Magnetic measurements as indicator of the equivalent firing temperature of ancient baked clays: New results, limits and cautions

Magnetic measurements as indicator of the equivalent firing temperature of ancient baked clays: New results, limits and cautions

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ABSTRACT

We present new experimental results on the variation of the magnetic properties of baked clays as a function of the temperature reached during laboratory treatments. Such experiments, including continuous monitoring of the magnetic susceptibility and magnetic moment versus temperature, were applied to a set of natural clays experimentally heated in the laboratory at 200 ºC, 400 ºC and 600 ºC as well as to archaeological baked clays collected from two archaeological sites in Northern Italy (Santhià and Carbonara Scrivia). The aim of this study is to investigate the reliability of the magnetic properties to identify the equivalent firing temperatures of ancient baked clay artefacts based on the reversible behavior of thermomagnetic diagrams. The results obtained indicate that the magnetic properties do not always succeed in estimating the firing temperature of the baked clays, mainly when clays have been heated only once and at relatively low temperatures, e.g. less than 300-400 ºC. On the contrary, magnetic properties of ancient clays that have been repeatedly heated at the past at temperatures higher than 400 ºC appear to be more stable and representative of

the equivalent firing temperature. This study confirms that the reversibility of thermomagnetic curves could be a useful indicator of ancient firing temperatures in the case of baked clays that have experienced multiple heatings at the past while caution should be paid on its general use as archaeo-temperature marker.

Keywords: Baked clay; Magnetic properties; Firing temperatures; Ancient technology

1. 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, manufacturing techniques and use of archaeological artifacts. The study of the firing conditions in archaeological kilns and ovens used for pottery or for food cooking provides useful information about the technology and fire control skills used by 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, magnetic measurements have also been involved in firing temperature studies, mainly based on the changes of magnetic properties occurring during the heating of clay minerals.

Clay minerals contain iron as a minor element that during heating is converted into Fe-oxides giving ferromagnetic properties to the clay matrix. Since the first pioneering magnetic studies (Le Borgne, 1960; 1965; Bouchez et al., 1974; Coey et al., 1979), which examined the effects of heating conditions on the Fe-oxides in fired soils and archaeological clays, several researchers have used magnetic measurements to investigate the magnetic enhancement and firing characteristics of ancient baked clays and pottery. In some cases, such firing temperatures were also related with pre-selection criteria for archaeointensity experiments and suitability of the materials for archaeomagnetic studies (e.g. Yang et al., 1993; Dalan and Banerjee, 1998; Jordanova et al., 2001; 2003; Beatrice et al., 2008; Tema et al., 2016; Kondopoulou et al., 2017). Linford and Platzman (2004) investigated the maximum firing temperature of burnt archaeological sediments based on isothermal remanent acquisition curves and hysteresis data. Spassov and Hus (2006) estimated the baking temperatures in a Roman pottery kiln by rock magnetic properties and analyzed the effect of thermochemical alteration on archaeointensity determinations. Rasmussen et al. (2012) proposed the use of magnetic susceptibility changes during stepwise laboratory heating of ceramics as an indicator of the maximum firing temperature experienced during their production, similarly to the method proposed by Hrouda et al. (2003) that used the monitoring of the magnetic susceptibility versus temperature as a palaeotemperature indicator of rocks. Recently, Kostadinova-Avramova et al. (2018) successfully used the magnetic susceptibility measurement method proposed by Rasmussen et al. (2012) to determine the firing temperatures of a large ceramic collection from Bulgaria while Jordanova et al. (2018) used the same approach to evaluate the paleo-firing temperatures of burnt daub material from the Neolithic site of Mursalevo-Deveboaz in Bulgaria.

This paper presents the results obtained investigating the change, after heating treatments, of several magnetic parameters from experimentally heated natural clay samples and archaeological material from three baked clay structures sampled at the archaeological sites of Santhià and Carbonara Scrivia (Northern Italy). The use of the magnetic properties in the estimation of firing temperatures in ancient baked clays is discussed together with the reliability and limits of such technique.

2. Materials and methods

2.1 Experimental samples

A set of 40 cylindrical samples with standard dimensions (diameter = 25.4 mm, height = 22 mm) was prepared at the laboratory using natural grey clay (Fig. 1). The clay used comes from the Arno River (Vinci, Firenze) and was bought from a Fine Arts shop as a bulk 5 kg piece (Fig. 1a). The samples prepared manually were divided in four groups of 10 samples each. The first group was heated at 200 °C for four hours in a Schonstedt furnace and then samples were left to naturally cool in ambient temperature outside the furnace. The same procedure was followed for the samples of the second and third group that were heated at 400 °C and 600 °C, respectively. The samples from the fourth group were not heated at all (untreated samples). The selection of three different increasing heating temperatures was made in order to investigate the variation of the magnetic properties at different critical temperatures: a low temperature (200 ºC), a medium temperature quite critical for the neo-crystallization of clay minerals (400 ºC) and a higher temperature, often experienced by ancient baked clays (600 ºC)

The bulk magnetic susceptibility of all samples was measured with a KLY-3 Kappabridge (Agico) at the CIMaN-ALP Palaeomagnetic Laboratory (Peveragno, Italy) and the mass susceptibility (χ) was calculated after weighing each sample with a precision balance. The Natural Remanent Magnetization (NRM) was measured with a JR6 Spinner magnetometer (Agico). Six samples from each group were stepwise thermally demagnetized up to 560-580 ºC following increasing temperature steps of 40 ºC. During thermal demagnetization, heating and cooling lasted around 30-45 min and were performed in a Schonstedt furnace. After each demagnetization step, the bulk magnetic susceptibility was measured at room temperature to monitor possible magnetic mineralogy alterations. The magnetic mineralogy of the samples before and after heating was investigated with Isothermal Remanent Magnetization (IRM) curves and three axes-IRM thermal demagnetization experiments (Lowrie, 1990). Moreover, continuous low-field monitoring of the magnetic susceptibility versus temperature (χ-T curves) was performed in air atmosphere at the IGGL Geomagnetic Laboratory (CEED, Oslo, Norway) with a MFK1-FA Kappabridge equipped with a CS-4 furnace (Agico).

Hysteresis loops and magnetic moment versus temperature profiles were measured with a Lake Shore 7400 Vibrating Sample Magnetometer (VSM) equipped with a thermo-resistance oven operating in inert Ar atmosphere to vent out residual gasses at the INRIM Institute (Torino, Italy). Small specimens (mass < 100 mg) of clay samples from the four different groups were used to obtain continuous thermomagnetic curves (M-T curves). First, the magnetic moment of one specimen from each group was continuously measured during heating up to 650 ºC and cooling back to room temperature. Then, for twin specimens from the same samples, the heating-cooling circle was repeated at different temperatures of 200 ºC, 300 ºC, 400 ºC, 500 ºC, 600 ºC and 700 ºC. Hysteresis loops have also been measured before and after thermal treatments applying a maximum intensity field, H_{max}, equal to 1 T.

2.2 Archaeological samples

Samples from three baked clay structures excavated at the archaeological sites of Santhià, and Carbonara Scrivia (Northern Italy) were collected and studied for ancient heating temperature determination.

The archaeological site of Santhià (45.30 ºN, 8.17 ºE), is situated in Northern Italy and was discovered during a rescue excavation carried out for the installation of methane gas tubes in the area. During the excavation, a late medieval kiln was found. The kiln was mainly built by baked clay while a part of the combustion chamber was made of bricks (Fig. 2). For magnetic analysis, brick samples from the inner side of the combustion chamber were collected both by direct drilling *in situ* and as bulk samples. In the case of bulk samples, they were drilled at the laboratory in order to obtain cylinders of standard dimensions (diameter = 25.4 mm, height = 22 mm).

In the site of Carbonara Scrivia (44.86 ºN, 8.85 ºE), two structures (US9 and US40) made by baked clay were excavated. This site was also a rescue excavation carried out during the installation of methane gas tubes. According to archaeological evidence, the cavities unearthed in the clay were tombs dated to the Roman period while the clear evidences of combustion residues are probably related to burial ceremonies (Giachino, 2015). In this case, the baked clay collected was very smooth and friable and sampling was therefore performed using nonmagnetic cylindrical plastic boxes.

These two archaeological sites were selected as case studies because of the completely different thermal history of the baked clay material collected. Bricks from the Santhià kiln were heated during their initial production, but they were also repeatedly re-heated for several times during the use of the kiln. On the contrary, samples from Carbonara Scrivia probably experienced only a unique firing in the antiquity related to religious ceremonies. Such different thermal history and heating conditions would be expected to be reflected to the magnetic properties of the studied structures.

3. Results

3.1 Variation of magnetic properties versus heating

The mean mass magnetic susceptibility calculated for the three different groups of the experimental samples, before and after heating at 200 ºC, 400 ºC and 600 ºC respectively, are plotted in Figure 3. The initial mass susceptibility of all 30 samples is very similar with mean value of 13.95 ± 0.3 x 10^{-8} m^3/kg. The obtained results show that heating at 200 ºC does not provoke any change of the magnetic susceptibility and its mean value after heating (14.3 x 10^{-8} m^3/kg) remains practically the same to the one before any thermal treatment. On the contrary, heating at higher temperatures leads to an important magnetic susceptibility enhancement. The mean mass susceptibility after heating at 400 ºC becomes 126.3 x 10^{-8} m^3/kg while after heating at 600 ºC it further importantly increases with mean value equal to 382 x 10^{-8} m^3/kg.

Changes in the magnetic mineralogy of the studied experimental samples can be observed from the IRM acquisition comparing the curves obtained from the samples before and after heating at various temperatures (Fig. 4). Clay samples that have not experienced any heating are not saturated at applied field of 1T, suggesting the presence of a high coercivity mineral. The same behavior is also noticed at samples heated at 200 ºC, where again saturation is not reached at 1T. On the contrary, samples heated at 400 ºC and 600 ºC are saturated in applied fields of around 0.2 T, indicating the presence of a low coercivity mineral and the absence of any high coercivity magnetic carriers. These results are also confirmed by the thermal demagnetization of a composite IRM component (Lowrie, 1990) diagrams that are very similar for the samples heated at 200 ºC and for those without any heating treatment. For these samples a drop of magnetization in the soft and medium coercivity components is observed around 250-300 ºC; such drop is not observed at the diagrams from samples heated at 400 ºC and 600 ºC. In all cases the obtained results show the dominance of the soft coercivity components while medium and high coercivity components are minor (for the samples of raw clay and those pre-heated at 200 °C) or negligible (for the samples pre-heated at 400 °C and 600 °C) (Fig. 5).

Hysteresis loops obtained after the subtraction of the paramagnetic contribution for raw clay samples and for samples pre-fired at 200°C, 400°C and 600 °C are reported in Fig. 6. These results show that the firing at temperature lower than 400 °C does not influence the magnetic granulometry of the samples. In fact, the loops of raw clay (black curve) and pre-fired clay at 200 °C (orange curve) overlap, being almost indistinct, characterized by a faint ferrimagnetic signal. After firing at 400 °C (red curve), a tenfold increase of both, saturation, M_S, and remanent magnetization, M_{RS}, arises; further increase of magnetization may be observed after firing at 600 °C (blue curve).

Measuring the bulk magnetic susceptibility at room temperature during the stepwise thermal demagnetization shows important differences among the samples initially heated at different temperatures. For the group pre-fired at 200 ºC, changes at the bulk susceptibility are registered around 320 ºC with an abrupt magnetic susceptibility increase clearly observed after heating at temperatures > 400 ºC (Fig. 7a). For temperatures from 200 ºC to 320 ºC, the magnetic susceptibility remains almost the same, even when the temperature exceeds the initial heating temperature experienced during the preparation of this sample group (200 ºC). For the group pre-fired at 400 ºC, the susceptibility measured at room temperature is very stable till 400 ºC and only very small variations can be observed after 420 ºC, with important changes noticed only at one sample after heating at 460 ºC (Fig. 7b). Finally, for the group pre-fired at 600 ºC, no variations at the magnetic susceptibility values are observed until heating up to 620 ºC (Fig. 7c).

Continuous monitoring of the low field magnetic susceptibility in air with repeated progressive heating and cooling cycles up to different maximum temperatures shows results similar to those obtained from the bulk magnetic susceptibility measured at room temperature during the thermal demagnetization. Indeed, the clay initially heated at 200 ºC shows reversible heating/cooling cycles up to 400 ºC (Fig. 8a-c) while important magnetic mineralogy changes are only noticed after heating at temperatures higher than 400 ºC (Fig. 8d). For the clay pre-fired at 400 ºC, magnetic susceptibility is completely reversible during heating/cooling at the same temperature (Fig. 8e), while only very minor differences may be observed when heated at higher temperatures (500 ºC and 600 ºC, Fig. 8 f-g).

Thermomagnetic curves of the magnetic moment versus temperature continuously measured up to 650 °C conducted in Ar atmosphere show that in the raw clay (Fig. 9a), the magnetic moment remains almost stable up to 350-400 °C, when a transformation starts producing an increase of the magnetic moment. Similar behavior is also observed for the pre-fired clay at 200 °C that shows its magnetic properties unchanged until 350-400 °C, when again some transformation appears increasing the magnetic moment. The thermomagnetic curves obtained from the samples pre-fired at 200 °C are actually undistinguishable from those obtained from the untreated samples (Fig. 9a and 9b). Similarly, thermomagnetic curves obtained from clay pre-fired at 400 ºC and 600 ºC show the same general trend, with irreversible behavior. However, in these cases no increase at the magnetic moment is observed at the heating curve (Fig. 9c and 9d).

The magnetic moment behavior after heating/cooling cycles at progressively increasing temperatures was also monitored for the various pre-fired clay groups. The obtained results for the untreated clay and for the clay pre-fired at 200 ºC show reversible curves till 300 ºC while at higher temperatures the magnetic moment registered during cooling is higher than the heating curve (Fig. 10 a, b). The same curves obtained for the clay pre-fired at 400 ºC show almost reversible behavior until 400 ºC, even though the heating and cooling curve of 300 ºC is not perfectly reversible. The difference of the curves obtained at 400 ºC and 500 ºC is not very important but then the curve obtained at 600 ºC is clearly distinguishable (Fig. 10c). Finally, the thermomagnetic curves obtained after heating/cooling at 500 ºC, 600 ºC and 700 ºC for the clay pre-fired at 600 ºC are almost never completely reversible with a clearly much higher magnetic moment measured after heating at 700 ºC (Fig. 10d).

3.2 Determining the heating temperatures of archaeological samples

Samples collected from the archaeological sites of Santhià and Carbonara Scrivia were also analyzed for the investigation of the heating temperatures experienced during their use in the past. The magnetic behavior as a function of temperature of small specimens (mass < 100 mg) collected from the bricks of the Santhià kiln and from the baked clay of the two structures excavated at Carbonara Scrivia, was analyzed mainly using the 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 at different temperatures. Each sample was heated at 200 ºC and cooled back to room temperature while its magnetization was continuously measured during both heating and cooling. Then, for the same sample, the heating-cooling circle was repeated up to around 300 ◦C, 400 ºC, 500 ºC, 600 ºC and finally up to 700 ◦C (Fig. 11a). Hysteresis loops were also measured before and after thermal treatments applying a maximum intensity field, H_{max}, equal to 1 T (Fig. 11b).

The results obtained show that most of samples have similar Curie points at around 580 ºC, corresponding to magnetite and/or Ti-magnetite. The samples from

Santhià show small variations of their magnetization, i.e. 2-3 % of change with respect to the initial value, until around 500 °C. At higher temperatures, generally above 600 °C, a sharp increment of the magnetic moment is observed, which further clearly increases at temperatures of 700°C. Such temperatures of changing magnetic behavior may vary from sample to sample but are generally observed at temperatures higher than 500-600 °C (Fig. 11). Differently, results from the baked clays sampled at Carbonara Scrivia give evidence of magnetic mineralogy changes at lower temperatures. The heating-cooling curves for both US9 and US40 structures are almost reversible up to temperatures of around 400-430 ºC while at higher temperatures important differences are noticed (Fig. 11a). These results are also confirmed by the hysteresis loops that clearly show variations after heating at 600 ºC for Santhià and 400-550 ºC for Carbonara Scrivia (Fig. 11b).

The bulk magnetic susceptibility measured at room temperature after stepwise thermal demagnetization of selected samples shows that the susceptibility does not significantly vary from the initial value up to temperatures of 500-600 °C for samples from Santhià. In the case of Carbonara Scrivia (US9) the susceptibility starts increasing at the temperature range from 300 °C to 400 ºC, with variations higher than 20 % observed for temperatures higher than 400 ºC (Fig. 12).

4. Discussion

The use of natural baked clay samples experimentally heated at known temperatures allowed us to test the reliability of magnetic measurements for the estimation of the equivalent firing temperatures of baked clays, based on the reversibility of thermomagnetic curves. Indeed, the obtained results lead to some interesting observations:

1. The mean magnetic susceptibility of the samples heated at 200 ºC is the same with that of the untreated clay, showing that heating at 200 ºC is not enough to cause any magnetic enhancement. Differently, the mean magnetic susceptibility measured after heating at 600 ºC is for all samples significantly higher than those heated at 400 ºC. This shows that heating at higher temperatures involves a larger number of iron sources from the clay matrix, as already previously observed by Kostadinova-Avramova and Kovacheva (2013).

2. Both raw clay and samples pre-heated at 200 °C show very similar magnetic properties. In both cases, χ-T and M-T curves remain completely reversible up to 300 °C showing a thermally stable behavior (even if they haven't experienced heating at that temperature before). Therefore, using the reversibility of the thermomagnetic curves for firing temperatures lower than 300 ºC should be used with caution as it could lead to erroneous conclusions.
3. As expected, most mineralogical transformations seem to occur at temperatures from 300 °C to 400 °C and lead to an important magnetic enhancement that can be easily detected by the abrupt changes of the magnetic properties after temperatures higher than 300 °C. This is probably related to the dehydration of clay minerals and the chemical transformation of maghemite, unstable to heating.
4. Samples pre-heated at 400 °C show reversible χ-T curves up to 600 °C, probably because most of the mineralogical changes have already taken place during the heating at 400 °C as previously discussed.
5. The M-T curves performed in argon atmosphere for samples pre-heated at 600 ºC, are not completely reversible after heating at the same temperature, suggesting that the laboratory heating of the samples for 4 hours at 600 ºC was not sufficient to achieve the thermal stability of the samples.

From these results, it is evident that caution should be exercised on the estimation of the firing temperatures of ancient baked clays based on the reversibility of the thermomagnetic curves. Undoubtedly, the mineralogical changes in clay during heating depend on the initial mineralogy of the raw clay and the neo-crystallized magnetic phases can affect the magnetic properties of the baked clay. However, in the case of ancient baked clays there are also several other factors that may affect the reversibility of the thermomagnetic curves and their effectiveness on reproducing the ancient firing temperature, such as the firing conditions and atmosphere (reducing or oxidizing), the presence of organic material, the type of kiln and fuel used, the cooling rate (Kostadinova-Avramova et al., 2018). In most of the cases, such information about the initial mineralogy of the clay and the ancient firing are not available and it is very difficult to reproduce the same firing conditions at the laboratory.

Our results presented here show that reversible χ-T curves up to 300 ºC does not necessarily indicate that the clays have experienced at the past firing at 300 ºC. They also show that heating at lower temperatures or not heating at all could also result on reversible curves up to 300 °C. Of course, this may depend on the initial mineralogy of the raw clay and may change from clay to clay. Nevertheless, such reversible curves can still be used to indicate that ancient heating has not exceeded this temperature, since important mineralogical changes that are clearly detected by magnetic measurements take place at 300-400 °C interval. On the other hand, caution should be also applied on the interpretation of reversible χ -T up to 600 °C: e.g. pre-fired samples at 400 °C show reversible χ-T curves even after heating to 600 °C. That is probably because most of the transformations have already taken place in the 300-400 °C temperature interval and therefore the samples have become thermally stable even if they haven't been heated at such high temperatures (e.g. 600 °C) before. The temperature range 300-400 °C is critical for clay minerals as it can be related to the transformation of unstable maghemite or the dihydroxylation of goethite (Trindade et al., 2010). Kostadinova-Avramova and Kovacheva (2013) have shown that for several clay types, at temperature of ~280 °C dehydration of supposed lepidocrocite begins and unstable (titano)maghemite is formed while at higher temperatures (~400 °C) a second transformation occurs and the maghemite converts into magnetite and hematite.

Even though the χ-T curves are generally considered to be more precise to the magnetic mineralogy of natural samples (Goguitchaichvili et al., 2001), our results suggest that the reversibility of the M-T thermomagnetic curves obtained in argon atmosphere, seems to reproduce better the firing history of the samples, even if they still not always succeed to precisely estimate the equivalent firing temperatures. Probably the Ar atmosphere prevents transformations caused by the oxidizing atmosphere in presence of air and improves the stability of the laboratory heating conditions.

Similarly to the χ-T curves, raw clay and samples pre-fired at 200 °C show completely reversible behavior up to 300 °C. These results confirm that low firing temperatures (<300 °C) cannot be detected based on the reversibility of the thermomagnetic curves. For higher firing temperatures (e.g. 400 and 600 °C), the M-T curves tend to show a relative reversible behavior (even if not completely reversible) after heating at temperatures close to those of the pre-firing. However, it's still hard to precisely detect the pre-firing temperatures, as they show important changes only when the initial firing temperature is strongly exceeded (e.g. 600 ºC for clays pre-fired at 400 ºC or 700 ºC for clays pre-fired at 600 ºC).

In the case of archaeological samples, the M-T curves show generally repeatable results for the different samples coming from the same structures. For the bricks sampled from the Santhià kiln, the repeated heating experienced by the samples during the use of the kiln resulted at a very stable magnetization up to 500 ºC, while important changes are noticed only after heating at 600 ºC. These results cannot guarantee that the bricks have not experienced higher temperatures at the past but however indicate that such higher heating (if applied) was not long enough to attain the thermal stability of the samples. On the other hand, baked clays from the Carbonara Scrivia funeral structures show relative low firing temperatures (less than 500 ºC). In particular, for the structure US40, the M-T curves are reversible only up to 340-430 ºC. Based on our data from the experimental samples, such results may show that the baked clay has not experienced long and repeated heating at temperatures higher than 400 ºC but heating at much lower temperatures cannot be excluded either (even less than 200 ºC).

5. Conclusions

The use of the reversibility of the thermomagnetic curves can be a useful tool for the estimation of the equivalent maximum heating temperatures but at the same time caution should be paid to their use in firing temperature determination of ancient baked clays. This is mainly because baked clays are often characterized by a complex thermal history, ~~that~~ which depends on several factors such as: ~~the~~ initial clay mineralogy, ~~the~~ heating temperature, ~~the~~ number of repeated firings ~~experienced~~ in the past, ~~the~~ duration of ~~the~~ heating, ~~and the~~ cooling rate, ~~the~~ firing atmosphere, ~~the~~ fuel and ~~the~~ technology used, ~~the~~ presence of organic material, and many others ~~that~~ in most cases ~~are~~ impossible to reproduce at the laboratory. Moreover, in baked clays, that are the most common material used in archaeomagnetic studies, most of the magnetic mineralogy changes occur in the temperature range from 300 ºC to 400 ºC. So, even though the monitoring of the magnetic susceptibility during stepwise laboratory heating is a reliable technique for well fired ceramics and baked clays, as already ~~shown~~ demonstrated in previous studies (Rasmussen et al., 2012~~),~~), – our results show ~~shows~~ that the reversibility of the χ-T and M-T curves alone cannot always be used as precise indicator of the maximum ancient heating temperatures, mostly in the case of single and weak heating at the past.

~~Our~~ The same results show that for temperatures lower than 300-400 ºC, clays are thermally stable even if they have no~~’~~t experienced similar temperatures in the past. Even for higher temperatures (>400 ºC) however, the reversibility or irreversibility of the thermomagnetic curves does not always indicate the limit of the maximum temperatures experienced in the past. The heating conditions and/or the time of heating at a certain temperature may importantly affect the achievement of the thermal stability. Indeed, the repeated heating experienced from the archaeological clays during their use in the past results to a clearer interpretation of the M-T curves in respect to the experimental samples that were heated at the laboratory only once. This study aims to point out that the reliability of the use of the reversibility of the thermomagnetic curves in baked clays is limited by several factors and should be ideally accompanied by other experimental techniques (e.g. XRF, thermoluminescence) to avoid erroneous estimations.

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Figure captions

Fig. 1. a-d) Photos from the preparation of the experimental samples. Cylinders of standard dimensions were prepared from the natural clay.

Fig. 2. Photos from the baked clay structures sampled at the archaeological sites of: a-b) Santhià and c-d) Carbonara Scrivia.

Fig. 3. Mean mass magnetic susceptibility measured for the experimental samples before any treatment and after heating at 200 ºC, 400 ºC and 600 ºC.

Fig. 4. Isothermal remanent magnetization curves obtained for the experimental samples a) before any thermal treatment, and after heating at b) 200 ºC, c) 400 ºC and d) 600 ºC.

Fig. 5. Stepwise thermal demagnetization of three IRM components following Lowrie (1990) for samples a) before any treatment, and samples pre-fired at b) 200 ºC, c) 400 ºC and d) 600 ºC. Symbols: dot= Soft- (0.12 T); diamond= Medium- (0.4 T); square= Hard- (1.2 T) coercivity component.

Fig. 6. Hysteresis loops for the untreated clay and for samples experimentally pre-fired at 200 ºC, 400 ºC and 600 °C. All curves are corrected for the para/diamagnetic contribution.

Fig. 7. Normalized bulk magnetic susceptibility measured at room temperature during stepwise thermal demagnetization for representative samples initially pre-fired at a) 200 ºC, b) 400 ºC and c) 600 ºC.

Fig. 8. Mass magnetic susceptibility versus temperature curves obtained in air after heating/cooling cycles at increasing temperatures for experimental clay samples pre-fired at a-d) 200 ºC and e-g) 400 ºC.

Fig. 9. Magnetic moment versus temperature curves up to 650 °C for a) untreated clay, and samples pre-fired at a) 200 ºC, b) 400 ºC and c) 600 ºC. All curves are measured in Ar atmosphere.

Fig. 10. Continuous magnetic moment versus temperature curves obtained in Ar atmosphere after heating/cooling at various maximum temperatures for samples a) before any treatment and samples pre-fired at b) 200 ºC, c) 400 ºC and d) 600 ºC.

Fig. 11. a) Thermomagnetic curves and b) hysteresis loops after subsequent thermal treatment at increasing temperatures (T range = 200 – 700 °C) for samples coming from the kilns of Santhià and Carbonara Scrivia.

Fig. 12. Normalized bulk magnetic susceptibility measured at room temperature during stepwise thermal demagnetization for representative samples from Santhià (blue lines) and Carbonara Scrivia (red lines).

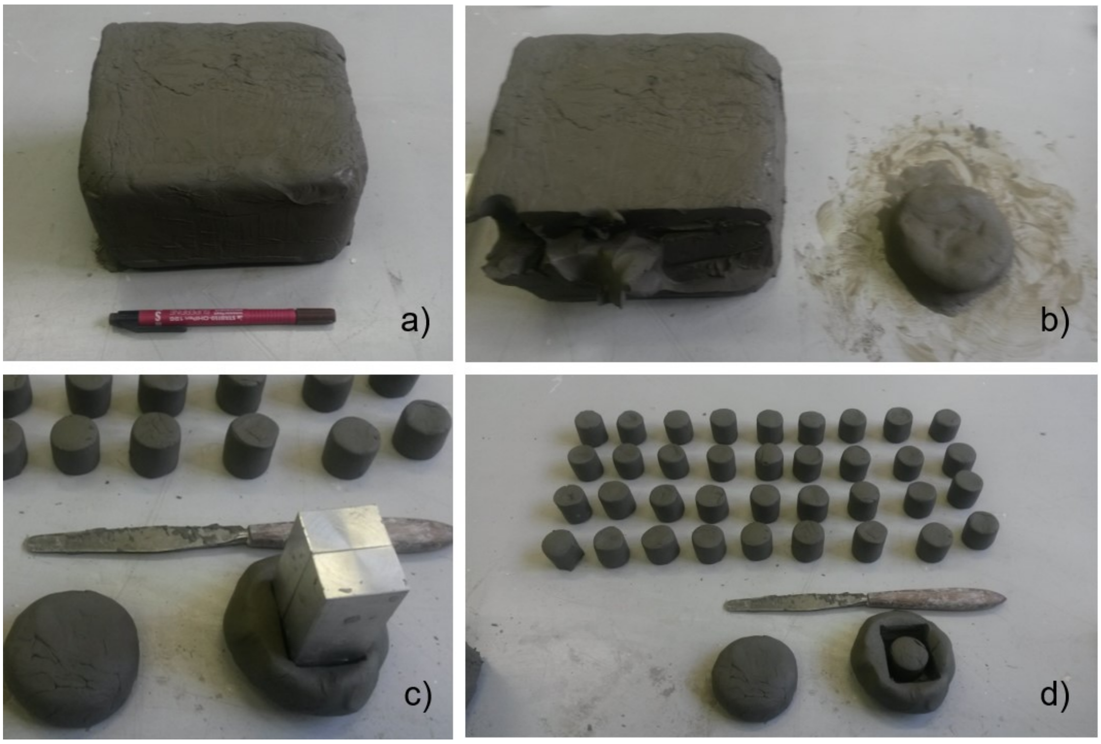


Fig. 1

Fig. 2

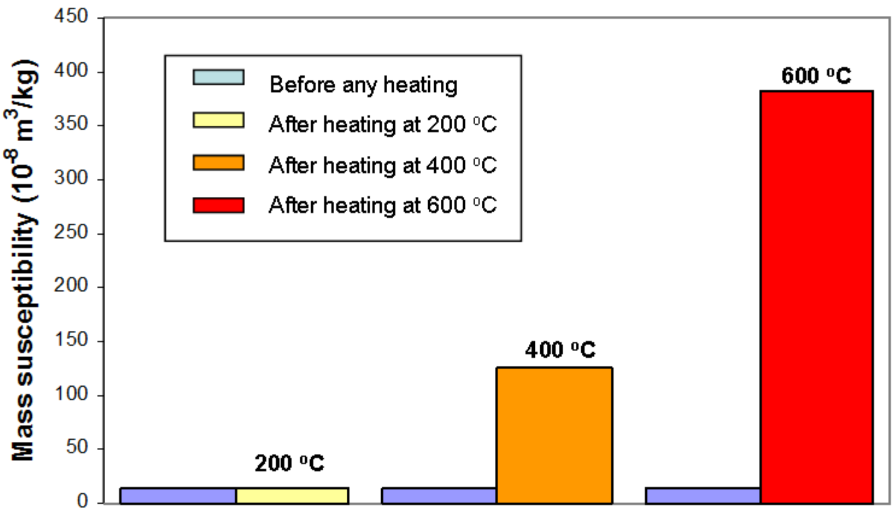

Mass susceptibility (10-8 m3/kg)
450
400
350
300
250
200
150
100
50
0
Before any heating
After heating at 200 °C
After heating at 400 °C
After heating at 600 °C
200 °C
400 °C
600 °C

Fig. 3

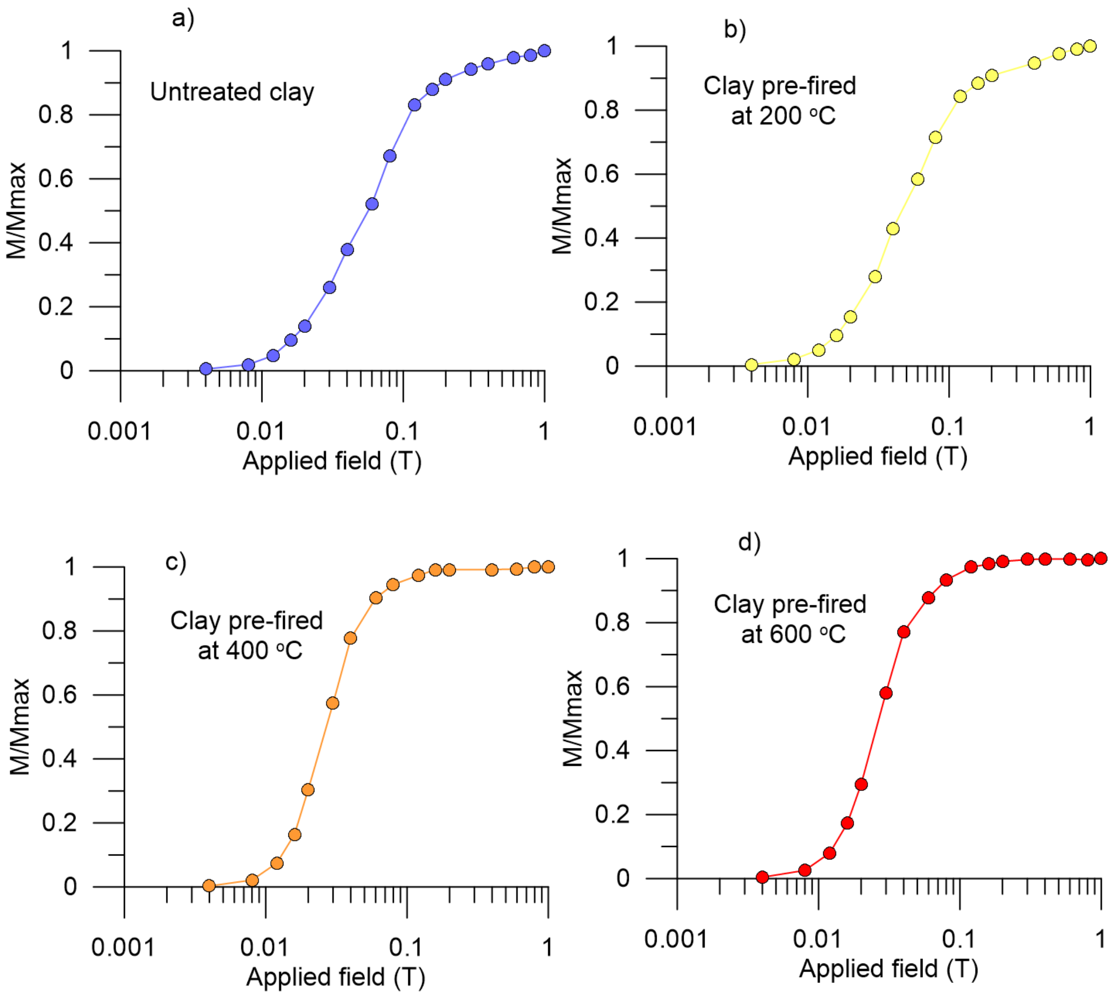

a)
Untreated clay
M/Mmax
1
0.8
0.6
0.4
0.2
0
0.001
0.01
0.1
1
Applied field (T)
b)
Clay pre-fired
at 200 °C
M/Mmax
Applied field (T)
c)
Clay pre-fired
at 400 °C
M/Mmax
Applied field (T)
d)
Clay pre-fired
at 600 °C
M/Mmax
Applied field (T)

Fig. 4

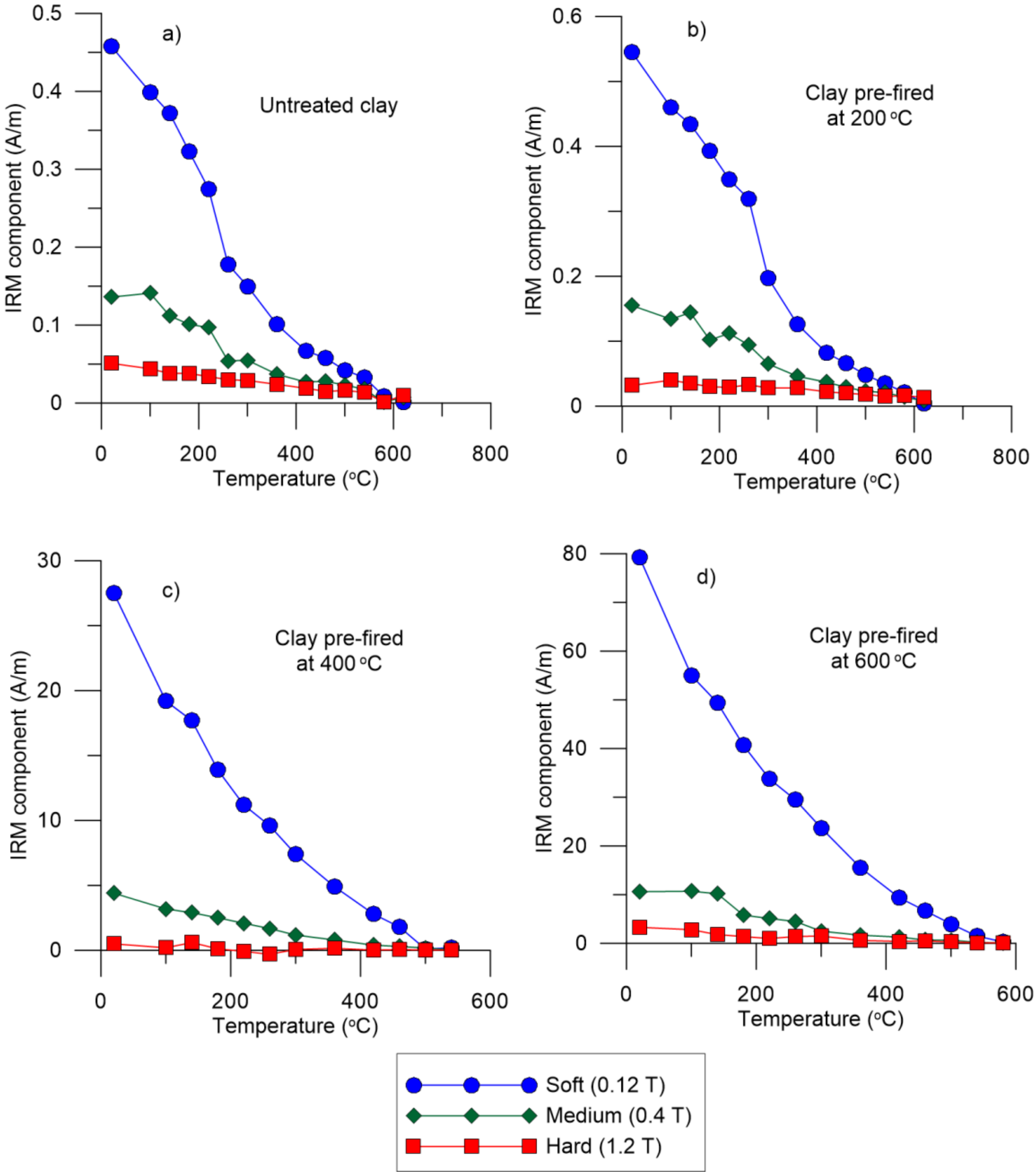
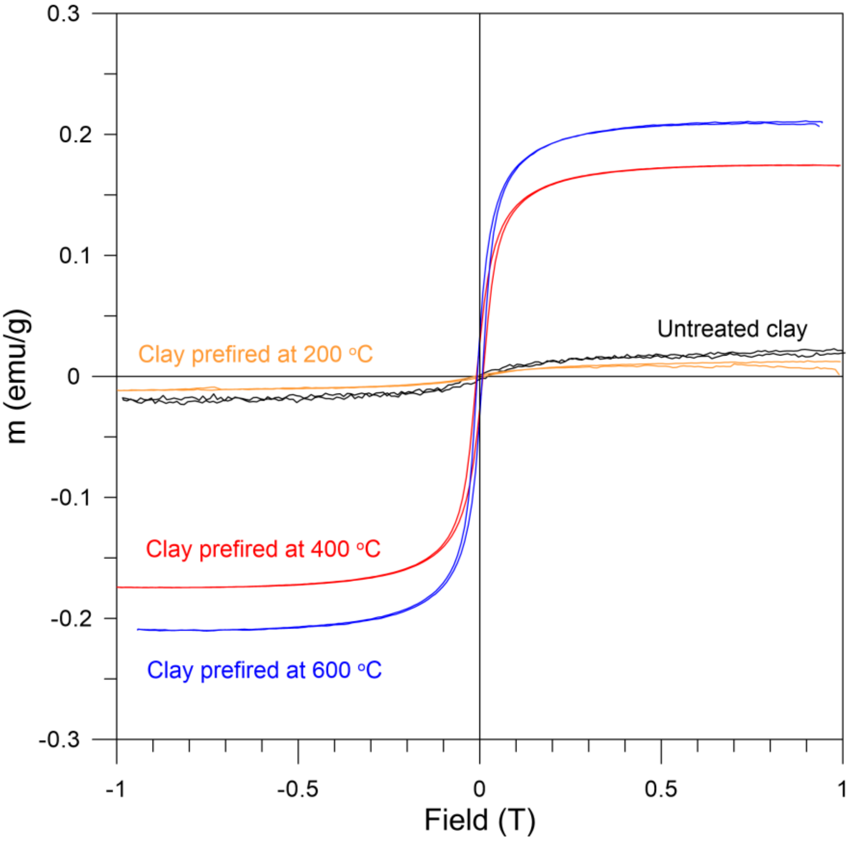

a)
Untreated clay
IRM component (A/m)
Temperature (°C)
b)
Clay pre-fired at 200 °C
c)
Clay pre-fired at 400 °C
d)
Clay pre-fired at 600 °C
Soft (0.12 T)
Medium (0.4 T)
Hard (1.2 T)

Fig. 5



0.3
0.2
0.1
0
-0.1
-0.2
-0.3
m (emu/g)
-1
-0.5
0
0.5
1
Field (T)
Untreated clay
Clay prefired at 200 °C
Clay prefired at 400 °C
Clay prefired at 600 °C

Fig. 6

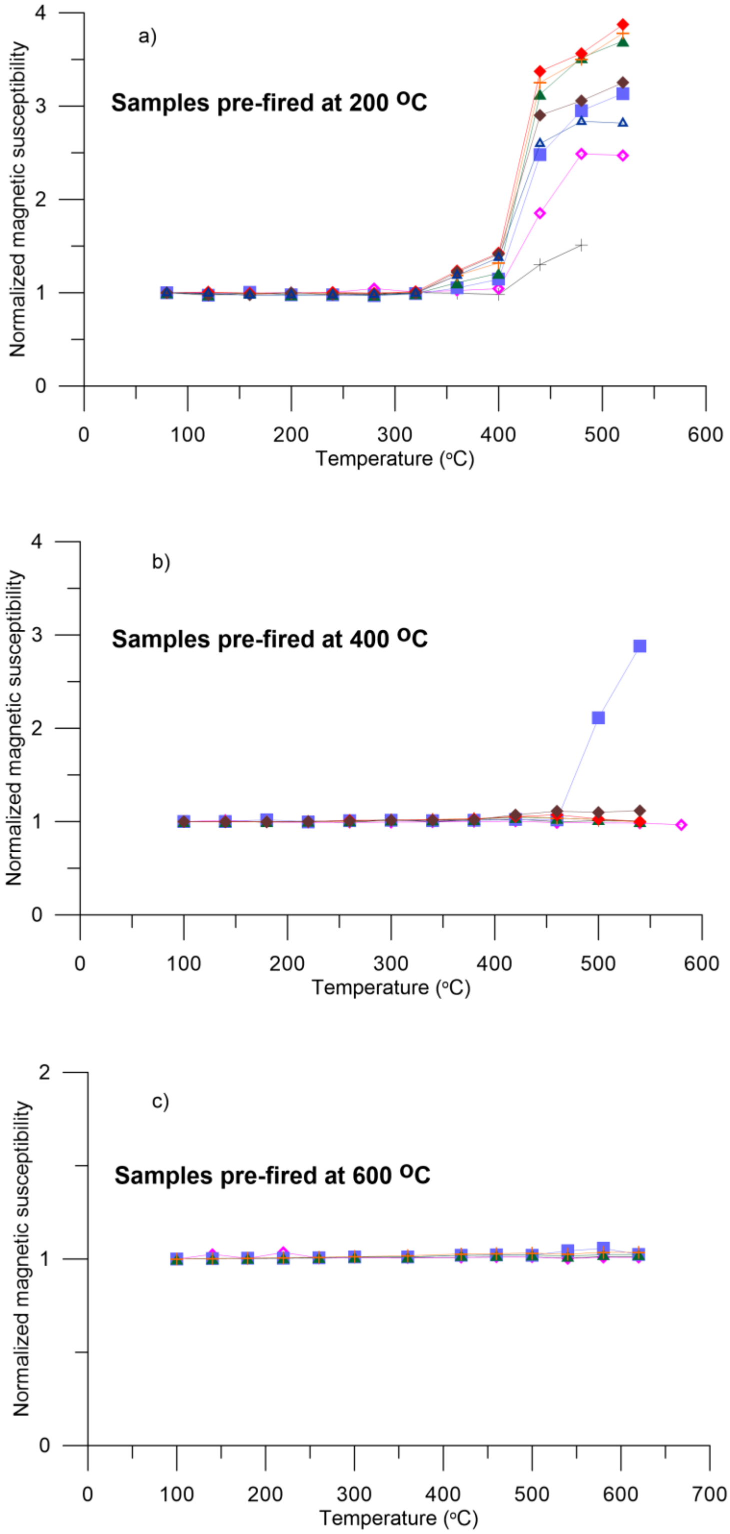
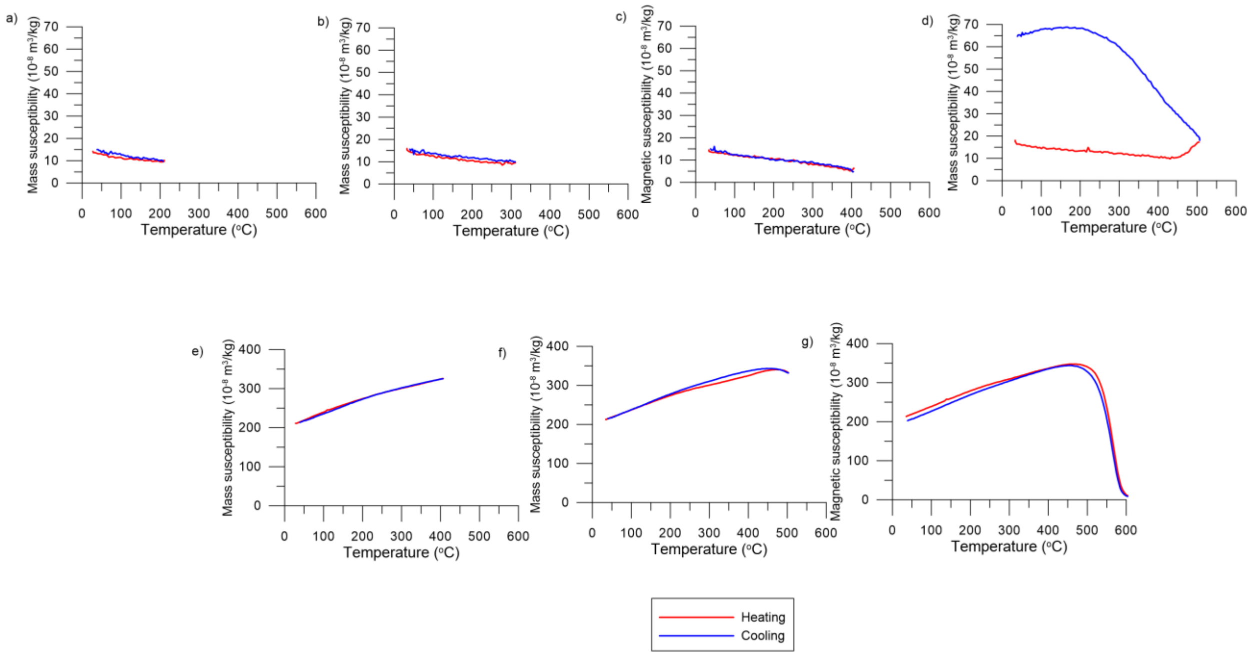
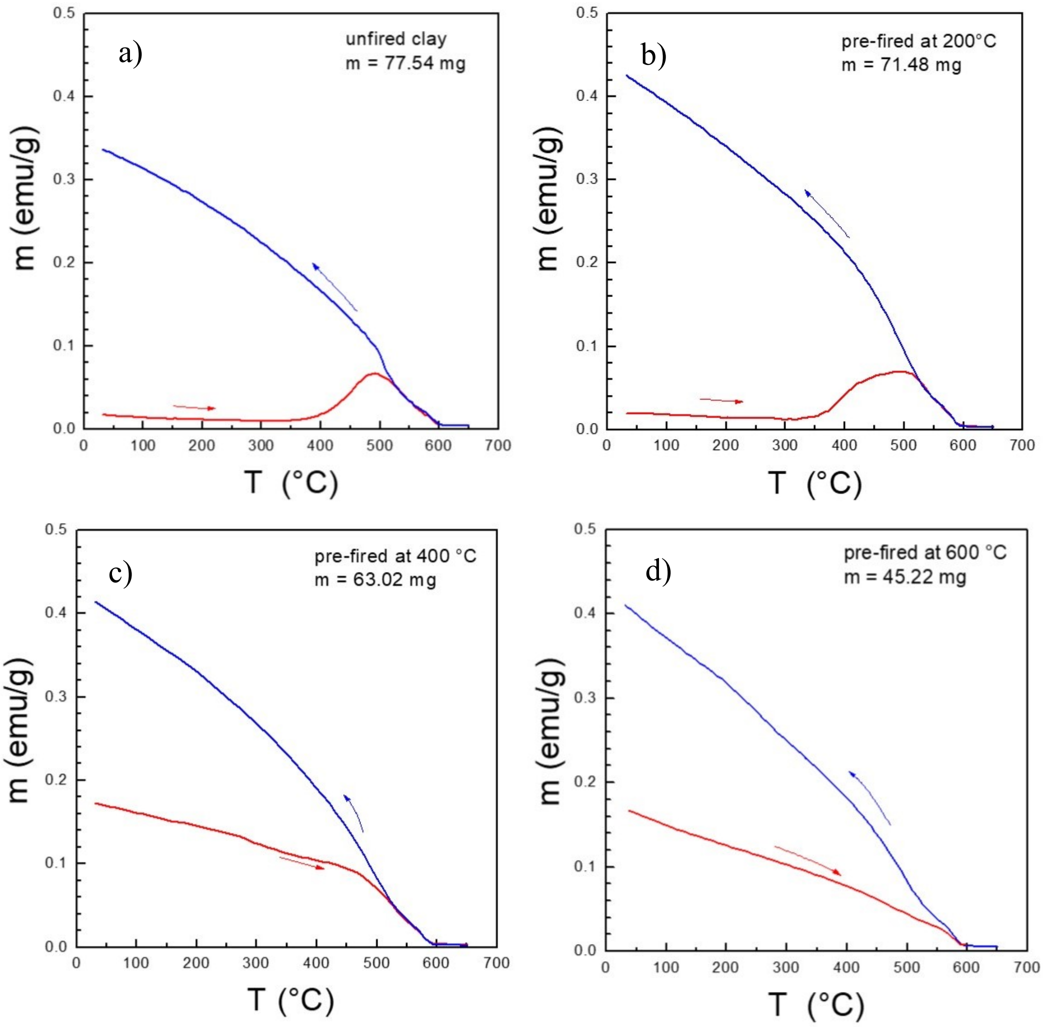

a)
Samples pre-fired at 200 °C
b)
Samples pre-fired at 400 °C
c)
Samples pre-fired at 600 °C
Normalized magnetic susceptibility
Temperature (°C)
0
1
2
3
4
100
200
300
400
500
600
700

Fig. 7



a)
b)
c)
d)
e)
f)
g)
Mass susceptibility (10⁻⁸ m³/kg)
Magnetic susceptibility (10⁻⁸ m³/kg)
Temperature (°C)
Heating
Cooling

Fig. 8



a)
unfired clay
m = 77.54 mg
b)
pre-fired at 200°C
m = 71.48 mg
c)
pre-fired at 400 °C
m = 63.02 mg
d)
pre-fired at 600 °C
m = 45.22 mg
m (emu/g)
T (°C)
0.0
0.1
0.2
0.3
0.4
0.5
0
100
200
300
400
500
600
700

Fig. 9

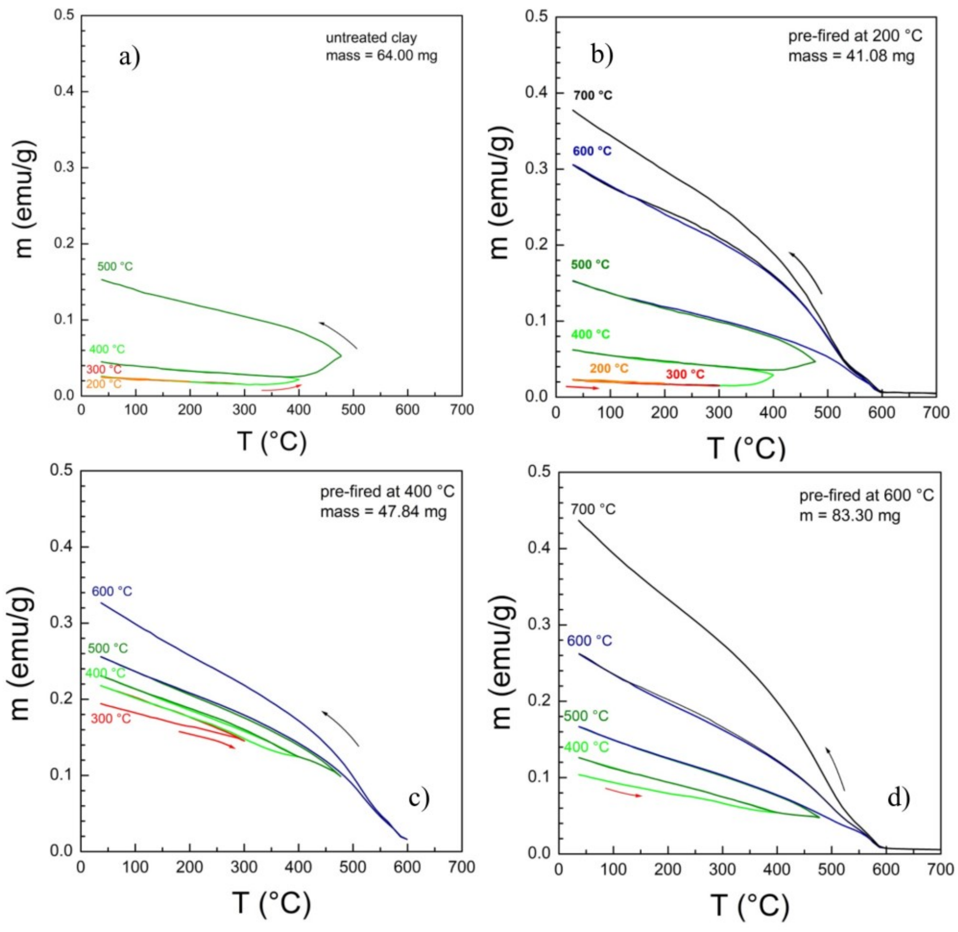
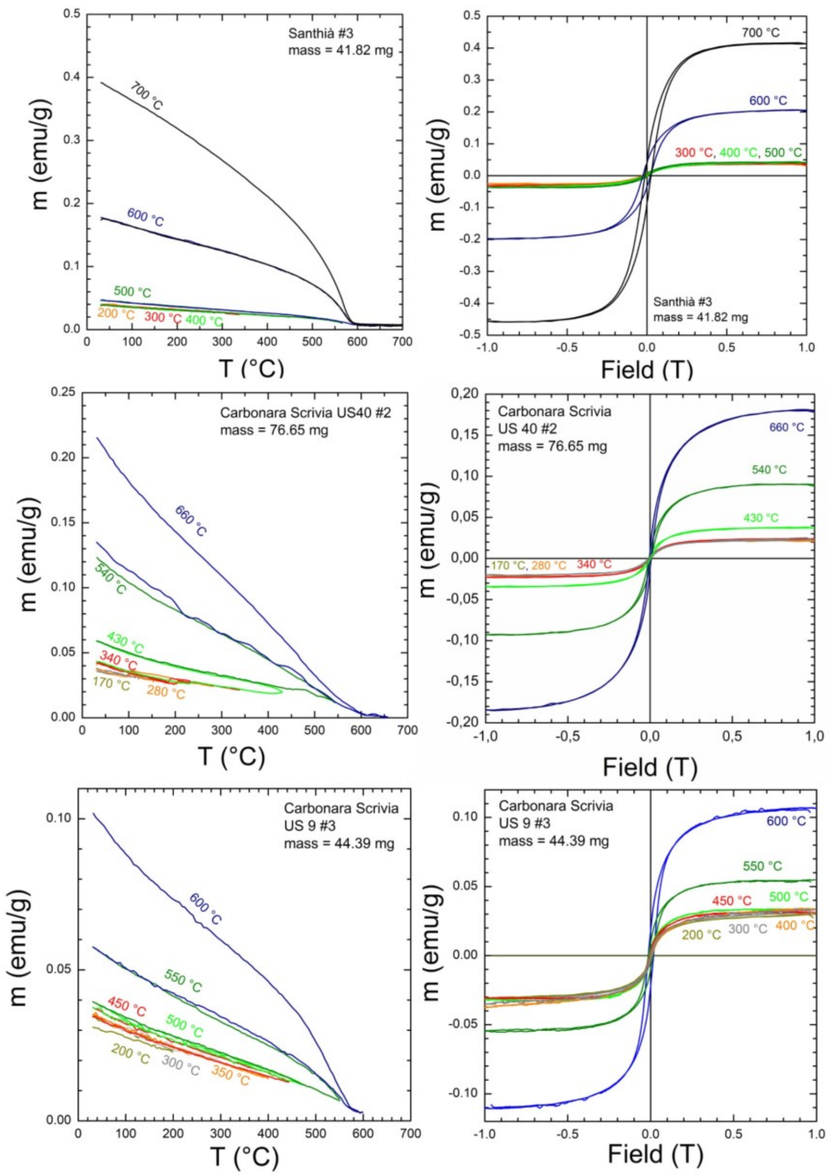

a)
untreated clay
mass = 64.00 mg
500 °C
400 °C
300 °C
200 °C
b)
pre-fired at 200 °C
mass = 41.08 mg
700 °C
600 °C
500 °C
400 °C
200 °C
300 °C
c)
pre-fired at 400 °C
mass = 47.84 mg
600 °C
500 °C
400 °C
300 °C
d)
pre-fired at 600 °C
m = 83.30 mg
700 °C
600 °C
500 °C
400 °C
m (emu/g)
T (°C)

Fig. 10


Santhià #3
mass = 41.82 mg
700 °C
600 °C
500 °C
200 °C
300 °C
400 °C
m (emu/g)
T (°C)
700 °C
600 °C
300 °C, 400 °C, 500 °C
Santhià #3
mass = 41.82 mg
m (emu/g)
Field (T)
Carbonara Scrivia US40 #2
mass = 76.65 mg
660 °C
540 °C
430 °C
340 °C
170 °C
280 °C
m (emu/g)
T (°C)
Carbonara Scrivia
US 40 #2
mass = 76.65 mg
660 °C
540 °C
430 °C
170 °C, 280 °C, 340 °C
m (emu/g)
Field (T)
Carbonara Scrivia
US 9 #3
mass = 44.39 mg
600 °C
550 °C
450 °C
500 °C
200 °C
300 °C
350 °C
m (emu/g)
T (°C)
Carbonara Scrivia
US 9 #3
mass = 44.39 mg
600 °C
550 °C
450 °C
500 °C
200 °C
300 °C
400 °C
m (emu/g)
Field (T)

(a) (b)

Fig. 11

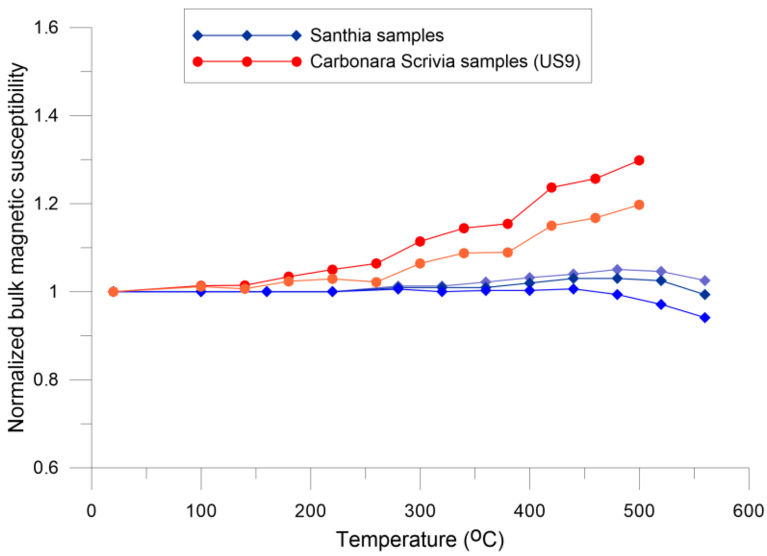

Santhia samples
Carbonara Scrivia samples (US9)
Normalized bulk magnetic susceptibility
1.6
1.4
1.2
1
0.8
0.6
0
100
200
300
400
500
600
Temperature (°C)

Fig. 12