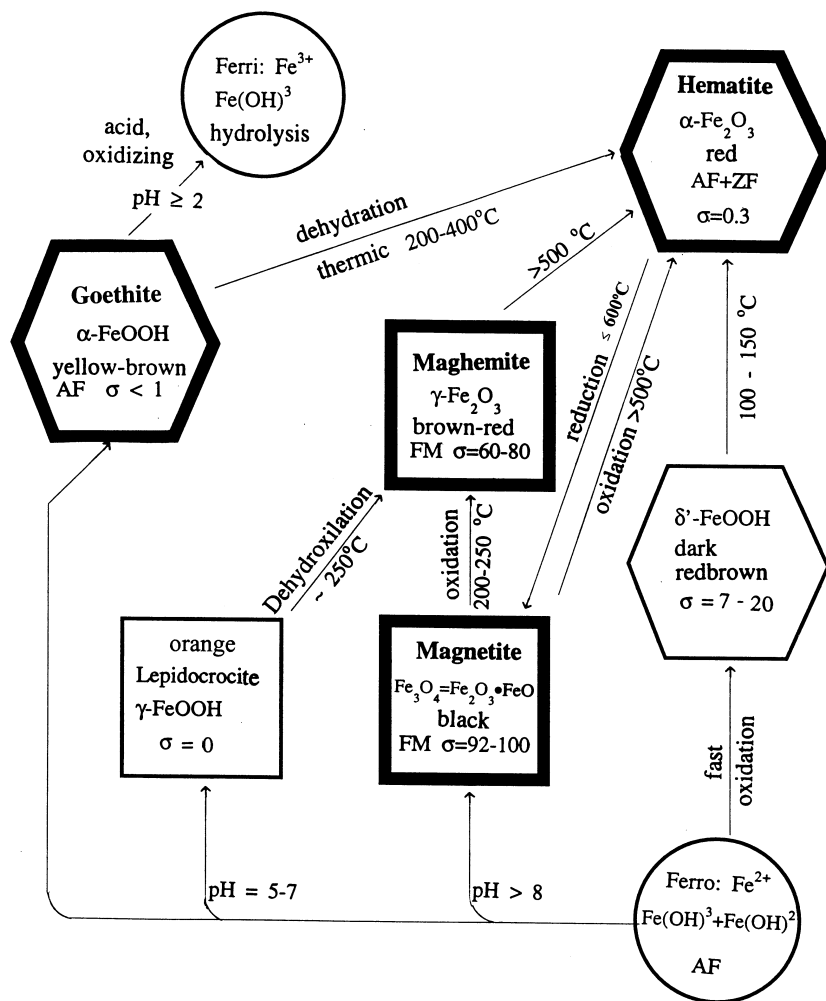


Figure 1 Schematic transformations below 750°C between iron oxides as adopted from Cornell and Schwertmann (1996). Solubles in circles, cubic structures in squares and hexagonal structures in hexagons. AF = antiferromagnetic, FM = ferrimagnetic, WF = weakly ferrimagnetic, σ = saturation magnetization in $\text{A m}^2 \text{kg}^{-1}$. Above 750°C silicate–Fe starts to exhibit super-paramagnetism with σ values between 0 and $5 \text{ A m}^2 \text{kg}^{-1}$. Colour hues are quoted for finely dispersed iron oxides.

Two other hydroxides (γ -FeOOH and δ -FeOOH) are already dehydrated below $\sim 250^\circ\text{C}$, as indicated in Figure 1. This scheme, adapted from the textbook by Cornell and Schwertmann (1996), shows that heating in oxidizing air ultimately shifts the oxides into hematite, while heating in a reducing CO atmosphere converts them back into magnetite. The scheme refers to pure oxide powders, but remains valid to a remarkable extent when the oxide particles are embedded in soft-baked pottery.

The two *high- σ oxides*, magnetite (black) and maghemite (red-brown), are in essence responsible for the magnetization of ceramics, magnetite being usually the most important one. The two *low- σ oxides*, hematite (red) and goethite (yellow) cause values close to zero and are—when diluted in ceramics at a 1% level—on the verge of being observable with the MG balance. Of these two, goethite can already dehydrate at relatively low temperatures.

THE MAGNETIZATION-GRAVITATION OR MG BALANCE

The MG balance for observing differences in the attraction of a NdFe magnet by potsherds is based on balancing magnetic and gravitational forces. In essence, a small flat magnet with a perpendicular magnetic induction ($B \approx 0.2\text{ T}$) is suspended on two thin wires of 60 cm length, with a celluloid foil to damp wobbling when hanging in air (Fig. 2). A potsherd put into contact with the magnet will be magnetized locally to within an area comparable with the NdFe area (chosen as $d^2 \approx 6 \times 6\text{ mm}^2$). The sherd then attracts the magnet, so that one can swing it aside by hand until it is released at a critical and easily to note angle α , at which the magnetic force becomes balanced by the gravitational pull.

Concerning the physics of magnetism underlying the instrument, see Cornél and Schwertmann (1996, especially chapter 13) and Coey *et al.* (1979); for details about NdFe,

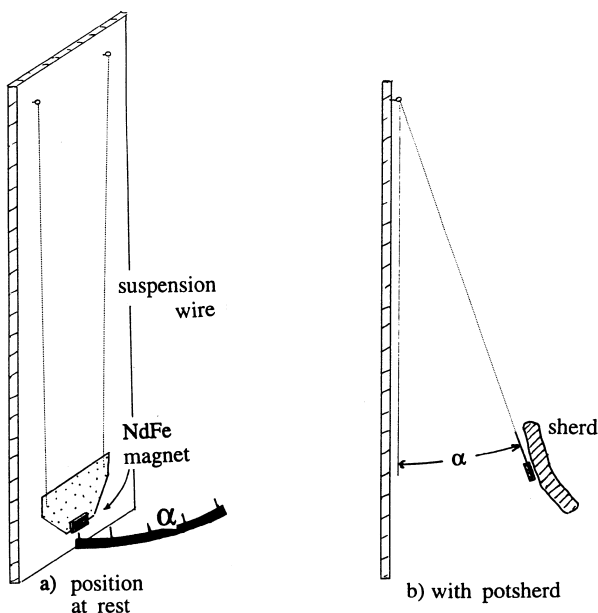


Figure 2 The MG balance on the left (a) with the NdFe magnet suspended at rest without any magnetic attraction, and on the right (b) with a potsherd pulling the little magnet aside until it loses contact at a critical angle α .

see references in Hoogduin and van Klinken (1997). In short, the little magnet represents an imaginary magnet coil that carries a formidable current of more than one thousand amperes! Its field magnetizes the iron oxides in a sherd to saturation, so that magnet and sherd attract each other by induced magnetization. The attraction decreases rapidly with decreasing distance z between sherd and magnet (at distances $0 \leq z \ll d$ the force is roughly proportional to $1/z^{2.6}$), which implies that the magnet is released abruptly at a sharp value of α . It also implies a mild preference for measurements with flat and smooth surfaces, which offer a close contact between magnet and sherd. Such conditions allow MG accuracies of 5%, while for irregular surfaces the inaccuracy may become larger than 10%. Rims with a radius of curvature less than the size of the NdFe magnet also only allow a partial contact.

The thickness of the magnet is not critical: 3 mm is about optimal, but one millimetre more or less reduces the sensitivity by little more than 10%. The magnetic induction will effectively penetrate into the contacting sherd by only 2–3 mm. This is less than the typical thickness of most potsherds, and it makes it meaningful to inspect a sherd at its outer and inner surfaces, since differences may have occurred due to thick plastering of one surface with a different clay species. However, a very thin surface layer (≤ 0.1 mm) will have little influence. Scanning sherds over distances of a few centimetres often showed a spread in α , but usually by no more than 25%, while sherds can differ from each other by one or two orders of magnitudes in the range $0.4^\circ < \alpha < 45^\circ$. In extreme cases—caused, for example, by an accidental tiny metallic Fe particle—a sherd can reach $\alpha = 90^\circ$, which simply means that the magnet remains ‘hanging’.

The magnetization of a sherd is proportional to $\sin \alpha$, or to α when the deflection is not too large. In the following, the magnetization will often be expressed in terms of the observed angle α referring to *comparative measurements* using one and the same NdFe magnet. However, it is possible to perform *absolute measurements* in terms of ‘magnetite equivalents’ by calibrating the MG balance with a plastic disc doped with finely grained black magnetite ($\sigma_{\text{magnetite}} \approx 96 \text{ A m}^2 \text{ kg}^{-1}$; Cornell and Schwertmann 1996). Then:

$$\sigma_{\text{sherd}}/\sigma_{\text{cal}} = \sin \alpha/\sin \alpha_{\text{cal}}$$

where α_{cal} is the angle observed with the calibrator disc with σ_{cal} . A disc doped with $10.0 \pm 0.8 \text{ mg cm}^{-3}$ magnetite pulled the NdFe magnet used in this work over $18^\circ \pm 1^\circ$. Diluted in sherds, this 10 mg cm^{-3} magnetite implies an Fe percentage of only 0.34 wt%.

MG APPLICATIONS WITH α CONTOURS, HISTOGRAMMING AND RAPID TESTING

Instead of attracting the NdFe magnet with a sherd, one can also attract it using the outside of a complete pot. This has been done with the *kugeltopf* shown in Figure 3. Scanning with the MG magnet produced iso- α contours with large variations, ranging from $\alpha = 34^\circ$ down to $\alpha = 4^\circ$. Evidently, this pot has been exposed to inhomogeneous fires fuelled by wood, which must have been a scarce commodity in coastal terp areas. Early medieval *kugeltopfs* are in any case notorious for showing all shades and mixes of the colours mentioned in Figure 1 in connection with changes in σ . The contours show two low- α loci; one as expected at the bottom and the other, unexpectedly, at the side. The latter one may tell us that the pot once experienced an unusually high temperature at that spot ($\geq 500^\circ\text{C}$, with oxidation to hematite) while lying on its side. The contours thus add a story to the *topf*. More prosaically: most *kugeltopfs* end up as sherds and these sherds will show a broad distribution in α . This suggests that the MG balance can assist pottery restoration: pieces that fit must have fitting α values.

The KVI sherds were all tempered with grit, but are otherwise diverse and often of the

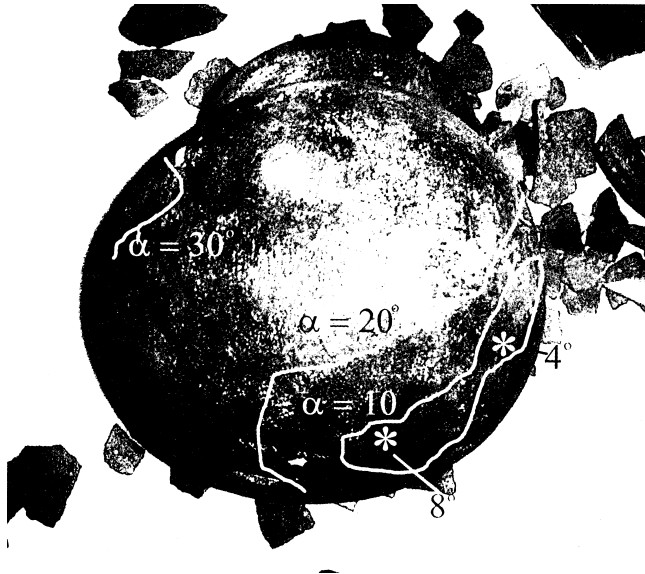


Figure 3 A *kugeltopf* (on loan from RUG-GIA) with α -contours showing two locations with minimum magnetization: one at 8° at the bottom and one with $\alpha = 4^\circ$ at the side.

kugeltopf type. Indeed, they show a broad distribution in α . Measuring a random number ($n = 105$) of greyish sherds, the angles ranged from $< 1^\circ$ to 45° (Fig. 4), when disregarding two exceptional 'hot spots' at the ultimate angle of 90° . For comparison, a number of sherds ($n = 14$) from a terp site north of Groningen have also been inspected. These sherds were baked very softly, with organic tempering materials. In contrast with the KVI sherds, they show a narrow and completely different distribution. Their inside bulk material was greyish black, but this hue could not be due to black high- σ magnetite, since they show distinctly small α values in Figure 4. This at first surprising observation leads below to a more detailed inspection of colours, which proves that the grey–black colour is caused by carbon derivatives and not by magnetite.

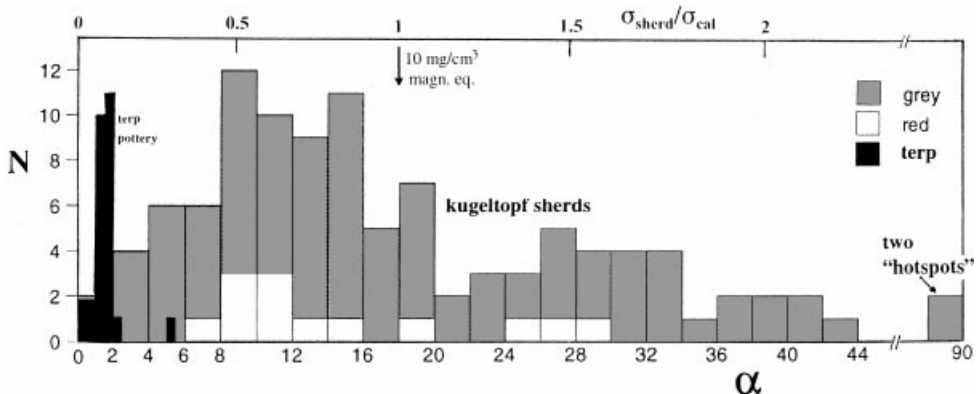


Figure 4 Histograms of magnetization values. The main broad distribution is obtained with a total of 103 grey KVI potsherds. A similar broad distribution resulted, with 13 sherds having a thin reddish surface. Sherds ($n = 14$) from a terp site show striking low α values as measured with the NdFe magnet used in this work. At the top, the magnetization is expressed in 'magnetite units', after calibration with a plastic disc containing 10 mg cm^{-3} of magnetite.

Sometimes a rapid field test may be helpful when an artefact is not recognized on the spot. *Unusually large magnetization* ($\alpha > 40^\circ$) may be due to an exceptional amount of magnetite, or even to straying particles of metallic iron, if they happen to be protected against oxidation by an accidental glazing layer. They can produce 'hot spots' which will already be visibly attracted by a conventional permanent magnet. At the KVI, items with an *unusually small magnetization* ($\alpha < 2^\circ$) often turned out to be Pingsdorf or other hard-baked imported pottery, or non-magnetic bone or limestone.

COLOURS

The focus of this paper is on the iron oxides as a source of magnetizability. However, these iron oxides are at the same time strong colouring agents, and are well known as early prehistoric pigments (Pomiès *et al.* 1999). Red hematite (= red ochre), black magnetite and perhaps also yellow goethite (= yellow ochre) can to a large degree determine the hues of unpainted pottery. When the KVI and terp sherds are heated in air to well above 600°C they all take the bright red colour of low- σ hematite; when they are thereafter reduced in CO at a somewhat lower temperature, they take the black colour of high- σ magnetite. In both cases σ and the colour are unmistakable and in agreement with Figure 1. Considering the chemical complexity of baked clays, and considering the fact that the 'free' iron oxides constitute only a minor fraction of the material, this agreement is already remarkable. However, while σ remains a clear-cut observable, the shades and hues of the sherds found at the KVI are more subtle than can be accounted for with the simplified indications of Figure 1 (the 'Munsell charts' are more indicative; Cornell and Schwertmann, 1996). To be specific, the grey to black colour of the sherds used for the histogram of Figure 4 does not always harmonize with an exclusive assignment to high- σ magnetite, because there are sherds which combine a grey-black hue with a small α value.

The histogram for the terp sherds centres at the low value of $\alpha = 1.5^\circ$, which makes it clear that a black colour is not always caused by high- σ magnetite. What is specific about this terp pottery? It has been soft-baked with organic tempering, it has a goethite-like yellow surface but is black inside, the thin yellow surface is not due to plastering, and the sherds show no signs of weathering during two millennia of deposition in the clay soil. Expecting the inside black colour being due to partially burned organic tempering, H. J. Streurman determined the carbon content of a sherd and found this to be true: the black material contained 1.54 wt% carbon (^{14}C -dated at 2580 y BP). This suggests that the baking temperature has been high enough to remove the organic material from the surface, but not to burn it on the inside. During tests at higher temperatures, described hereafter, all carbon derivatives disappear, while the yellow goethite transforms into red hematite without a significant change in σ .

Some KVI sherds had a red or reddish surface colour caused by sudden oxidation to low- σ hematite at the end of the firing process. The surface layer is, however, too thin (≤ 0.1 mm) to influence a MG measurement. Indeed, histogramming a number of such reddish sherds ($n = 13$) showed, on average, at most a marginal preference for lower values of α as compared to the grey-black sherds (Fig. 4).

CHANGES IN MAGNETIZATION INDUCED BY OXIDATION AND REDUCTION

The thermal history of ancient pottery ended in most cases when it broke into sherds, although it remains possible that the sherds were thrown as debris into a fireplace to experience secondary firing. I assume that after that the magnetization σ remained unchanged. However, σ can be

changed again in the laboratory by firing or 're-baking', which will not change the total Fe contents of the sherds, but which will interchange the four 'free' iron oxides. When staying below 750°C, our interpretation can be simplified by ascribing all observations with $\alpha > 1^\circ$, to the two combined high- σ oxides and those with $\alpha < 1^\circ$ to the two low- σ oxides. At higher firing temperatures, a slow restructuring of silicate-Fe may cause a small but observable increase in σ , which falls outside the scope of Figure 1 and to which I will return below.

Three grit-tempered KVI sherds have been inspected in closer detail. They are identified in Table 1: W selected upon showing wweak, M medium and H high magnetization. Most likely, these sherds originate from selected local clays with quartz and albite as major components. Furthermore, X-ray diffraction showed illite in W and microcline in M. Observations of α before starting tests yielded the Fe-element contents presented in line (i): W containing no, M a small amount and H a relatively large amount of the high- σ oxides. The sherds have been oxidized in air for 3 h at 560°C and 890°C successively, and reduced by heating between 550°C and 650°C in CO in a closed oven with charcoal. After each heat treatment the α values have been recorded and averaged for a number of points on both sides of the sherds. In the case of *complete* oxidation to hematite, followed by *complete* reduction to magnetite, the finally observed angle α will be a measure of the percentage of the four 'free' oxides combined. The minimal α values at 890°C indicate that this oxidation into red low- σ hematite has been fairly complete. However, the intended complete reduction to magnetite cannot be ascertained so easily. After increasing the reduction time stepwise from 2 h to 17 h and 26 h at temperatures between 550°C and 650°C, I arrived at α values of 40°, 30° and 21° respectively. For W and M, these values may indicate the initial (high- σ plus low- σ) percentage, but this cannot be true for H. This sherd did not return to its original value $\alpha = 40^\circ$. This may be due to a too high oxidation temperature of 890°C, due to which the magnetite-Fe partly 'disappears' (depending on the microstructure of the ceramic environment) to substitutional sites in silicate matrices.

Table 1 *MG results (α) and colour indications with three sherds W, M and H after subsequent heat treatments. The α determinations will be accurate to 10% at larger angles and to 30% at small angles around $\alpha = 1^\circ$. Below follow deduced initial iron percentages by weight from before the heating tests. The total Fe content (deduced from proton-activation analyses) is distributed over fractions: i) Fe in high- σ magnetite and maghemite, ii) Fe in low- σ hematite and goethite, iii) Fe in silicate matrices*

Sherd (thickness)	W (7.0 mm)		M (3.4 mm)		H (4.3 mm)	
	α	Colour	α	Colour	α	Colour
Starting at room temperature:	0.8°	Grey + yellow	12°	Red	40°	Mostly gray
After oxidizing in air						
at 560°C	~1°	Bright yellow	11°	Red	34°	Yellowish
at 890°C	1.0°	Bright red	0.8°	Bright red	1.2°	Bright red
After reduction in CO at 650°C	40°	Black	30°	Black	21°	Black
Total Fe content (p-activation)	2.0 ± 0.2%		2.4 ± 0.2%		1.8 ± 0.2%	
Distributed over:						
(i) Fe in magnetite + maghemite:	≤ 0.01%		0.17 ± 0.03%		0.52 ± 0.05%	
(ii) Fe initial hematite + goethite:	0.52 ± 0.04%		0.23 ± 0.05%		Minor?	
(iii) Fe bound in silicates:	~1.5%		~2%		~1.3%	

Despite some uncertainty concerning complete reduction, it is possible to estimate the distribution of all iron atoms over both the 'free' and silicate-bound fractions. For this purpose, the total Fe abundances have been determined via induced radioactivities after activating the sherds with 150 MeV protons (van Klinken *et al.* in preparation). These total percentages are larger than those of line (i) for the high- σ and of line (ii) for the low- σ 'free' iron oxides, the 'free' to 'bound' ratio being of order of 1 : 3. This is not as small as a ratio of 1 : 7 deduced for ancient Iranian ceramics (Coey *et al.* 1979), possibly because Iranian clays have a larger amount of Fe bound in silica matrices.

A test sequence with a typical terp sherd yielded results similar to the above sherd W. The MG measurements showed minimal angles ($\alpha \leq 1^\circ$) for both the typical yellow surface and the black bulk material. After that, parts from the sherd have been oxidized in 10 firing steps of 3 h each, at temperatures increasing from 150°C to 900°C, without showing any change in α until firing at 700°C. However, a visible darkening of the yellow surface and a slight reddening of the black bulk had already started after firing at 380°C, while the conversion to low- σ red hematite became evident after firing at 440°C. In sharp contrast, a sequence of reduction steps already showed the onset of a change in α after firing in CO at 380°C, by an increase in α from $\leq 1^\circ$ to 3.5°C for the yellow material. Further reduction at 630°C showed that both the initial yellow and black material contained a notable large fraction of 'free' iron, causing angles of $\sim 45^\circ$ and the black colour of true magnetite (black carbon derivatives having already disappeared at 400°C). Tentative explanations for the initial yellow surface colour could be to ascribe it to goethite (if only its dehydration can be postponed somehow to temperatures around 380°C) or to a kiln temperature significantly lower than 380°C. This may be a topic for further investigation but, independent of the origin of the yellow colour, the changes that start at 380°C do already suggest that the sherd has not been exposed to higher temperatures; not in air and certainly not when kiln-fired with charcoal.

I noticed at first, with some surprise, that α increased again after firing at 790°C and 900°C, reaching small but distinct values of $4.5 \pm 0.5^\circ$, and too high to be caused by hematite. It appears that a similar increase has already been noticed by Coey *et al.* (1979), with a modest maximum at 1100°C. They showed by chemical treatments that the effect is not due to 'free' iron oxides but to a partial reorganization of Fe in the silica lattice, into fine iron oxide particles with superparamagnetic σ values from 0 to $10 \text{ A m}^2 \text{ kg}^{-1}$, a range that reaches one 10th of the value of high- σ magnetite.

OUTLOOK AND FINAL REMARKS

In conclusion, I attempted to demonstrate the potential of rapid magnetization measurements for archaeometry. It has led to the introduction of an easy to handle and non-destructive MG balance with applications that are possibly of broader interest, such as:

- (1) Recording iso- α contours (Fig. 3) of a *kugeltopf* to reveal some of its thermal history.
- (2) Histogramming of α distributions (Fig. 4) as characteristics for specific archaeological sites.
- (3) Rapid attribution of a grey/black colour to magnetite or to carbon derivatives.
- (4) On-site recognition of items with exceptionally low or exceptionally high α values.
- (5) α -labelling of candidate sherds for pottery restoration.

These applications do not depend on a complete knowledge of all relevant chemical reactions, but a broader materials science study—for example, on the role of goethite—will be seminal for

a full understanding of the iron reactions during firing processes at temperatures between 350°C and 750°C.

The MG balance has been introduced as an inexpensive tool for non-destructive measurements with 10% or better accuracy, requiring no laboratory infrastructure. While it seems hard to improve its simplicity it must, however, be possible to make a pencil-sized electronic probe with sophisticated and convenient digital recording and graphical plotting of contours like those of Figure 3. For a trial of this possibility, I connected a thin Hall to a small (0.15 T) NdFe magnet and then touched it with a plastic calibration disc doped with 5 mg cm^{-3} of magnetite. The induced magnetization of the doped plastic increased the field by about $25 \mu\text{T}$. The available field probe had a read-out sensitivity of $5 \mu\text{T}$, which (related to the $25 \mu\text{T}$) does not yet compare well with the 5–10% accuracy of the MG balance. However, electronic improvements are conceivable, be it with a Hall probe, or with a torque balance or with yet other methods. These can improve the low- σ measurements ($0^\circ < \alpha \leq 1^\circ$)—a regime that is rather difficult for the present MG balance—but it would be of interest to investigate harder-baked low- σ ceramics and materials with a large (super-) paramagnetism.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the interest and help of the archaeologists P. B. Kooi, H. A. Groenendijk, L. Jacobs and A. van As. F. Kiestra made MG balances with artistic woodcraft. F. van der Horst from the RUG (Solid State Physics) offered help with X-ray diffraction and H. J. Streurman from the RUG-CIO suggested and performed a determination of the carbon contents. This work has been supported by the Stichting voor Fundamenteel Onderzoek der Materie (FOM) with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

REFERENCES

- Coey, J. M. D., Bouchez, R., and N. van Dang, 1979, Ancient techniques, *Journal of Applied Physics*, **50**, 7772–7.
- Cornell, R. M., and Schwertmann, U., 1996, *The iron oxides*, VCH Publishers, Germany.
- Hoogduin, J. M., and van Klinken, J., On properties of $\text{R}_2\text{Fe}_{14}\text{B}$ magnets, 1997, *Nuclear Instruments and Methods*, **B134**, 149–52.
- Pomiès, M.-P., Menu, M., and Vignaud, C., 1999, Red palaeolithic pigments; natural hematite or heated goethite?, *Archaeometry*, **41**(2) 275–85.
- Reinders, J., Hambach, U., Krumsiek, K., Sanke, M., and Strack, N., 1999, An archaeomagnetic study of pottery kilns from Brühl-Pingsdorf (Germany), *Archaeometry*, **41**(2), 413–19.
- Van Es, W. A., 1968, Paddepoel, excavations of frustrated terp, *Palaeohistoria*, **XIV**, 187–352.
- Van Klinken, J., Beijers, J. P. M., Ostendorf, R. W., Venema, L. B., in preparation.
- Velde, B., 1995, *Origin and mineralogy of clays*, Springer-Verlag, Berlin.