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

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4   Evdokia Tema<sup>a,\*</sup>, Enzo Ferrara<sup>b</sup>

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7       <sup>a</sup> Dipartimento di Scienze della Terra, Università degli Studi di Torino, via Valperga  
8   Caluso 35, 10125 Torino, Italy.

9       <sup>b</sup>Istituto Nazionale di Ricerca Metrologica, Strada delle Cacce 91, I-10135 Torino,  
10   Italy

11  
12  
13       \*Corresponding author at: Dipartimento di Scienze della Terra, Università degli Studi  
14       di Torino, via Valperga Caluso 35, 10125 Torino, Italy. Tel.: +39 011 6708395  
15       E-mail address: [evdokia.tema@unito.it](mailto:evdokia.tema@unito.it)

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18  
19       **ABSTRACT**

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

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

38

39 **Keywords:** Baked clay; Magnetic properties; Firing temperatures; Ancient  
40 technology

41

42

### 43 **1. Introduction**

44 During the last decades, several laboratory-based techniques have been used in  
45 archaeology to provide information about the dating, mineralogy, heating conditions,  
46 material provenance, manufacturing techniques and use of archaeological artifacts.  
47 The study of the firing conditions in archaeological kilns and ovens used for pottery  
48 or for food cooking provides useful information about the technology and fire control  
49 skills used by ancient populations. Mineralogical investigation, X-ray diffraction,  
50 thermal analysis (e.g. thermal dilatometry), color studies, or Mössbauer and  
51 luminescence techniques are usually applied to infer the equivalent firing  
52 temperatures and gain information on the duration and prevalent atmospheric  
53 conditions (reducing/oxidizing) during the ancient heating. Among these techniques,  
54 magnetic measurements have also been involved in firing temperature studies, mainly  
55 based on the changes of magnetic properties occurring during the heating of clay  
56 minerals.

57 Clay minerals contain iron as a minor element that during heating is  
58 converted into Fe-oxides giving ferromagnetic properties to the clay matrix. Since the  
59 first pioneering magnetic studies (Le Borgne, 1960; 1965; Bouchez et al., 1974; Coey  
60 et al., 1979), which examined the effects of heating conditions on the Fe-oxides in  
61 fired soils and archaeological clays, several researchers have used magnetic  
62 measurements to investigate the magnetic enhancement and firing characteristics of  
63 ancient baked clays and pottery. In some cases, such firing temperatures were also  
64 related with pre-selection criteria for archaeointensity experiments and suitability of  
65 the materials for archaeomagnetic studies (e.g. Yang et al., 1993; Dalan and Banerjee,  
66 1998; Jordanova et al., 2001; 2003; Beatrice et al., 2008; Tema et al., 2016;  
67 Kondopoulou et al., 2017). Linford and Platzman (2004) investigated the maximum

68 firing temperature of burnt archaeological sediments based on isothermal remanent  
69 acquisition curves and hysteresis data. Spassov and Hus (2006) estimated the baking  
70 temperatures in a Roman pottery kiln by rock magnetic properties and analyzed the  
71 effect of thermochemical alteration on archaeointensity determinations. Rasmussen et  
72 al. (2012) proposed the use of magnetic susceptibility changes during stepwise  
73 laboratory heating of ceramics as an indicator of the maximum firing temperature  
74 experienced during their production, similarly to the method proposed by Hrouda et  
75 al. (2003) that used the monitoring of the magnetic susceptibility versus temperature  
76 as a palaeotemperature indicator of rocks. Recently, Kostadinova-Avramova et al.  
77 (2018) successfully used the magnetic susceptibility measurement method proposed  
78 by Rasmussen et al. (2012) to determine the firing temperatures of a large ceramic  
79 collection from Bulgaria while Jordanova et al. (2018) used the same approach to  
80 evaluate the paleo-firing temperatures of burnt daub material from the Neolithic site  
81 of Mursalevo-Deveboaz in Bulgaria.

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

88

## 89 **2. Materials and methods**

### 90 *2.1 Experimental samples*

91 A set of 40 cylindrical samples with standard dimensions (diameter = 25.4  
92 mm, height = 22 mm) was prepared at the laboratory using natural grey clay (Fig. 1).  
93 The clay used comes from the Arno River (Vinci, Firenze) and was bought from a  
94 Fine Arts shop as a bulk 5 kg piece (Fig. 1a). The samples prepared manually were  
95 divided in four groups of 10 samples each. The first group was heated at 200 °C for  
96 four hours in a Schonstedt furnace and then samples were left to naturally cool in  
97 ambient temperature outside the furnace. The same procedure was followed for the  
98 samples of the second and third group that were heated at 400 °C and 600 °C,  
99 respectively. The samples from the fourth group were not heated at all (untreated  
100 samples). The selection of three different increasing heating temperatures was made  
101 in order to investigate the variation of the magnetic properties at different critical

102 temperatures: a low temperature (200 °C), a medium temperature quite critical for the  
103 neo-crystallization of clay minerals (400 °C) and a higher temperature, often  
104 experienced by ancient baked clays (600 °C)

105 The bulk magnetic susceptibility of all samples was measured with a KLY-3  
106 Kappabridge (Agico) at the CIMaN-ALP Palaeomagnetic Laboratory (Peveragno,  
107 Italy) and the mass susceptibility ( $\chi$ ) was calculated after weighing each sample with a  
108 precision balance. The Natural Remanent Magnetization (NRM) was measured with a  
109 JR6 Spinner magnetometer (Agico). Six samples from each group were stepwise  
110 thermally demagnetized up to 560-580 °C following increasing temperature steps of  
111 40 °C. During thermal demagnetization, heating and cooling lasted around 30-45 min  
112 and were performed in a Schonstedt furnace. After each demagnetization step, the  
113 bulk magnetic susceptibility was measured at room temperature to monitor possible  
114 magnetic mineralogy alterations. The magnetic mineralogy of the samples before and  
115 after heating was investigated with Isothermal Remanent Magnetization (IRM) curves  
116 and three axes-IRM thermal demagnetization experiments (Lowrie, 1990). Moreover,  
117 continuous low-field monitoring of the magnetic susceptibility versus temperature ( $\chi$ -  
118 T curves) was performed in air atmosphere at the IGGL Geomagnetic Laboratory  
119 (CEED, Oslo, Norway) with a MFK1-FA Kappabridge equipped with a CS-4 furnace  
120 (Agico).

121 Hysteresis loops and magnetic moment versus temperature profiles were  
122 measured with a Lake Shore 7400 Vibrating Sample Magnetometer (VSM) equipped  
123 with a thermo-resistance oven operating in inert Ar atmosphere to vent out residual  
124 gasses at the INRIM Institute (Torino, Italy). Small specimens (mass < 100 mg) of  
125 clay samples from the four different groups were used to obtain continuous  
126 thermomagnetic curves (M-T curves). First, the magnetic moment of one specimen  
127 from each group was continuously measured during heating up to 650 °C and cooling  
128 back to room temperature. Then, for twin specimens from the same samples, the  
129 heating-cooling circle was repeated at different temperatures of 200 °C, 300 °C, 400  
130 °C, 500 °C, 600 °C and 700 °C. Hysteresis loops have also been measured before and  
131 after thermal treatments applying a maximum intensity field,  $H_{\max}$ , equal to 1 T.

132

133

134 *2.2 Archaeological samples*

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

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

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

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

162

### 163 **3. Results**

#### 164 *3.1 Variation of magnetic properties versus heating*

165 The mean mass magnetic susceptibility calculated for the three different  
166 groups of the experimental samples, before and after heating at 200 °C, 400 °C and  
167 600 °C respectively, are plotted in Figure 3. The initial mass susceptibility of all 30  
168 samples is very similar with mean value of  $13.95 \pm 0.3 \times 10^{-8} \text{ m}^3/\text{kg}$ . The obtained

169 results show that heating at 200 °C does not provoke any change of the magnetic  
170 susceptibility and its mean value after heating ( $14.3 \times 10^{-8} \text{ m}^3/\text{kg}$ ) remains practically  
171 the same to the one before any thermal treatment. On the contrary, heating at higher  
172 temperatures leads to an important magnetic susceptibility enhancement. The mean  
173 mass susceptibility after heating at 400 °C becomes  $126.3 \times 10^{-8} \text{ m}^3/\text{kg}$  while after  
174 heating at 600 °C it further importantly increases with mean value equal to  $382 \times 10^{-8}$   
175  $\text{m}^3/\text{kg}$ .

176 Changes in the magnetic mineralogy of the studied experimental samples can  
177 be observed from the IRM acquisition comparing the curves obtained from the  
178 samples before and after heating at various temperatures (Fig. 4). Clay samples that  
179 have not experienced any heating are not saturated at applied field of 1T, suggesting  
180 the presence of a high coercivity mineral. The same behavior is also noticed at  
181 samples heated at 200 °C, where again saturation is not reached at 1T. On the  
182 contrary, samples heated at 400 °C and 600 °C are saturated in applied fields of  
183 around 0.2 T, indicating the presence of a low coercivity mineral and the absence of  
184 any high coercivity magnetic carriers. These results are also confirmed by the thermal  
185 demagnetization of a composite IRM component (Lowrie, 1990) diagrams that are  
186 very similar for the samples heated at 200 °C and for those without any heating  
187 treatment. For these samples a drop of magnetization in the soft and medium  
188 coercivity components is observed around 250-300 °C; such drop is not observed at  
189 the diagrams from samples heated at 400 °C and 600 °C. In all cases the obtained  
190 results show the dominance of the soft coercivity components while medium and high  
191 coercivity components are minor (for the samples of raw clay and those pre-heated at  
192 200 °C) or negligible (for the samples pre-heated at 400 °C and 600 °C) (Fig. 5).

193 Hysteresis loops obtained after the subtraction of the paramagnetic  
194 contribution for raw clay samples and for samples pre-fired at 200°C, 400°C and 600  
195 °C are reported in Fig. 6. These results show that the firing at temperature lower than  
196 400 °C does not influence the magnetic granulometry of the samples. In fact, the  
197 loops of raw clay (black curve) and pre-fired clay at 200 °C (orange curve) overlap,  
198 being almost indistinct, characterized by a faint ferrimagnetic signal. After firing at  
199 400 °C (red curve), a tenfold increase of both, saturation,  $M_s$ , and remanent  
200 magnetization,  $M_{RS}$ , arises; further increase of magnetization may be observed after  
201 firing at 600 °C (blue curve).

202 Measuring the bulk magnetic susceptibility at room temperature during the  
203 stepwise thermal demagnetization shows important differences among the samples  
204 initially heated at different temperatures. For the group pre-fired at 200 °C, changes at  
205 the bulk susceptibility are registered around 320 °C with an abrupt magnetic  
206 susceptibility increase clearly observed after heating at temperatures > 400 °C (Fig.  
207 7a). For temperatures from 200 °C to 320 °C, the magnetic susceptibility remains  
208 almost the same, even when the temperature exceeds the initial heating temperature  
209 experienced during the preparation of this sample group (200 °C). For the group pre-  
210 fired at 400 °C, the susceptibility measured at room temperature is very stable till 400  
211 °C and only very small variations can be observed after 420 °C, with important  
212 changes noticed only at one sample after heating at 460 °C (Fig. 7b). Finally, for the  
213 group pre-fired at 600 °C, no variations at the magnetic susceptibility values are  
214 observed until heating up to 620 °C (Fig. 7c).

215 Continuous monitoring of the low field magnetic susceptibility in air with  
216 repeated progressive heating and cooling cycles up to different maximum  
217 temperatures shows results similar to those obtained from the bulk magnetic  
218 susceptibility measured at room temperature during the thermal demagnetization.  
219 Indeed, the clay initially heated at 200 °C shows reversible heating/cooling cycles up  
220 to 400 °C (Fig. 8a-c) while important magnetic mineralogy changes are only noticed  
221 after heating at temperatures higher than 400 °C (Fig. 8d). For the clay pre-fired at  
222 400 °C, magnetic susceptibility is completely reversible during heating/cooling at the  
223 same temperature (Fig. 8e), while only very minor differences may be observed when  
224 heated at higher temperatures (500 °C and 600 °C, Fig. 8 f-g).

225 Thermomagnetic curves of the magnetic moment versus temperature  
226 continuously measured up to 650 °C conducted in Ar atmosphere show that in the raw  
227 clay (Fig. 9a), the magnetic moment remains almost stable up to 350-400 °C, when a  
228 transformation starts producing an increase of the magnetic moment. Similar behavior  
229 is also observed for the pre-fired clay at 200 °C that shows its magnetic properties  
230 unchanged until 350-400 °C, when again some transformation appears increasing the  
231 magnetic moment. The thermomagnetic curves obtained from the samples pre-fired at  
232 200 °C are actually undistinguishable from those obtained from the untreated samples  
233 (Fig. 9a and 9b). Similarly, thermomagnetic curves obtained from clay pre-fired at  
234 400 °C and 600 °C show the same general trend, with irreversible behavior. However,

235 in these cases no increase at the magnetic moment is observed at the heating curve  
236 (Fig. 9c and 9d).

237 The magnetic moment behavior after heating/cooling cycles at progressively  
238 increasing temperatures was also monitored for the various pre-fired clay groups. The  
239 obtained results for the untreated clay and for the clay pre-fired at 200 °C show  
240 reversible curves till 300 °C while at higher temperatures the magnetic moment  
241 registered during cooling is higher than the heating curve (Fig. 10 a, b). The same  
242 curves obtained for the clay pre-fired at 400 °C show almost reversible behavior until  
243 400 °C, even though the heating and cooling curve of 300 °C is not perfectly  
244 reversible. The difference of the curves obtained at 400 °C and 500 °C is not very  
245 important but then the curve obtained at 600 °C is clearly distinguishable (Fig. 10c).  
246 Finally, the thermomagnetic curves obtained after heating/cooling at 500 °C, 600 °C  
247 and 700 °C for the clay pre-fired at 600 °C are almost never completely reversible  
248 with a clearly much higher magnetic moment measured after heating at 700 °C (Fig.  
249 10d).

250

### 251 *3.2 Determining the heating temperatures of archaeological samples*

252 Samples collected from the archaeological sites of Santhià and Carbonara  
253 Scrivia were also analyzed for the investigation of the heating temperatures  
254 experienced during their use in the past. The magnetic behavior as a function of  
255 temperature of small specimens (mass < 100 mg) collected from the bricks of the  
256 Santhià kiln and from the baked clay of the two structures excavated at Carbonara  
257 Scrivia, was analyzed mainly using the Vibrating Sample Magnetometer (VSM  
258 model: Lakeshore 7410). On three samples from the Santhià kiln, and on five samples  
259 from Carbonara Scrivia (two samples from Unit 9, and three samples from Unit 40)  
260 the variation of the magnetic moment has been continuously recorded at different  
261 temperatures. Each sample was heated at 200 °C and cooled back to room temperature  
262 while its magnetization was continuously measured during both heating and cooling.  
263 Then, for the same sample, the heating-cooling circle was repeated up to around 300  
264 °C, 400 °C, 500 °C, 600 °C and finally up to 700 °C (Fig. 11a). Hysteresis loops were  
265 also measured before and after thermal treatments applying a maximum intensity  
266 field,  $H_{\max}$ , equal to 1 T (Fig. 11b).

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

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

281 The bulk magnetic susceptibility measured at room temperature after stepwise  
282 thermal demagnetization of selected samples shows that the susceptibility does not  
283 significantly vary from the initial value up to temperatures of 500-600 °C for samples  
284 from Santhià. In the case of Carbonara Scrivia (US9) the susceptibility starts  
285 increasing at the temperature range from 300 °C to 400 °C, with variations higher than  
286 20 % observed for temperatures higher than 400 °C (Fig. 12).

287

#### 288 **4. Discussion**

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

- 294 **1.** The mean magnetic susceptibility of the samples heated at 200 °C is the same  
295 with that of the untreated clay, showing that heating at 200 °C is not enough to  
296 cause any magnetic enhancement. Differently, the mean magnetic  
297 susceptibility measured after heating at 600 °C is for all samples significantly  
298 higher than those heated at 400 °C. This shows that heating at higher  
299 temperatures involves a larger number of iron sources from the clay matrix, as  
300 already previously observed by Kostadinova-Avramova and Kovacheva  
301 (2013).

- 302       2. Both raw clay and samples pre-heated at 200 °C show very similar magnetic  
303       properties. In both cases,  $\chi$ -T and M-T curves remain completely reversible up  
304       to 300 °C showing a thermally stable behavior (even if they haven't  
305       experienced heating at that temperature before). Therefore, using the  
306       reversibility of the thermomagnetic curves for firing temperatures lower than  
307       300 °C should be used with caution as it could lead to erroneous conclusions.
- 308       3. As expected, most mineralogical transformations seem to occur at  
309       temperatures from 300 °C to 400 °C and lead to an important magnetic  
310       enhancement that can be easily detected by the abrupt changes of the magnetic  
311       properties after temperatures higher than 300 °C. This is probably related to  
312       the dehydration of clay minerals and the chemical transformation of  
313       maghemite, unstable to heating.
- 314       4. Samples pre-heated at 400 °C show reversible  $\chi$ -T curves up to 600 °C,  
315       probably because most of the mineralogical changes have already taken place  
316       during the heating at 400 °C as previously discussed.
- 317       5. The M-T curves performed in argon atmosphere for samples pre-heated at 600  
318       °C, are not completely reversible after heating at the same temperature,  
319       suggesting that the laboratory heating of the samples for 4 hours at 600 °C was  
320       not sufficient to achieve the thermal stability of the samples.

321

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

334       Our results presented here show that reversible  $\chi$ -T curves up to 300 °C does not  
335       necessarily indicate that the clays have experienced at the past firing at 300 °C. They

336 also show that heating at lower temperatures or not heating at all could also result on  
337 reversible curves up to 300 °C. Of course, this may depend on the initial mineralogy  
338 of the raw clay and may change from clay to clay. Nevertheless, such reversible  
339 curves can still be used to indicate that ancient heating has not exceeded this  
340 temperature, since important mineralogical changes that are clearly detected by  
341 magnetic measurements take place at 300-400 °C interval. On the other hand, caution  
342 should be also applied on the interpretation of reversible  $\chi$ -T up to 600 °C: e.g. pre-  
343 fired samples at 400 °C show reversible  $\chi$ -T curves even after heating to 600 °C. That  
344 is probably because most of the transformations have already taken place in the 300-  
345 400 °C temperature interval and therefore the samples have become thermally stable  
346 even if they haven't been heated at such high temperatures (e.g. 600 °C) before. The  
347 temperature range 300-400 °C is critical for clay minerals as it can be related to the  
348 transformation of unstable maghemite or the dihydroxylation of goethite (Trindade et  
349 al., 2010). Kostadinova-Avramova and Kovacheva (2013) have shown that for several  
350 clay types, at temperature of ~280 °C dehydration of supposed lepidocrocite begins  
351 and unstable (titano)maghemite is formed while at higher temperatures (~400 °C) a  
352 second transformation occurs and the maghemite converts into magnetite and  
353 hematite.

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

362 Similarly to the  $\chi$ -T curves, raw clay and samples pre-fired at 200 °C show  
363 completely reversible behavior up to 300 °C. These results confirm that low firing  
364 temperatures (<300 °C) cannot be detected based on the reversibility of the  
365 thermomagnetic curves. For higher firing temperatures (e.g. 400 and 600 °C), the M-T  
366 curves tend to show a relative reversible behavior (even if not completely reversible)  
367 after heating at temperatures close to those of the pre-firing. However, it's still hard to  
368 precisely detect the pre-firing temperatures, as they show important changes only

369 when the initial firing temperature is strongly exceeded (e.g. 600 °C for clays pre-  
370 fired at 400 °C or 700 °C for clays pre-fired at 600 °C).

371 In the case of archaeological samples, the M-T curves show generally repeatable  
372 results for the different samples coming from the same structures. For the bricks  
373 sampled from the Santhià kiln, the repeated heating experienced by the samples  
374 during the use of the kiln resulted at a very stable magnetization up to 500 °C, while  
375 important changes are noticed only after heating at 600 °C. These results cannot  
376 guarantee that the bricks have not experienced higher temperatures at the past but  
377 however indicate that such higher heating (if applied) was not long enough to attain  
378 the thermal stability of the samples. On the other hand, baked clays from the  
379 Carbonara Scrivia funeral structures show relative low firing temperatures (less than  
380 500 °C). In particular, for the structure US40, the M-T curves are reversible only up to  
381 340-430 °C. Based on our data from the experimental samples, such results may show  
382 that the baked clay has not experienced long and repeated heating at temperatures  
383 higher than 400 °C but heating at much lower temperatures cannot be excluded either  
384 (even less than 200 °C).

385

## 386 5. Conclusions

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

402 always be used as precise indicator of the maximum ancient heating temperatures,  
403 mostly in the case of single and weak heating at the past.

404 ~~Our~~ The same results show that for temperatures lower than 300-400 °C, clays  
405 are thermally stable even if they have not experienced similar temperatures in the  
406 past. Even for higher temperatures (>400 °C) however, the reversibility or  
407 irreversibility of the thermomagnetic curves does not always indicate the limit of the  
408 maximum temperatures experienced in the past. The heating conditions and/or the  
409 time of heating at a certain temperature may importantly affect the achievement of the  
410 thermal stability. Indeed, the repeated heating experienced from the archaeological  
411 clays during their use in the past results to a clearer interpretation of the M-T curves  
412 in respect to the experimental samples that were heated at the laboratory only once.  
413 This study aims to point out that the reliability of the use of the reversibility of the  
414 thermomagnetic curves in baked clays is limited by several factors and should be  
415 ideally accompanied by other experimental techniques (e.g. XRF,  
416 thermoluminescence) to avoid erroneous estimations.

417

418

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433

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525 **Figure captions**

526

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

529

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

532

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

535

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

539

540 Fig. 5. Stepwise thermal demagnetization of three IRM components following Lowrie  
541 (1990) for samples a) before any treatment, and samples pre-fired at b) 200 °C, c) 400  
542 °C and d) 600 °C. Symbols: dot= Soft- (0.12 T); diamond= Medium- (0.4 T); square=  
543 Hard- (1.2 T) coercivity component.

544

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

548

549 Fig. 7. Normalized bulk magnetic susceptibility measured at room temperature during  
550 stepwise thermal demagnetization for representative samples initially pre-fired at a)  
551 200 °C, b) 400 °C and c) 600 °C.

552

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

556

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

560

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

564

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

568

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

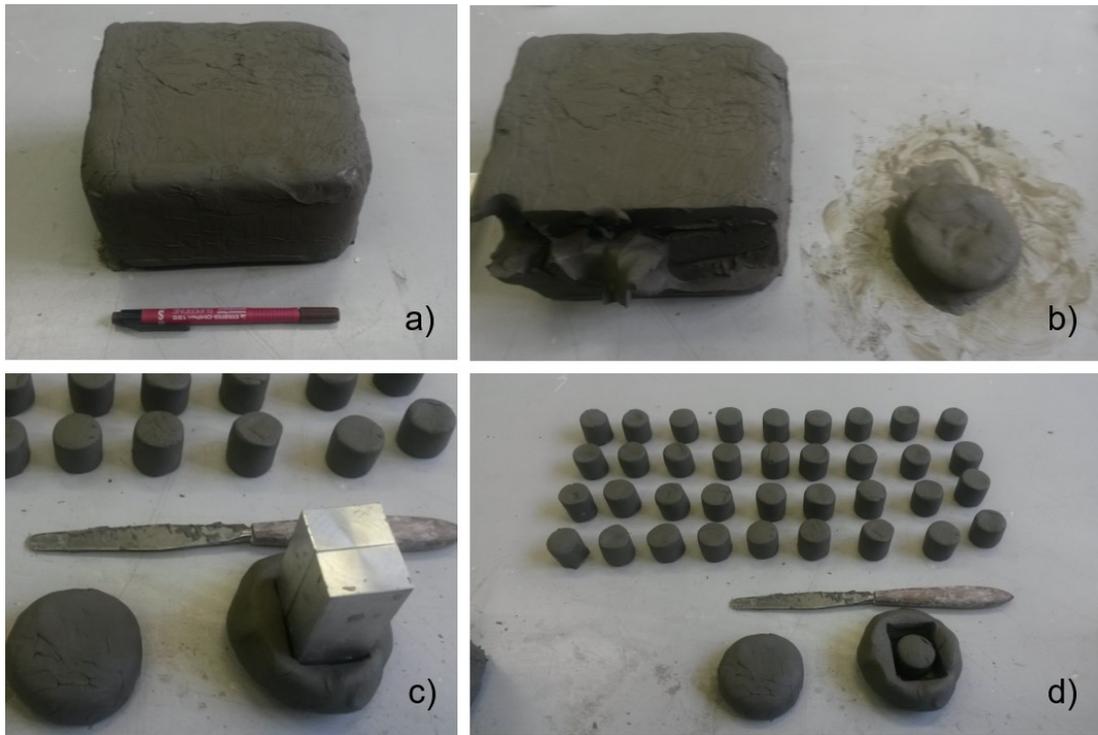
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Fig. 1

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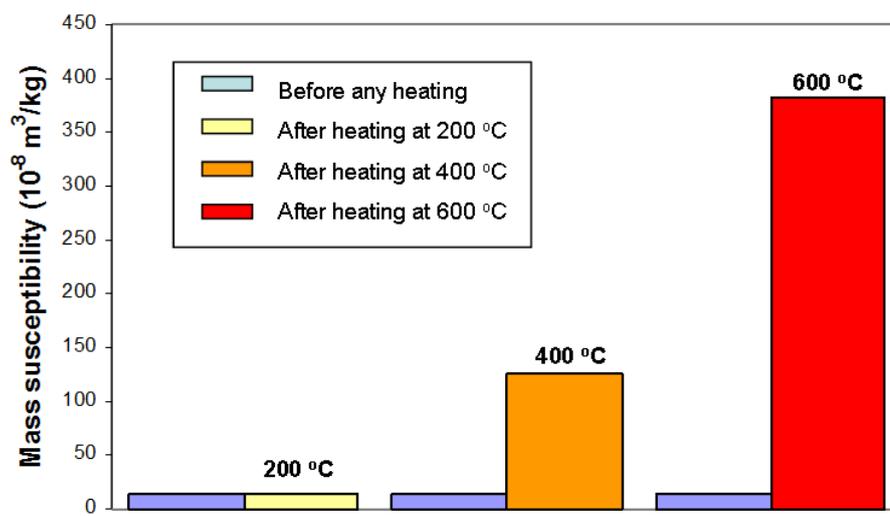
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Fig. 2

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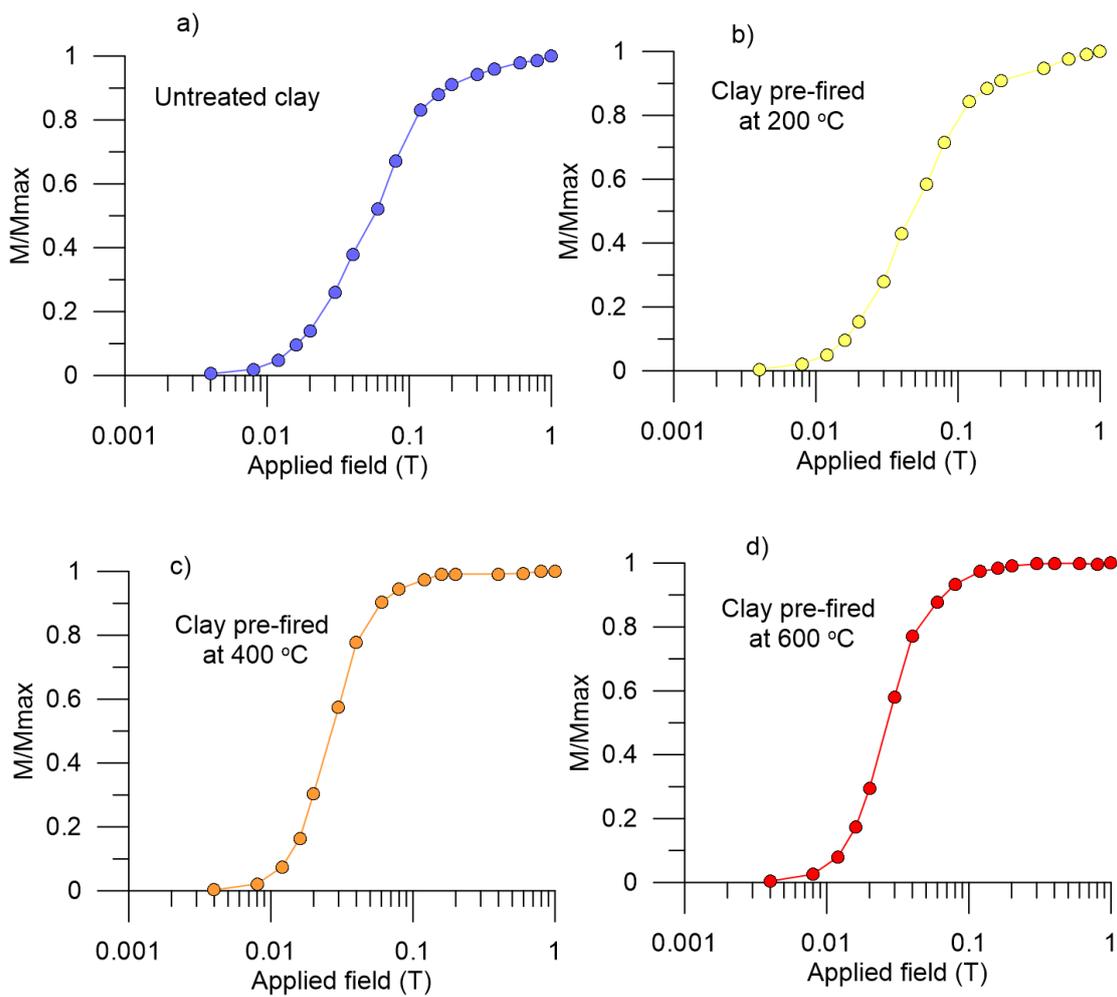
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Fig. 3

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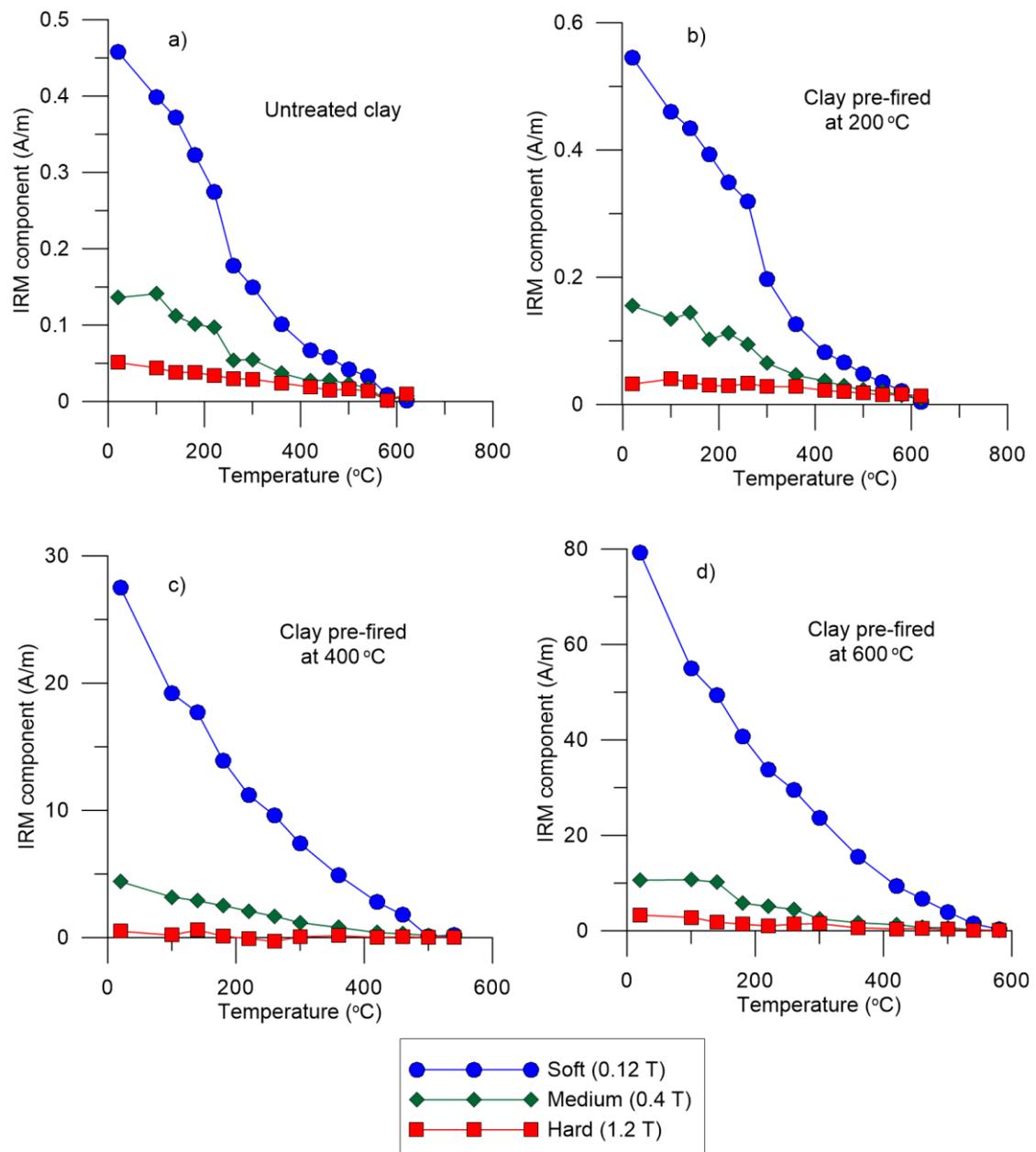
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Fig. 4

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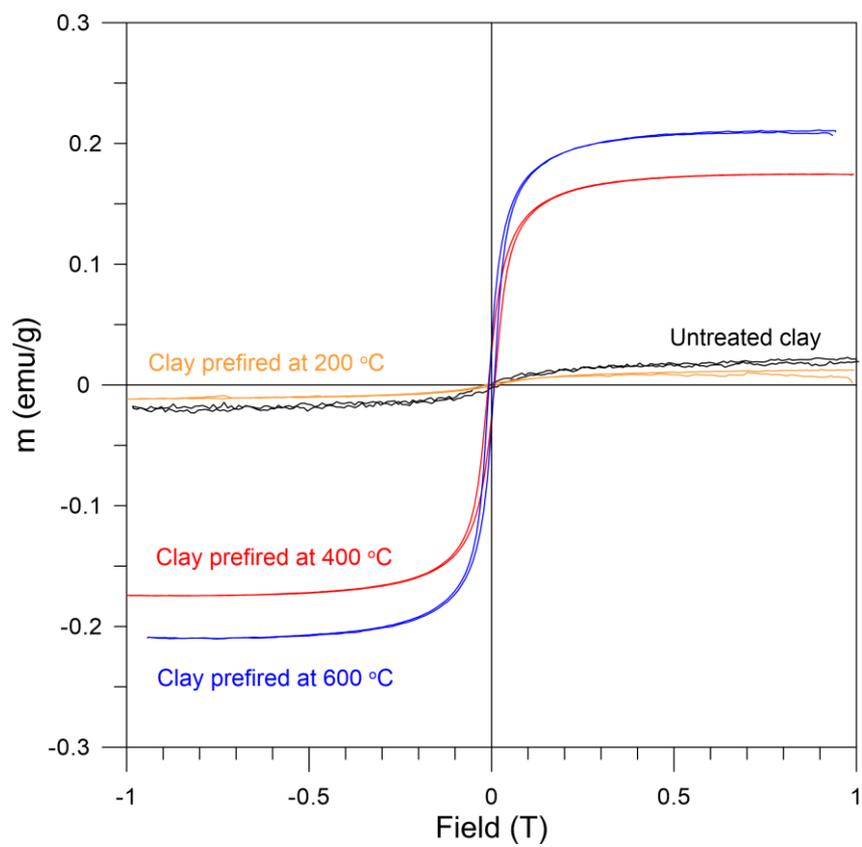
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Fig. 5



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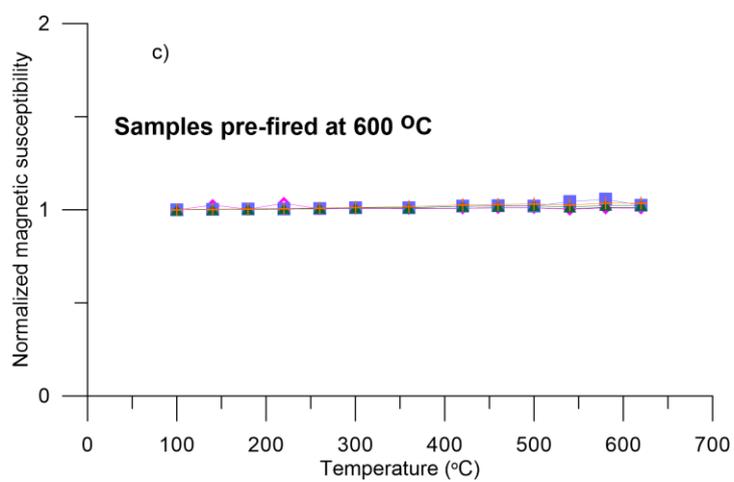
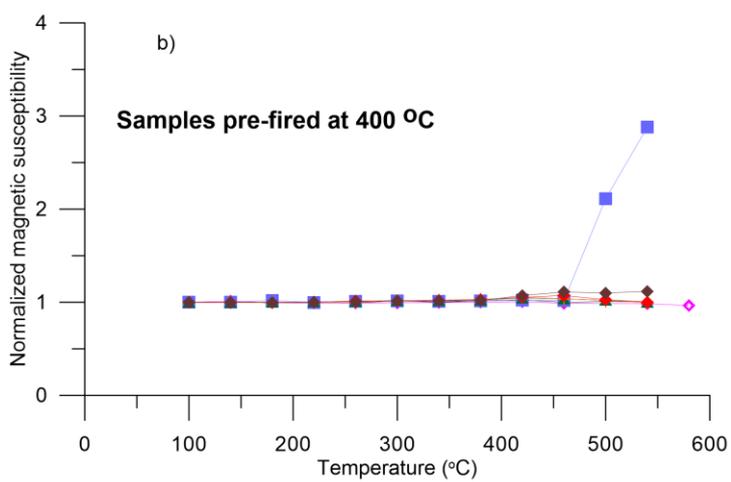
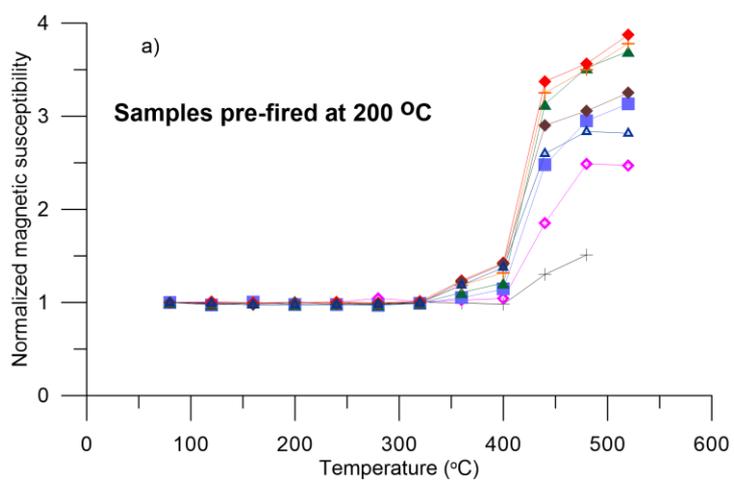
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Fig. 6



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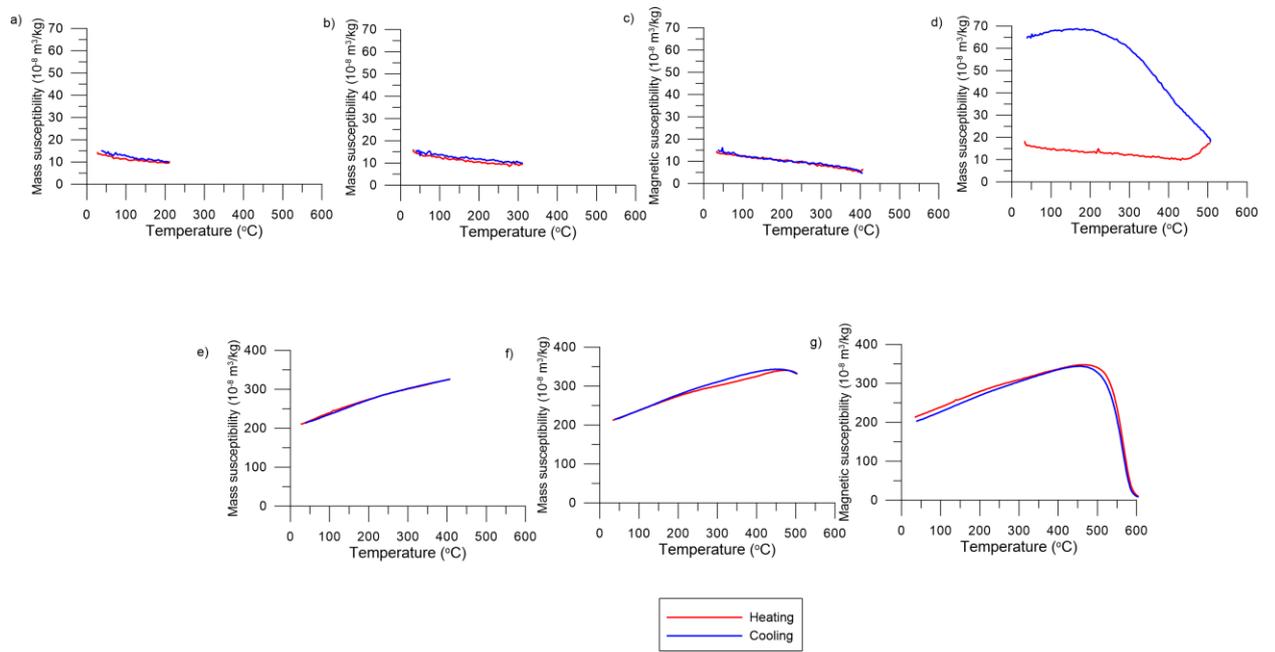
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Fig. 7

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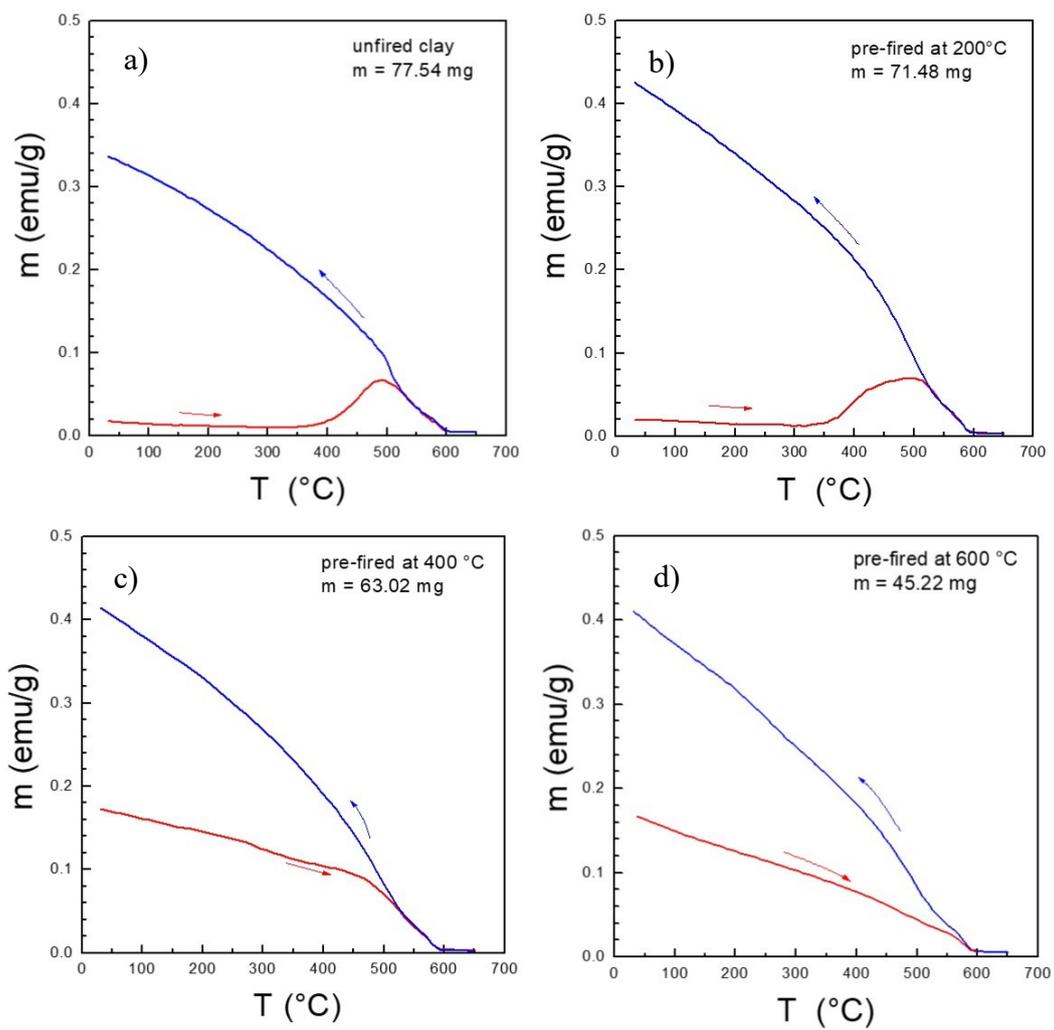
Fig. 8

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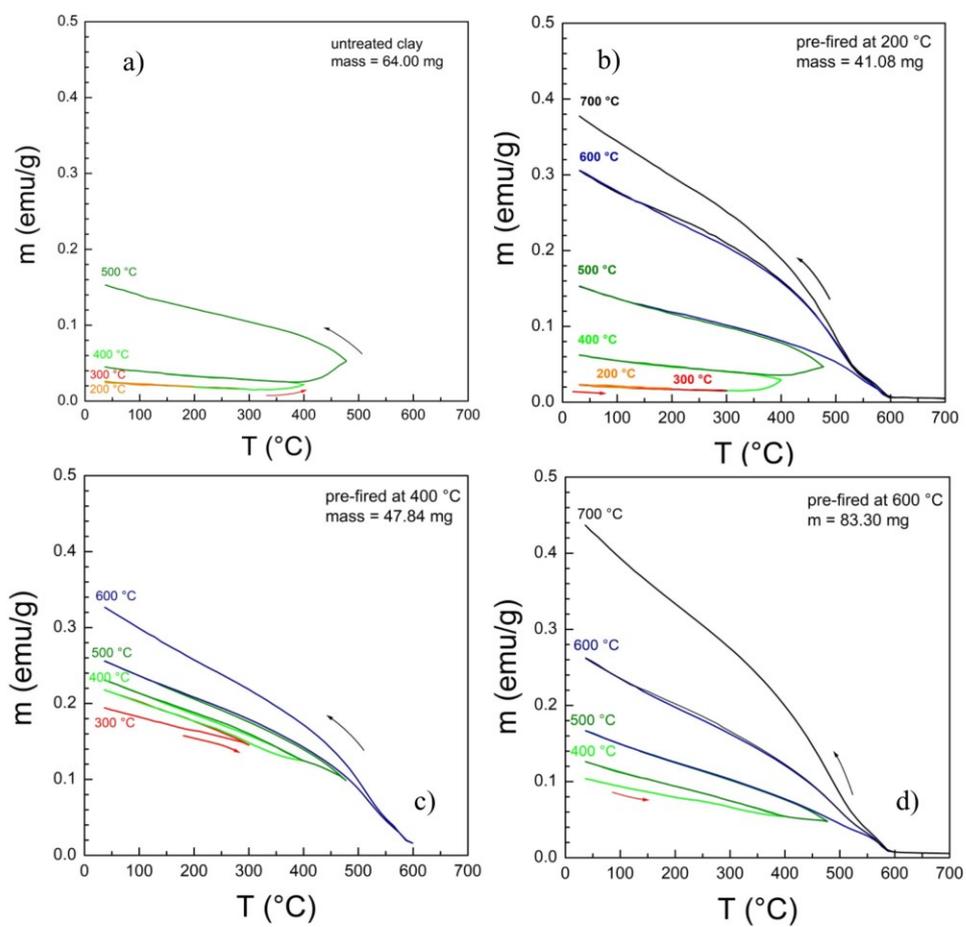
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Fig. 9



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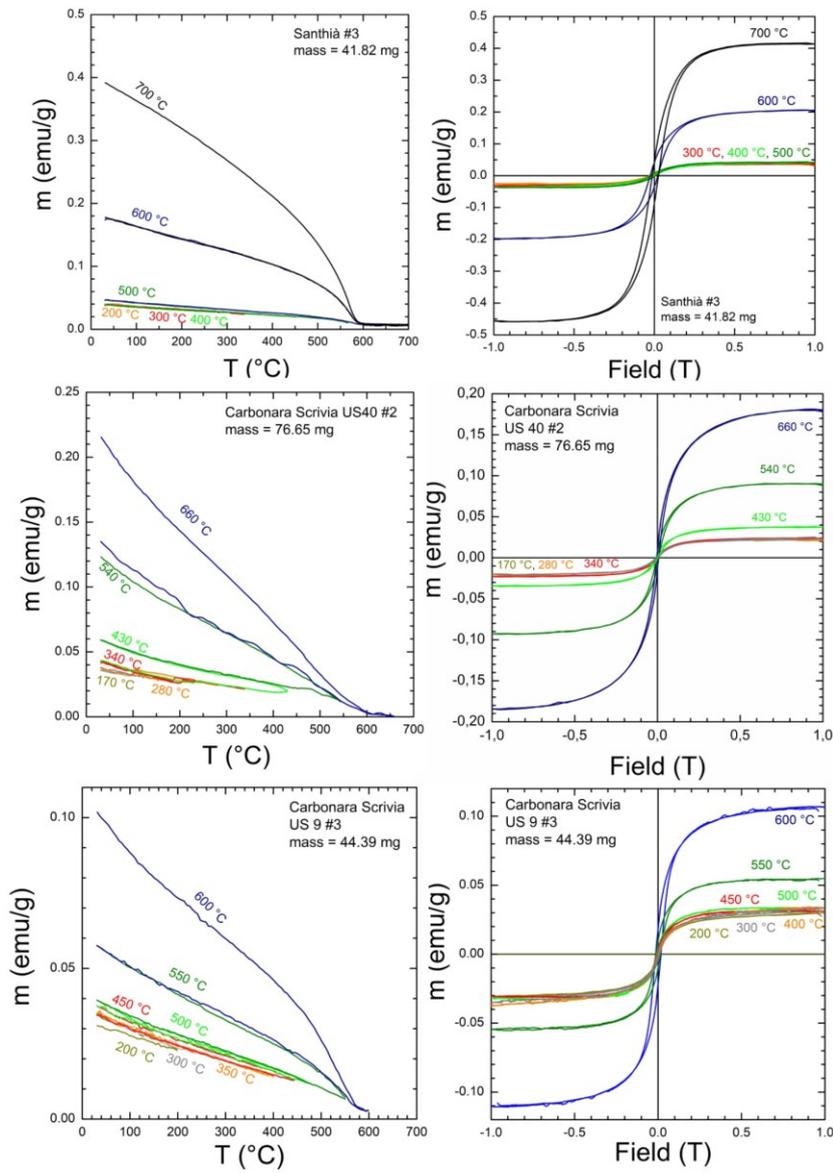
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Fig. 10



(a)

(b)

Fig. 11

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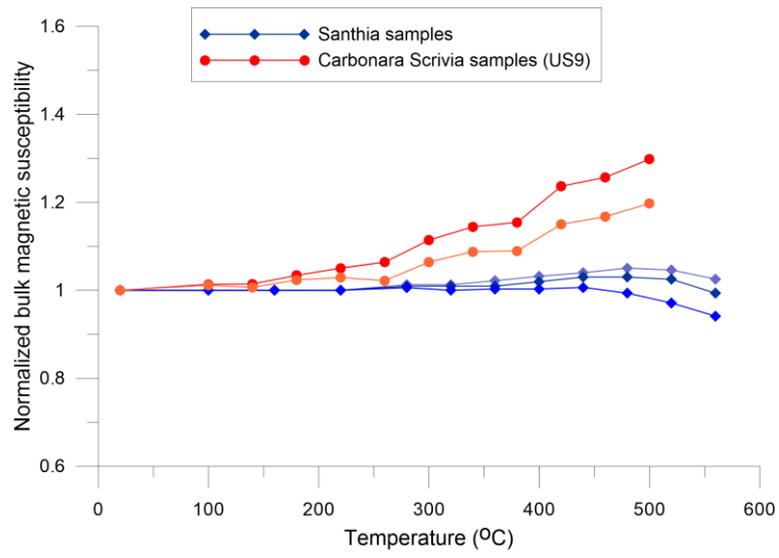
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Fig. 12