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Estimating the equivalent firing temperature of ancient baked clay artifacts through magnetic measurements

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***Abstract* – Magnetic measurements are usually applied in archeology for dating purposes through archaeomagnetic applications, but they can also be used to study ceramics technology, from the production stage through distribution and use. Actually, the study of the firing temperatures achieved in ancient baked clay structures can offer important insights to the establishment of the ancient technology used in a certain region or historical period, contributing to the archaeological research of technology developments in both space and time. In this work, we investigated the changes observed on the magnetic properties of baked clay samples collected from one furnace and two burnt funeral walls, in order to identify the equivalent firing temperature occurred in these structures. Such investigations are based on the onset change of the initial magnetic properties observed after subsequent thermal treatments of the studied materials.**

I. INTRODUCTION

During the last decades, several laboratory-based techniques have been used in archaeology to provide information about the dating, mineralogy, heating conditions, material provenance, and use of archaeological artefacts. The study of the firing conditions in archaeological ovens used for pottery or for food cooking provides useful information about the technology and fire control skills of ancient populations. Mineralogical investigation, X-ray diffraction, thermal analysis (e.g. thermal dilatometry), color studies, or Mössbauer and luminescence techniques are usually applied to infer the equivalent firing temperatures and gain information on the duration and prevalent atmospheric conditions (reducing/oxidizing) during the ancient heating. Among these techniques, archaeomagnetism based on the magnetic properties of ancient artefacts, has been rapidly developed in the last years, offering nowadays a reliable dating technique and possibly a useful tool for estimating also the equivalent firing temperature of ancient baked clay structures.

The investigation of the firing temperatures of archaeological artifacts is furthermore an important aspect of the classical archaeomagnetic studies, as low heating temperatures experienced by the samples in ancient times could result in the acquisition of only a partial thermoremanent magnetization that may reflect an unreliable archaeomagnetic record. Magnetic mineralogy, thermal stability, and domain state analysis are therefore often performed preliminary to archaeomagnetic studies, to establish the suitability of samples to dating procedures that include successive thermal demagnetization procedures at progressively increasing temperatures.

Magnetic properties such as the magnetic susceptibility, coercive field, and magnetic moment can be continuously measured at increasing temperatures monitoring their evolution with heating. Clay minerals contain, in fact, iron as a minor element that during heating is almost entirely converted into Fe-oxides giving the ferromagnetic properties to the clay matrix. Since the pioneering studies (La Borgne, 1965; Bouchez et al. 1974; Coey et al. 1979), which examined the effects of heating conditions on the Fe-oxides embedded within ceramic bodies, several researchers have used magnetic measurements to investigate technology and firing of ancient pottery (e.g. Yang et al., 1993; Dalan and Banerjee, 1998; Hus et al., 2002; Beatrice et al., 2008; Rasmussen et al., 2012; Tema et al., 2016). The use of hysteresis cycles can also be useful for monitoring the thermal behavior of the baked clays. Their comparison at room temperature, before and after laboratory heating at increasing temperatures, can also be used to appreciate the technological conditions applied for production, as temperature, atmosphere, and duration of firing can results in different magnetic features and shape of the hysteresis cycles.

For this work, the estimation of the equivalent firing temperature has been associated to the reversibility/irreversibility onset of the thermomagnetic curves and the change in features of the hysteresis cycles.

When the magnetic moment *m* versus temperature *T* curves show reversible behavior during the heating/cooling circles, it is supposed that no mineralogical transformations have taken place, suggesting the thermal stability of the samples at a given temperature. While laboratory heating is increasing at temperatures higher than those experienced in the past by the studied material, irreversible behaviors are expected, suggesting that the material has probably experienced induced alterations at temperatures not previously reached during ancient heating (Spassov and Hus, 2006). Additional information on the magnetic mineralogy and thermal stability is obtained through the analysis of the shape of the hysteresis cycles and Curie point estimated by the thermomagnetic curves, often corresponding to Ti-magnetite transition ($T_C \sim 540/560$ °C).

II. EXPERIMENTAL PROCEDURES

This paper presents the results obtained investigating the change, after heating treatments, of several magnetic parameters for the estimation of the equivalent firing temperatures of three baked clay structures sampled at the archaeological sites of Santhià, and Carbonara Scrivia, both in Northern Italy. At the site of Santhià (Novara) a kiln made of bricks and baked clay has been excavated, dated to the XVII century. From this kiln, brick samples from the inner side of the combustion chamber have been collected for magnetic analyses.

In the case of Carbonara Scrivia, two structures (US9 and US40) completely made of baked clay have been sampled, probably related to burial ceremonies of the Roman age, with clear evidence of combustion residuals.

Several magnetic properties have been investigated at the INRIM Institute (Torino, Italy) and the ALP Palaeomagnetic Laboratory (Peveragno, Italy) before and after thermal treatments. The magnetic behavior as a function of temperature of small specimens (mass < 100 mg) collected from the bricks or baked clay constituting the walls and pavement of the three studied structures, has been analyzed mainly using a Vibrating Sample Magnetometer (VSM model: Lakeshore 7410). On three samples from the Santhià kiln, and on five samples from Carbonara Scrivia – two samples from Unit 9, and three samples from Unit 40 – the variation of the magnetic moment has been continuously recorded during heating treatments, carried out in subsequently increasing steps, from room temperature to about 700 °C. In the VSM, heating was applied using a thermal-resistance set-up directly placed around the specimen, As well a constant field having flux intensity H = 0.2 T has been applied continuously during heating and cooling processes.

Furthermore, one sample from each site was thermally treated separately up to T = 560 °C (heating duration ~ 1 hour) using a ASC Scientific TD 48-SC furnace available at CIMAN, and then the resulting magnetic properties were analyzed at INRIM using an Alternating Field Gradient Magnetometer – AGFM Princeton Micro Mag model. In addition to the thermomagnetic curves, hysteresis cycles (maximum flux intensity of the applied field H = ± 1T) of the samples have been attained using the VSM set-up at room temperature after each thermal treatment.

Finally, samples from the Santhià and Carbonara Scrivia sites have also been stepwise thermally demagnetized at CIMAN with the ASC Scientific TD 48-SC furnace and, after each heating step, the bulk magnetic susceptibility was measured with an AGICO KLY-3 bridge in order to monitor possible magnetic mineralogy changes during heating.

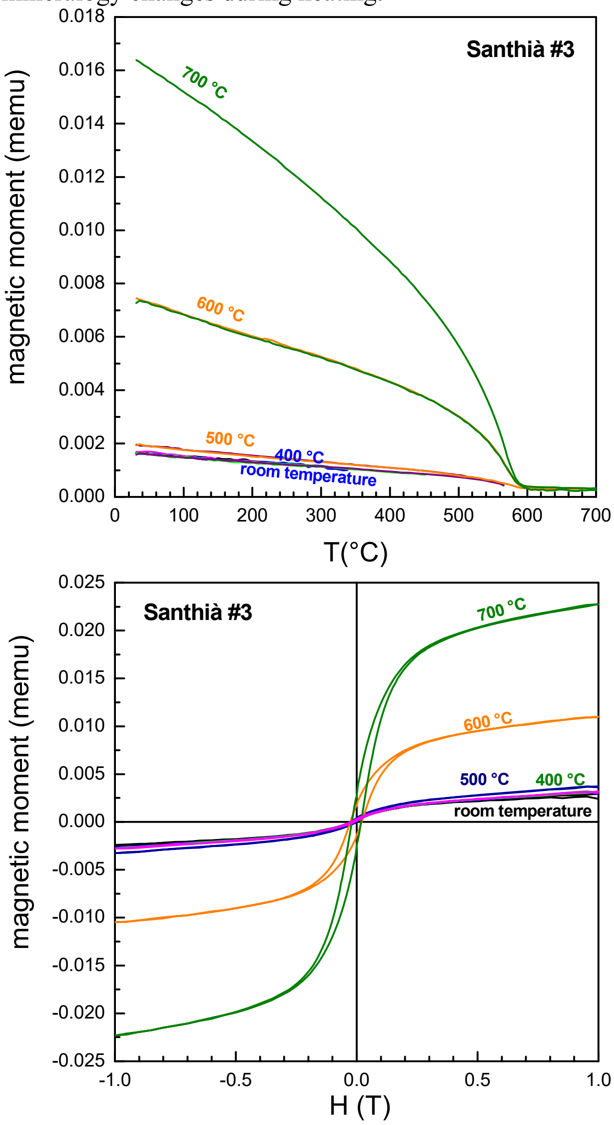

Fig. 1. Thermomagnetic curves (above) and hysteresis loops (below) after subsequent thermal treatment at increasing temperatures (T range = 200 – 700 °C) of sample #3 coming from a brick extracted from the kiln of Santhià.

III. RESULTS AND DISCUSSION

The results obtained using the VSM setup are shown in fig. 1 (Santhià), fig. 2 (Carbonara Scrivia US 9), and fig. 3 (Carbonara Scrivia US 40), which report the thermomagnetic curves (up) and the corresponding hysteresis loops for each temperature after cooling (down) as obtained on samples representative of the three furnaces. Observing the collected data, one notes that the samples show similar Curie points corresponding to Ti-magnetite transition, as it can be appreciated from thermomagnetic curves in figs. 1-3 for temperatures above 500 °C. In only one case, the Curie point of Ti-hematite was observed at T ~ 660 °C.

Moreover, the samples from Santhià show small variations of the magnetic properties, i.e. 2-3 % of change with respect to the initial value, until ~ 500 °C. At higher temperatures, generally above 600 °C, a sharp increment of the magnetic moment is observed, which further increases at temperatures of 700°C. Such onset temperatures of changing magnetic behavior may vary from sample to sample, mainly depending on the position in the kiln while heating, but generally, the temperature range 600-700 °C can be considered as the maximum heating experienced in the past for this kiln. Differently, results from the baked clays sampled at Carbonara Scrivia give evidence of lower heating temperatures. According to the experimental results (thermomagnetic curves and hysteresis loops) it appears that the maximum heating temperature attained in both the studied structures (US9 and US40) was between 400 °C and 500 °C. These results are in agreement with the archaeological evidence, expecting relatively high heating temperatures for a kiln used for brick production while temperatures reached during burial ritual firings are expected to be low.

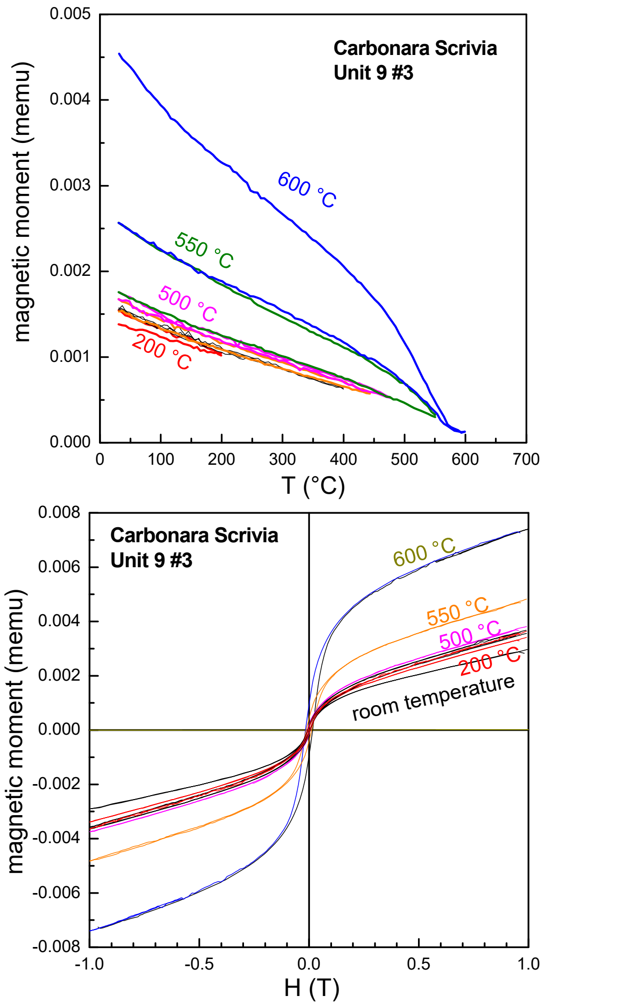

Fig. 2. Thermomagnetic curves (above) and hysteresis loops (below) after stepwise thermal treatment at increasing temperatures (T range = 200 – 600 °C) of sample #3 consisting of baked clay collected from the walls of Unit 9 in Carbonara Scrivia.

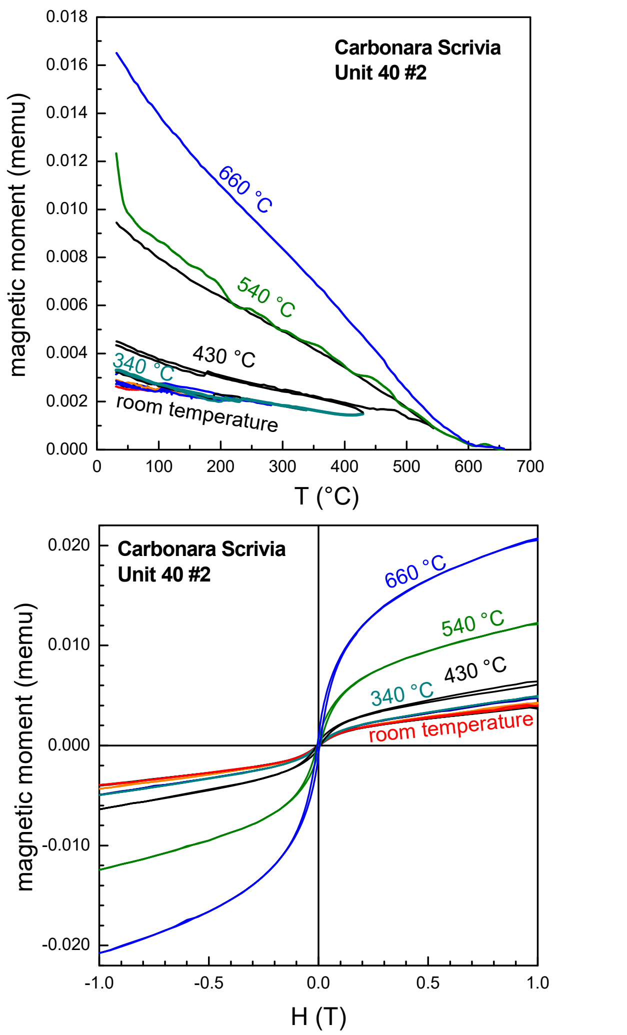

Fig. 3. Thermomagnetic curves (above) and hysteresis loops (below) after stepwise thermal treatment at increasing temperatures (T range = 200 – 600 °C) of sample #2 consisting of baked clay collected from the walls of Unit 40 in Carbonara Scrivia.

These estimated heating temperatures appear to be also confirmed from the variation of the bulk magnetic susceptibility measured at room temperature after stepwise increasing heating performed during the thermal demagnetization of selected samples. Fig. 4 illustrates the behavior of the susceptibility measured on two samples from Carbonara Scrivia (Unit 9) and three samples from Santhià. It is observed that in the case of Santhià, susceptibility does not importantly vary from the initial value up to temperatures of 500-600 °C. On the contrary, in the case of Carbonara Scrivia (US9) the same quantity starts increasing at the temperature range from 300 °C to 400 °C, while variations higher than 20 % are observed for temperatures higher than 400 °C.

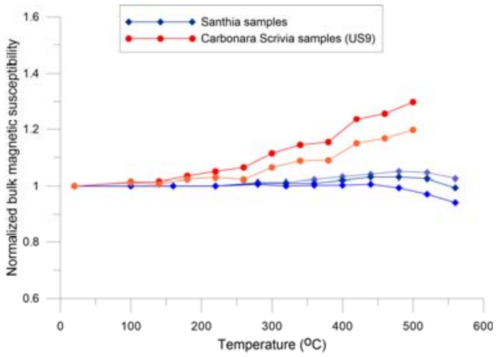

Fig. 4. Normalized bulk magnetic susceptibility measured at room temperature during stepwise thermal demagnetization for representative samples from Santhià (blue lines) and Carbonara Scrivia (red lines).

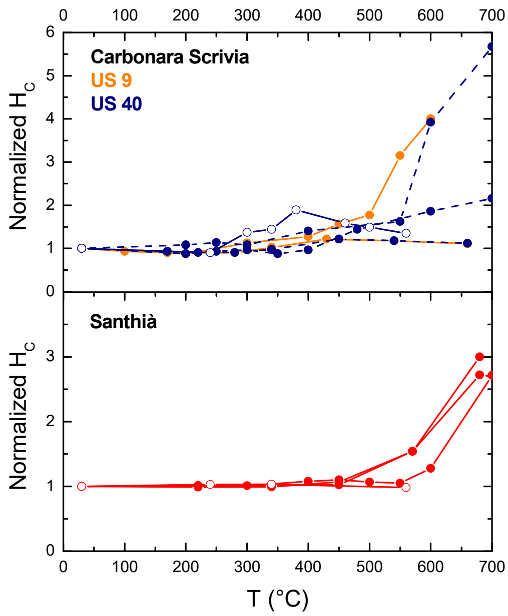

Fig. 5. Normalized H_c values of samples from Carbonara Scrivia (above; blue = US 40, red = US 9) and Santhià (below) obtained by hysteresis loops after stepwise thermal treatment at increasing temperatures (T = 200 – 700 °C). Open circles correspond to measurements done by AGFM on samples heated in conventional ovens.

Finally, fig. 5 and fig. 6 resume the ensemble of normalized magnetic parameters, H_c and $m_{Hp=0.2T}$, obtained by the hysteresis loops and thermomagnetic curves, respectively, as those reported in figs. 1-3. The experimental data obtained using AGFM to characterize one sample from each site, separately heated in a conventional furnace, are also reported in figs. 5 and 6 as open circles. Yet, no difference is observed between the differently treated samples when temperatures are the same, showing that in either cases the effects of firing can be appreciated as the the onset of magnetic change though a series of thermal treatments at increasing temperature.

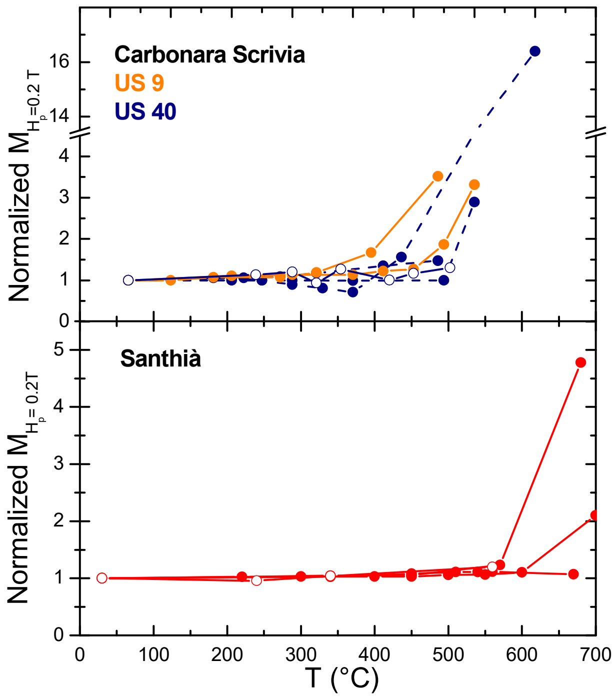

Fig. 6. Changes of the magnetic moment (applied field H_p = 0.2 T) with temperature of samples from Carbonara Scrivia (above) and Santhià (below) as obtained by thermomagnetic curves after stepwise thermal treatment at increasing temperatures (T range = 200 – 700 °C). Open circles correspond to measurements done by AGFM on samples heated in conventional ovens.

In all the samples, the investigated behavior of magnetic parameters as a function of subsequent thermal treatments provide different results for the sites of Santhià (higher firing temperatures) and Carbonara Scrivia (lower firing temperatures): in the latter, the two detached structures US 40 and US 9 show almost identical results. Still, the change observed versus temperature through variation of the resulting coercive force, H_c, which is reached by the hysteresis cycles, appears as having major sensitivity than the change of the magnetic moment *m* obtained through thermomagnetic experiments.

IV. CONCLUSIONS

As a summary, magnetic measurements based on the monitoring of the magnetic susceptibility, magnetic moment, and hysteresis cycles are suitable for determining the equivalent firing conditions of ancient baked clay structures. Although deeper clues about firing technology can be reached by comparison with a set of other techniques such as X-ray diffraction, assessing mineralogical features, magnetic measurements too allow establishing the maximum temperature to which ceramic materials have been subjected in the past, providing also information on the magnetic mineralogy of the investigated samples.

The aim of the present paper was to provide a summary and critical assessment of the particular contribution magnetic measurements can provide to the reconstruction and interpretation of the firing temperature of ancient furnaces through the presentation of two selected case studies. Throughout, this information, which integrates archaeological observations, is valuable also to confirm the importance of considering the overall environmental, technological, and historical context in which the furnaces were prepared and used.

REFERENCES

[1] C. Beatrice, M. Coïsson, E. Ferrara, E. S. Olivetti, 2008. Relevance of magnetic properties for the characterisation of burnt clays and archaeological tiles. Physics and Chemistry of the Earth, 33, 458–464.

[2] R. Bouchez, J. Coey, R. Coussement, K. Schmidt, M. Van Rossum, J. Aprahamian, J. Deshayes, 1974. Mossbauer study of firing conditions used in the manufacture of the grey and red ware of Tureng-Tepe. Journal of Physique, 35, 541–546.

[3] J. Coey, R. Bouchez, N.V. Dang, 1979. Ancient techniques. Journal of Applied Physics, 50, 7772 – 7777.

[4] R.A. Dalan, S.K. Banerjee, 1998. Solving archaeological problems using techniques of soil magnetism. Geoarchaeology, 13, 3 – 36.

[5] E. La Borgne, 1965. Les proprietes magnetiques du sol. Application à la prospection des sites archaeologiques. Archaeo-Physika, 1, 1–20 (in French).

[6] K. L. Rasmussen, G. A. De la Fuente, A. D. Bond, K. K. Mathiesen, S. D. Vera, 2012. Pottery firing temperatures: a new method for determining the firing temperature of ceramics and burnt clay. Journal of Archaeological Science, 39, 1705 – 1716.

[7] S. Spassov, J. Hus, 2006. Estimating baking temperatures in a Roman pottery kiln by rock magnetic properties: implications of thermochemical alteration on archaeointensity determinations. Geophys. J. Int., 167, 592-604.

[8] E. Tema, E. Ferrara, P. Camps, C. Conati Barbaro, S. Spatafora, C. Carvallo, Th. Poidras, 2016. The Earth's magnetic field in Italy during the Neolithic period: New data from the Early Neolithic site of Portonovo (Marche, Italy). Earth and Planetary Science Letters, 448, 49-61, doi: http://dx.doi.org/10.1016/j.epsl.2016.05.003.

[9] S. Yang, J- Shaw, T. Rolph, 1993. Archaeointensity studies of Peruvian pottery from 1200 BC to 1800 AD. Journal of Geomagnetism and Geoelectricity, 45, 1193–1207.