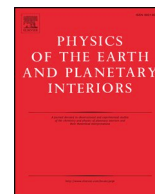


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Further progress in the study of epsilon iron oxide in archaeological baked clays

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ABSTRACT

The occurrence of ϵ -Fe₂O₃ in archaeological samples that have been subjected to high temperatures is gradually being detected by the use of micrometric structural characterization techniques. This work provides new information by revealing that the ϵ -Fe₂O₃ is formed as a response to temperature, the aggregation state and the position within the baked clay with respect to the nearest heat source. In addition, depending mainly on the atmospheric environment, the temperature reached by the combustion structure, the distance from the heating source and the particle aggregation, other iron oxide magnetic phases are produced. In the baked clay studied here, hematite is found over the whole range of samples studied but its magnetic contribution is negligible. Magnetite is observed at the sample surface, probably due to local atmospheric environment closest to the combustion source. Maghemite is found at all depths up to 6 cm below the sample surface. ϵ -Fe₂O₃ has a limited distribution, found within 2–3 cm of the sample surface. Furthermore, the viability of this compound as a palaeofield marker has been evaluated in both archaeological and synthetic samples. The results indicate that ϵ -Fe₂O₃ is able to register the direction of the magnetic field. Linear palaeointensity plots have been obtained in synthetic samples, although the value of the palaeofield could be, sometimes, overestimated.

1. Introduction

Unanswered questions arise when the ϵ -Fe₂O₃ polymorph is studied in the context of the optimal natural or artificial environments that promote its growth and chemical stability. The discovery of this iron III oxide polymorph was made in 1934 by Forestier and Guiot-Guillain (1934), although the correct determination of its orthorhombic crystal structure, with lattice parameters $a = 5.095 \text{ \AA}$, $b = 8.789 \text{ \AA}$ and $c = 9.437 \text{ \AA}$, was not made until 1998 (Tronc et al., 1998). Regarding its magnetic properties, this phase has a coercive field of 2 T in its single magnetic domain state and a saturation magnetization of 15–20 emu g⁻¹ at room temperature (Zboril et al., 2002; Popovici et al., 2004; Gich et al., 2005; Tucek et al., 2010). The development of sensitive micrometric structural characterization techniques such as confocal Raman spectroscopy (CRS) enabled a better understanding of the nature and formation of this polymorph (Dejoie et al., 2014; Lopez-

Sanchez et al., 2016a, 2016b, 2017a, 2017b, 2019).

In relation to archaeomagnetism, the existence of a stable high-coercivity magnetic compound with a Curie temperature close to 200–250 °C was discovered by McIntosh et al. (2007). This phase, named by the authors as HCSLT (high coercivity, thermally stable, and low unblocking temperature), was found in numerous archaeological sites around the world (McIntosh et al., 2011). Combining CRS and magnetic characterization, HCSLT was shown to be a ϵ -Fe₂O₃ phase substituted with cation substitutions (probably Ti and/or Al atoms) (Lopez-Sanchez et al., 2017a). In addition, a nanomineral called luogufengite with a giant coercive field was recently discovered in Late Pleistocene basalt scoriae (Xu et al., 2017). This mineral has structural analogies with ϵ -Fe₂O₃ with Al, Ti and Mg substitutions (Xu et al., 2017; Lee and Xu, 2018; Lee et al., 2019). Therefore, natural and mankind alteration of more common minerals provide suitable scenarios for the formation of this polymorph.

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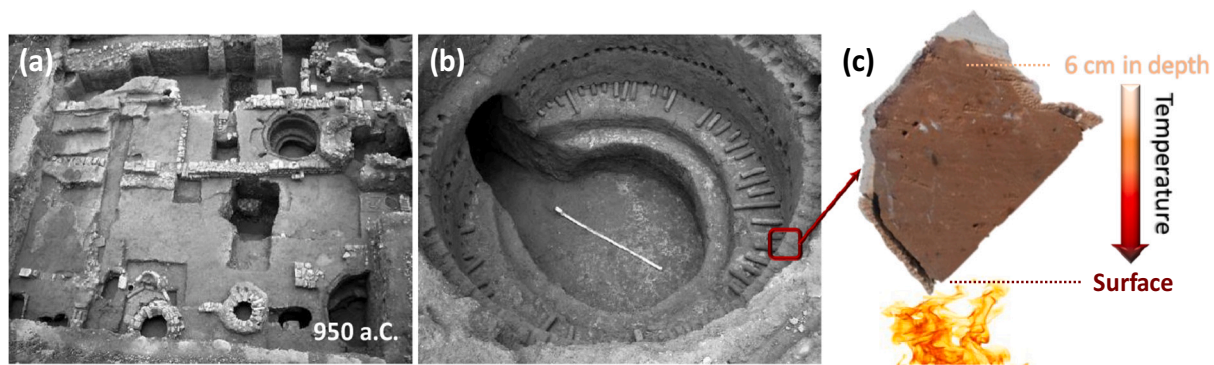


Fig. 1. (a) Image of the Las Ollerías Islamic pottery complex (Molina and Salinas, 2013) and (b) kiln COO62. (c) Baked clay block COO62.5 chosen for magnetic and CRS analyses.

Although ϵ -Fe₂O₃ is a thermally stable phase that can contribute to the natural remanence of archaeological materials, its magnetic properties are quite different to other more common phases such as magnetite (Fe₃O₄) or maghemite (γ -Fe₂O₃). For example, the Cisowski R-ratio (Cisowski, 1981) of samples containing ϵ -Fe₂O₃ is comprised between 0.3 and 0.4 (McIntosh et al., 2007, 2011). R-ratio values < 0.5 may indicate a non-ideal single domain (SD) behaviour which complicates palaeointensity determinations since the demagnetization process requires lower energy than magnetization (Cisowski, 1981). Therefore, one important question that remains open is whether this new phase can adequately record the past geomagnetic field. In this sense, several studies have been performed to examine its suitability as a palaeointensity recorder. For example, bricks containing ϵ -Fe₂O₃ from the beginning of the 20th century (CE) was investigated by Donadini et al. (2007), who obtained palaeointensities in agreement with expected observatory values. Linear Arai plots were also obtained from Neolithic remains, most of them containing ϵ -Fe₂O₃ in variable amounts (Kostadinova-Avramova et al., 2019). However, it was observed in a compilation carried out by McIntosh et al. (2011) that ϵ -Fe₂O₃ was sometimes able to carry a stable direction with ideal palaeointensity behaviour and other times not. Furthermore, in some baked clay samples where ϵ -Fe₂O₃ was identified and useful palaeointensity values have been often obtained only above the Curie temperature of this material, for example beginning from 250 °C (site COO, Molina-Cardin et al., 2018). In this context, experiments on synthetic samples can help to clarify the palaeomagnetic behaviour of this hard magnetic phase in archaeological samples.

Typical sizes of synthetic ϵ -Fe₂O₃ samples do not exceed 100 nm, mainly because of the low surface energy (Machala et al., 2011). For its synthesis, the employment of a mesoporous matrix comes in to play, where iron oxide nanoparticles remain embedded without excessive agglomeration. This system promotes the formation of metastable phases such as ϵ -Fe₂O₃ at high temperatures (Gich et al., 2005, 2006; Ohkoshi et al., 2007, 2015, 2017; Tadic et al., 2008, 2017, 2020; Namai and Ohkoshi, 2011, 2018; Nikolic et al., 2017a, 2017b; Wang et al., 2017; Ma et al., 2019, 2020). These chemical synthetic routes are based on a silica matrix, capable of withstanding high densification temperatures (> 900 °C) and the Si atoms do not interact with the Fe atoms in an oxidizing atmosphere (Chaneac et al., 1995). In an uncontrolled way, the same processes might occur in natural and archaeological high temperature environments. This point is essential since the ϵ -Fe₂O₃ phase can have a strong influence in the magnetic properties of non-synthetic samples (Lopez-Sanchez et al., 2017a; McIntosh et al., 2007, 2011). As with synthetic methods, specific conditions of temperature, particle concentration and reaction atmosphere must be fulfilled for the formation of this elusive polymorph (Machala et al., 2011).

The first objective of this work is to carry out localized structural and magnetic studies to determine the most likely place where ϵ -Fe₂O₃ can be found within heated archaeological materials. For this purpose,

a cross-section has been made through a baked clay block from an Islamic pottery kiln (COO62, Molina-Cardin et al., 2018), where ϵ -Fe₂O₃ was previously identified (Lopez-Sanchez et al., 2017a). The second objective deals with the ability of this material to properly record both the direction and intensity of the geomagnetic field. To test this, two types of analysis have been carried out. In a first analysis, archaeological samples containing ϵ -Fe₂O₃ from the sites COO62, COO88, COO90 and COO94 (Molina-Cardin et al., 2018) have been reanalyzed to determine if the direction and intensity of the geomagnetic field has been adequately recorded within the blocking temperature of this phase. In a second analysis, synthetic samples rich in ϵ -Fe₂O₃ phase have been synthesized and palaeointensity experiments have been carried out. Therefore, this work not only provides the basis for a local and effective identification of the ϵ -Fe₂O₃ phase in archaeological samples, but also evaluates its ability to properly record the geomagnetic field.

2. Archaeological samples

Archaeological samples have been taken from several kilns (COO structures) belonging to an Islamic pottery complex: Las Ollerías site located in Córdoba, southern Spain (Fig. 1a–b). Las Ollerías was discovered during the construction of new buildings at Las Ollerías avenue (Córdoba city). Excavations revealed 17 pottery kilns, dated by archaeological remains from 950 CE up to 1200 CE (Molina and Salinas, 2013). Four combustion structures (COO62, COO88, COO90 and COO94) were selected to reanalyze previous palaeomagnetic results obtained by Molina-Cardin et al. (2018). COO62 corresponds to a 2.5 m diameter circular kiln ascribed to the (1200 ± 100) CE period. A first Raman identification of ϵ -Fe₂O₃ was obtained with a sample from this structure (Lopez-Sanchez et al., 2017a). Therefore, the COO62 kiln was chosen to perform a Raman profile study to reconstruct the distribution of ϵ -Fe₂O₃ within a lateral block of baked clay. For this purpose, specimens have been taken along a 6 cm depth profile within the baked clay block COO62.5, parallel to the expected temperature gradient (Fig. 1c).

Additional samples were taken from the COO88 structure corresponding to a circular oven dated at (1200 ± 100) CE which overlays an older structure, COO90, a circular table oven dated (950 ± 50) CE. Finally, COO94 consists of a well-preserved circular table oven with a diameter of 1.8 m with an age of (1200 ± 100) CE. New palaeointensity results of the four COO structures are presented in Section 5.2.

3. Sol-gel synthesis of ϵ -Fe₂O₃ particles

Synthetic ϵ -Fe₂O₃ samples have been obtained in powder form by the sol-gel method, following a chemical route adding glycerol (polyalcohol) as a steric agent (Lopez-Sanchez et al., 2017b, 2019). This

approach is intended to simulate the environmental conditions in which the ε -Fe₂O₃ polymorph might have formed in archaeological samples. The following points are crucial to obtain a successful synthesis: i) the use of a mesoporous silica matrix, and ii) densification treatments performed at temperatures above 960 °C (Lopez-Sanchez et al., 2016a, 2016b). Specifically, a hydroethanolic solution was prepared adding iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O, Sigma-Aldrich > 98%), barium nitrate (Ba(NO₃)₂, Sigma-Aldrich > 98%), and tetraethyl orthosilicate (SiC₈H₂₀O₄, Sigma-Aldrich > 98%) in a 1:0.02:1 molar ratio. In addition, a few drops of glycerol (Sigma-Aldrich > 99.5%) were added to promote hydrolysis/polycondensation processes. After several days under a vigorous stirring at room temperature, the resulting sol was dried for two weeks at 60 °C. Final densification has been performed at high temperatures in air. Following this synthetic route, samples rich in ε -Fe₂O₃ with particle sizes below 14 nm were obtained at temperatures close to 960 °C (Lopez-Sanchez et al., 2017b). As observed in other works (Dejoie et al., 2014; Lopez-Sanchez et al., 2017a; Gurylev et al., 2019), ε -Fe₂O₃ phases detected in archaeological samples are much larger (few micrometers) and surrounded by a large amount of hematite, the most chemically stable iron III oxide (Cornell and Schwertmann, 2003). Therefore, a densification temperature of 1100 °C for 3 h was used to promote larger ε -Fe₂O₃ and hematite polymorph sizes (Ohkoshi et al., 2015).

4. Experimental methods

The crystal structure and compositional properties of the archaeological samples were examined by CRS and X-ray diffraction (XRD). XRD pattern was obtained with a PANalytical X-ray diffractometer at the CAI de Técnicas Físicas of the Complutense University of Madrid, using Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation in a Bragg-Brentano configuration. Raman spectra were acquired using a confocal Raman microscope (ALPHA 300RA, WITEC, at the Institute of Ceramics and Glass-Spanish National Research Council (ICV-CSIC)), with a Nd:YAG laser source (532 nm) in p-polarization. The optical resolution of the system is about $\sim 200 \text{ nm}$ in the lateral axes and $\sim 500 \text{ nm}$ in the vertical axis. The spectral resolution of the system is 0.02 cm^{-1} . Spectra were acquired in the spectral range $0\text{--}3600 \text{ cm}^{-1}$ by using a 600 g mm^{-1} grating. Samples were placed on a piezo-driven scan platform with a positioning accuracy of 4 nm in the lateral direction and 0.5 nm in the vertical direction. Raman measurements were performed at room temperature, working with a $100\times$ objective with a numerical aperture of 0.95. The output laser power chosen was set at 0.7 mW in order to avoid undesirable phase transformations induced by the laser. Data were processed and analyzed using the WITEC Project Plus software. To avoid fluorescence effects caused by large differences between focal planes, these samples were embedded in epoxy resin and polished before being measured with the CRS system. This procedure presents a significant advantage since it allows the possibility of studying powder samples as a thin film. The areas of particular interest are localized, which allows to return to the same point afterward if necessary.

Magnetic properties of both archaeological and synthetic samples were studied with a vibrating sample magnetometer attached to a physical property measurement system (PPMS Model 6000 controller – Quantum Design) at the Applied Magnetism Institute (IMA-UCM-ADIF). Magnetic hysteresis loops were obtained at room temperature with a maximum applied magnetic field of 5 T.

The behaviour of the synthetic ε -Fe₂O₃ powder used for palaeointensity determinations was evaluated by Thellier-Thellier experiments (referred to as TH hereafter) at the Palaeomagnetism Laboratory of the Complutense University of Madrid using a MMTDSC (Magnetic Measurements) oven and a superconducting magnetometer (2G). To avoid physical rotation of the particles when a magnetic field is externally applied, the synthetic powder was embedded in epoxy resin. Palaeointensity experiments were carried out using the following steps: i) acquisition of a controlled thermal remanent magnetization

(TRM) by heating the synthetic samples up to 235 °C (close to the melting point of epoxy) in a 50 μT field applied along the Z axis for 45 min; ii) thermal demagnetization following the TH demagnetization protocol (Thellier and Thellier, 1959), including partial TRM (pTRM) checks and anisotropy correction. The heating steps were of 50 °C up to 200 °C followed by steps of 5 °C from 200 °C up to 235 °C. The anisotropy determination of the TRM tensor was calculated at 230 °C following the method described by Veitch et al. (1984) and Chauvin et al. (2000).

COO specimens from four combustion structures (see Section 2 for details) were sampled using a plaster of Paris and oriented with magnetic and sun compasses. Samples were cut with a circular saw into 2 cm cubic specimens. Stepwise alternating field (AF) as well as thermal demagnetizations were conducted on different sets of specimens from every structure. The TH procedure included pTRM checks and anisotropy experiments. A variety of rock magnetic experiments were carried out, including hysteresis loops, isothermal remanent magnetization (IRM) acquisition and back-field demagnetization, thermomagnetic curves and thermal demagnetization of orthogonal IRMs (Lowrie, 1990), in order to demonstrate the presence of ε -Fe₂O₃. All experiments were conducted in the Palaeomagnetism Laboratory of the Complutense University of Madrid.

5. Results

5.1. Magnetic hysteresis loops and Raman characterization along a depth profile

The magnetic and Raman results corresponding to the top, intermediate and bottom region of the COO62.5 depth profile are represented in Fig. 2. Saturation magnetization and coercivity values are listed in Table 1. In the top region, which corresponds to the surface closest to the firing source, magnetic properties are dominated by a high-remnant, magnetically soft phase compatible with maghemite or magnetite (Dunlop and Ozdemir, 1997; Cornell and Schwertmann, 2003) dominates the magnetic behaviour (Fig. 2a). A representative optical image of the sample is shown in Fig. 2b along with a Raman intensity XY image calculated from the yellow square (Fig. 2c). For clarity, only Raman bands corresponding to magnetite (from 693 cm^{-1} to 735 cm^{-1} in light blue) and hematite (from 1300 cm^{-1} to 1400 cm^{-1} in red) are integrated. The average Raman spectra of the studied areas are shown in Fig. 2d. CRS data also collected signal of large quartz crystals and relatively small rutile-TiO₂ phase aggregates (not shown).

Although magnetite and maghemite have the same crystalline structure and closely related lattice parameters (Cornell and Schwertmann, 2003), it is possible to discern between them through CRS experiments. Specifically, the position of the most intense Raman band of magnetite is around 690 cm^{-1} and, in the case of maghemite, around 720 cm^{-1} (Jubb and Allen, 2010). Moreover, the two neighbouring vibrational modes going towards lower wavenumbers have the same shape, but different Raman frequencies. For example, the first mode is found at around 550 cm^{-1} in magnetite and at around 500 cm^{-1} in maghemite (Jubb and Allen, 2010). Additionally, second order harmonics/overtone (from $\sim 800 \text{ cm}^{-1}$) are practically absent while contributing significantly to the Raman spectrum of maghemite (from 1100 cm^{-1} to 1450 cm^{-1} approximately) (de Faria et al., 1997). Taking into account these features, the abovementioned Raman characteristics for magnetite are observed in the top region below 1100 cm^{-1} . Higher Raman frequencies are possibly contaminated by hematite (Fig. 2d). Accordingly, the low coercivity magnetic phase shown in Fig. 2a is identified as magnetite. The observed magnetic mineralogy might be explained by the low-oxygen environment produced by combustion, which promotes the formation of magnetite instead of maghemite (more oxidized) near the wall surface (Parkinson, 2016).

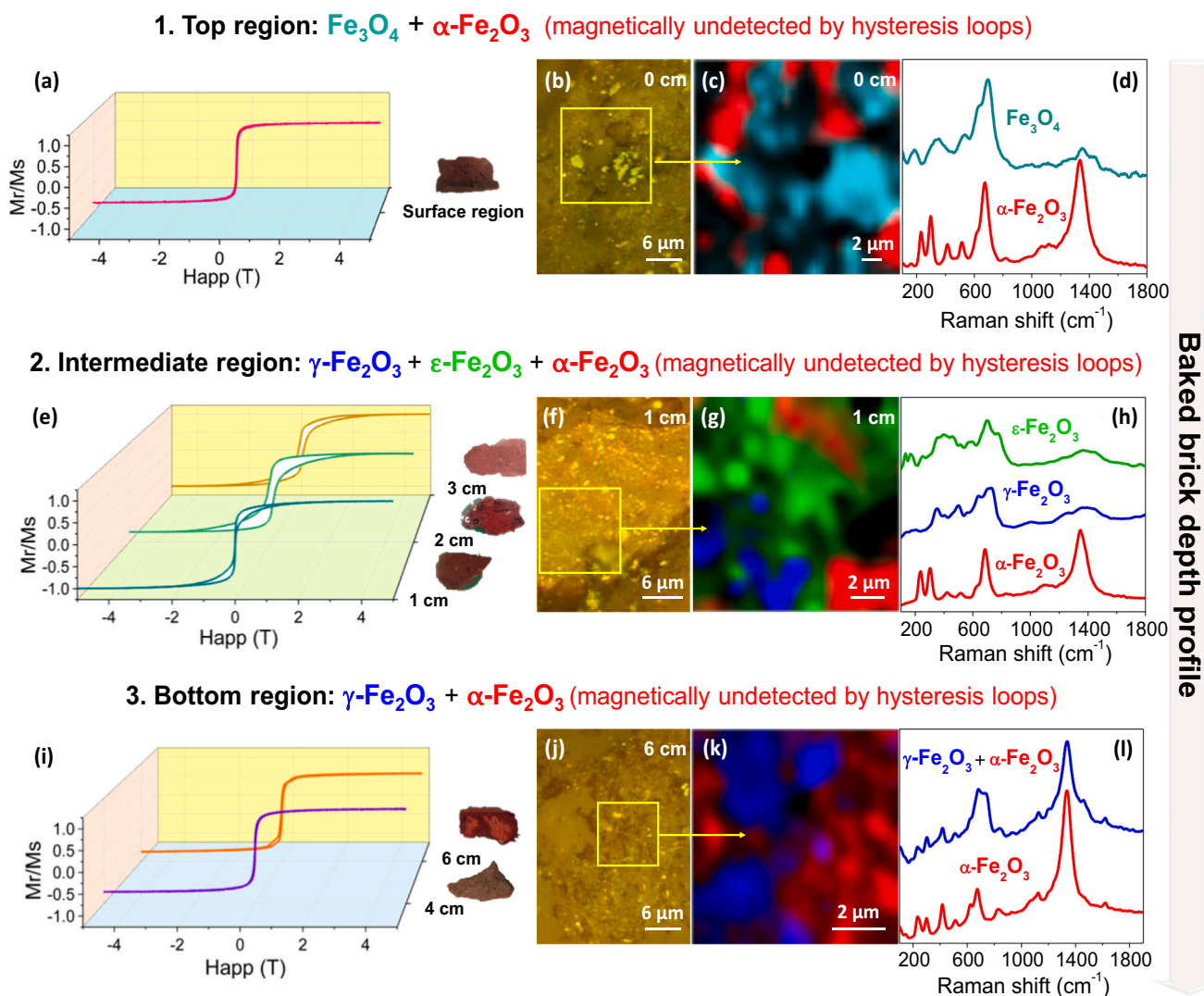


Fig. 2. Magnetic and Raman characterization of the top, intermediate and bottom regions corresponding to the depth profile performed in sample COO62.5: Magnetic hysteresis loops obtained at room temperature for (a) surface region, (e) 1–3 cm in depth and (i) 4–6 cm in depth; Optical micrographs from representative regions with magnetic signature of (b) 0 cm in depth, (f) 1 cm in depth and (j) 6 cm in depth; (c, g and k) In-plane Raman intensity images obtained from mapping the area indicated with a yellow square in figures b, f and j. Magnetite (light blue), hematite (red), $\varepsilon\text{-Fe}_2\text{O}_3$ (green) and maghemite (dark blue) are detected; (d, h and l) Average Raman spectra calculated from in-plane Raman images (figures c, g and k). Note that $\alpha\text{-Fe}_2\text{O}_3$ is not detectable by magnetic measurements in these samples, most probably due to its low saturation magnetization, but is easily observed from CRS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Saturation magnetization and coercivity values related to samples chosen from surface to 6 cm in depth. The colors representing each depth match their respective colors shown in the magnetic hysteresis loops in Fig. 2a, e and i.

Depth profile sample	Saturation magnetization ($\text{A m}^2 \text{kg}^{-1}$)	Coercivity (mT)
Surface	0.10	5
1 cm	0.11	7
2 cm	0.67	124
3 cm	0.31	100
4 cm	0.20	1
6 cm	0.18	15

It is important to note that the presence of hematite, confirmed by CRS, is not directly visible by the magnetic hysteresis loops owing to its low saturation magnetization of $0.3 \text{ A m}^2 \text{kg}^{-1}$ (Morrish, 1995; Cornell and Schwertmann, 2003), one order of magnitude smaller than that of

magnetite ($92\text{--}100 \text{ A m}^2 \text{kg}^{-1}$) (Dunlop and Ozdemir, 1997; Cornell and Schwertmann, 2003).

Going into the intermediate region between 1 and 3 cm, the magnetic hysteresis loops become wasp-waisted (Fig. 2e), as observed in archaeological samples containing $\varepsilon\text{-Fe}_2\text{O}_3$ (McIntosh et al., 2007, 2011; Lopez-Sanchez et al., 2017a; Molina-Cardin et al., 2018; Calvo-Rathert et al., 2019; Kostadinova-Avramova et al., 2019; Lee et al., 2019; Kostrov et al., 2020). The wasp-waisted hysteresis shape is due to two distinct magnetic populations with highly contrasting coercivities (Fig. 2e): (1) a low coercivity, high remanence contribution, and (2) a high coercivity, low remanence contribution (Tauxe et al., 1996). Raman mappings detected large areas covered by hematite (not shown here), along with localized maghemite and $\varepsilon\text{-Fe}_2\text{O}_3$ aggregates, as shown in a representative area located at 1 cm from the heat source (Fig. 2f–g). Apart from these minerals, large areas covered by quartz, pseudobrookite (Fe_2TiO_5) and rutile aggregates are also detected (not shown here). The average Raman spectra obtained by integrating non-overlapping bands are displayed in Fig. 2h. These bands range from

1300 cm^{-1} to 1400 cm^{-1} for hematite, 320 cm^{-1} to 400 cm^{-1} for maghemite and 100 cm^{-1} to 200 cm^{-1} for $\epsilon\text{-Fe}_2\text{O}_3$. Combining both magnetic and Raman analyses at the three depths, the low coercivity, high remanence contribution is attributed to maghemite and the high coercivity, low remanence contribution is attributed to the $\epsilon\text{-Fe}_2\text{O}_3$ phase (Fig. 2e). A pronounced widening of the magnetic hysteresis loop is observed at 2 cm in depth, accompanied by an increase in coercivity from 7 mT at 1 cm to 124 mT at 2 cm in depth. This would indicate that a higher amount of $\epsilon\text{-Fe}_2\text{O}_3$ is encountered at a depth of 2 cm. Possible magnetic contributions from hematite would not be distinguishable from the hysteresis loop, since $\epsilon\text{-Fe}_2\text{O}_3$ possess the high coercivity responsible for hysteresis opening at large fields.

The magnetic properties of the bottom region between 4 and 6 cm depth indicates the predominance of a low coercivity, high-remnance magnetic phase (Fig. 2i). Apart from hematite (detected by CRS but not in the magnetic hysteresis loops), the only magnetic compound detected by CRS is maghemite, which has been identified from the peaks at 690 cm^{-1} to 750 cm^{-1} and at 1400 cm^{-1} to 1500 cm^{-1} in the spectral range (Fig. 2l). This maghemite is found to be mixed with hematite. Raman mapping also reveals anatase-TiO₂ aggregates and large areas covered by quartz and hematite (not shown here). The formation of anatase-TiO₂ aggregates requires lower temperatures than rutile-TiO₂ (detected in the top region), which might be indicative for the lower temperatures reached by the bottom region, compared to the surface (Hanaor and Sorrell, 2011).

5.2. Reevaluation of Las Ollerías archaeomagnetic results

Palaeointensity reevaluations have been carried out in four ceramic hearths (COO62, COO88, COO90 and COO94) to check the directions and intensities recorded by the $\epsilon\text{-Fe}_2\text{O}_3$ phase and compare them with the values obtained from the other magnetic phases (Fig. 3 and Table 2). These specimens contain different amounts of $\epsilon\text{-Fe}_2\text{O}_3$. They were analyzed previously by Molina-Cardin et al. (2018), by considering only the NRM fraction that demagnetize between 250 and 600 °C, above the $\epsilon\text{-Fe}_2\text{O}_3$ Curie temperature of 227 °C. In this re-analysis of previous data, the NRM range has been extended to include the fraction between 100 and 250 °C unblocking range.

Single-specimen directions, together with the mean and error for each structure, are shown in Fig. 3a–d (cyan and dark blue lines) and they are summarized in Table 2. Many of the specimens subjected to alternating field treatment were not fully demagnetized at a maximum applied field of 100 mT (Fig. 3e, dark blue line). The residual NRM can be ascribed to the $\epsilon\text{-Fe}_2\text{O}_3$ phase. Based on this, specimens that at the end of the demagnetization process kept more than 10% of their initial natural remanent magnetization (NRM) were selected for analysis. NRM directions were calculated between 10 and 100 mT (taken to be free of important $\epsilon\text{-Fe}_2\text{O}_3$ contribution) and compared to the direction calculated from 100 mT to the origin of the demagnetization plot (which should mainly be due to $\epsilon\text{-Fe}_2\text{O}_3$). These two groups of directions were statistically indistinguishable.

Complete isolation of $\epsilon\text{-Fe}_2\text{O}_3$ contribution in specimens subjected to TH treatment (Thellier and Thellier, 1959), is not fully possible, since its unblocking temperature spectrum overlaps with that of other remanence carriers (Fig. 3f). The determination of a well-constrained direction is difficult because only few temperature steps are available for calculations and the low blocking temperature range might be affected by viscous overprints. Therefore, this study is focused on the regions where NRM intensity drops significantly between about 200 and 250 °C, close to the Curie temperature of $\epsilon\text{-Fe}_2\text{O}_3$ (Fig. 3f). Direction recorded by $\epsilon\text{-Fe}_2\text{O}_3$ and other phases are calculated using the 100–250 and 250–575 °C temperature ranges. The resulting directions obtained for the $\epsilon\text{-Fe}_2\text{O}_3$ contribution are more scattered than those obtained from AF demagnetization, due to the small fraction of NRM considered and possibly due to magnetically soft, viscous components, resulting in large α_{95} values. Nevertheless, the directions from the $\epsilon\text{-Fe}_2\text{O}_3$

and the other magnetic phases are still consistent (magenta and yellow lines in Fig. 3a, d). The detailed data are presented in Table 2. In order to allow comparison with the AF results, no anisotropy corrections have been made. However, these corrections are small (Molina-Cardin et al., 2018). In Fig. 3a–d, the joint direction of the isolated $\epsilon\text{-Fe}_2\text{O}_3$ phase from both methods (AF high and TH low components, red line) and the joint direction of the other magnetic phases (AF low and TH high, green line) are shown. Based on the similarity in the recorded directions, $\epsilon\text{-Fe}_2\text{O}_3$ formed during firing in archaeological materials is capable to acquire and hold a remanent magnetization in the field direction.

To address the palaeointensity determinations, the TH specimens are selected with the same criteria used for the directional calculations. Accordingly, specimens without an important $\epsilon\text{-Fe}_2\text{O}_3$ contribution have been ruled out (Fig. 4c1–2) because no reliable palaeointensity results from this low temperature component have been obtained. It is important to point out that an important fraction of the ferrimagnetic component might also be demagnetized in the low temperature range of $\epsilon\text{-Fe}_2\text{O}_3$ unblocking (100–250 °C, magenta color), as demonstrated by the results of a Lowrie test (Fig. 4a2). Therefore, the palaeointensity behaviour of $\epsilon\text{-Fe}_2\text{O}_3$ is best evaluated for COO62 and COO94, where the $\epsilon\text{-Fe}_2\text{O}_3$ contribution is higher. Selected specimens from these samples exhibit Arai plots with a linear trend (Fig. 4b1–2) and their intensities from both $\epsilon\text{-Fe}_2\text{O}_3$ and other magnetic phases were statistically compatible. Further statements cannot be obtained since the comparison is based on a low number of specimens and some errors are quite large even when all specimens are used to calculate the mean value for non- ϵ phases (Fig. 4a1, Table 3).

5.3. Structural and magnetic remanence results performed in synthetic $\epsilon\text{-Fe}_2\text{O}_3$

In this section, the possibility of carrying out palaeomagnetic studies on synthetic samples rich in $\epsilon\text{-Fe}_2\text{O}_3$ phase is evaluated. For this purpose, hematite particles and a silica matrix have been synthesized using the recipe described in Section 2 (Lopez-Sanchez et al., 2017b, 2019), simulating a certain degree of heterogeneity as found in archaeological samples. The synthesized samples do not contain $\gamma\text{-Fe}_2\text{O}_3$, because of the elevated densification temperature of 1100 °C (Ohkoshi et al., 2015). Fig. 5a shows XRD pattern with diffraction peaks corresponding to two silica polymorphs α -quartz (Gordon and Leroy, 1963) and β -cristobalite (Demuth et al., 1999), as well as $\epsilon\text{-Fe}_2\text{O}_3$ (Kelm and Mader, 2005) and hematite (Wolska and Schwertmann, 1989). Considering the Scherrer relation (Scherrer, 1912), the average crystal domain sizes are ($\sim 32 \pm 1$) nm and ($\sim 50 \pm 1$) nm for $\epsilon\text{-Fe}_2\text{O}_3$ and hematite respectively. For $\epsilon\text{-Fe}_2\text{O}_3$, the coercivity has been reported to be 2.0 T at room temperature and a stable magnetization is expected (Ohkoshi et al., 2015). The average crystal domain size is relatively large compared to those commonly obtained in synthetic samples (Lopez-Sanchez et al., 2017b) and it might result in particle agglomerates as found in the intermediate region of the COO62.5 sample (Fig. 2e–h).

The averages of the single Raman spectra obtained in the areas indicated by crosses in Fig. 5b show both synthetic $\epsilon\text{-Fe}_2\text{O}_3$ and hematite Raman vibrational modes (Fig. 5c) (Lopez-Sanchez et al., 2016a, 2016b, 2017b). The shape of these spectra resembles those displayed in Fig. 2h, with variations in the number of the Raman modes detected and their positions in frequency probably due to substitutions by other elements such as Ti, Al and/or Mg present in the COO samples (Lopez-Sanchez et al., 2017a). In addition, the hematite Raman signature in the synthetic case overlaps the $\epsilon\text{-Fe}_2\text{O}_3$ Raman spectrum at around 230 cm^{-1} , 300 cm^{-1} and 1320 cm^{-1} (Fig. 5c). Therefore, $\epsilon\text{-Fe}_2\text{O}_3$ aggregates could have smaller sizes and they could be more mixed with hematite than in the case of the archaeological samples (Fig. 2g, h).

Looking at the magnetic properties, the hysteresis loop shown in Fig. 5d (light green line) shows the typical characteristics of $\epsilon\text{-Fe}_2\text{O}_3$

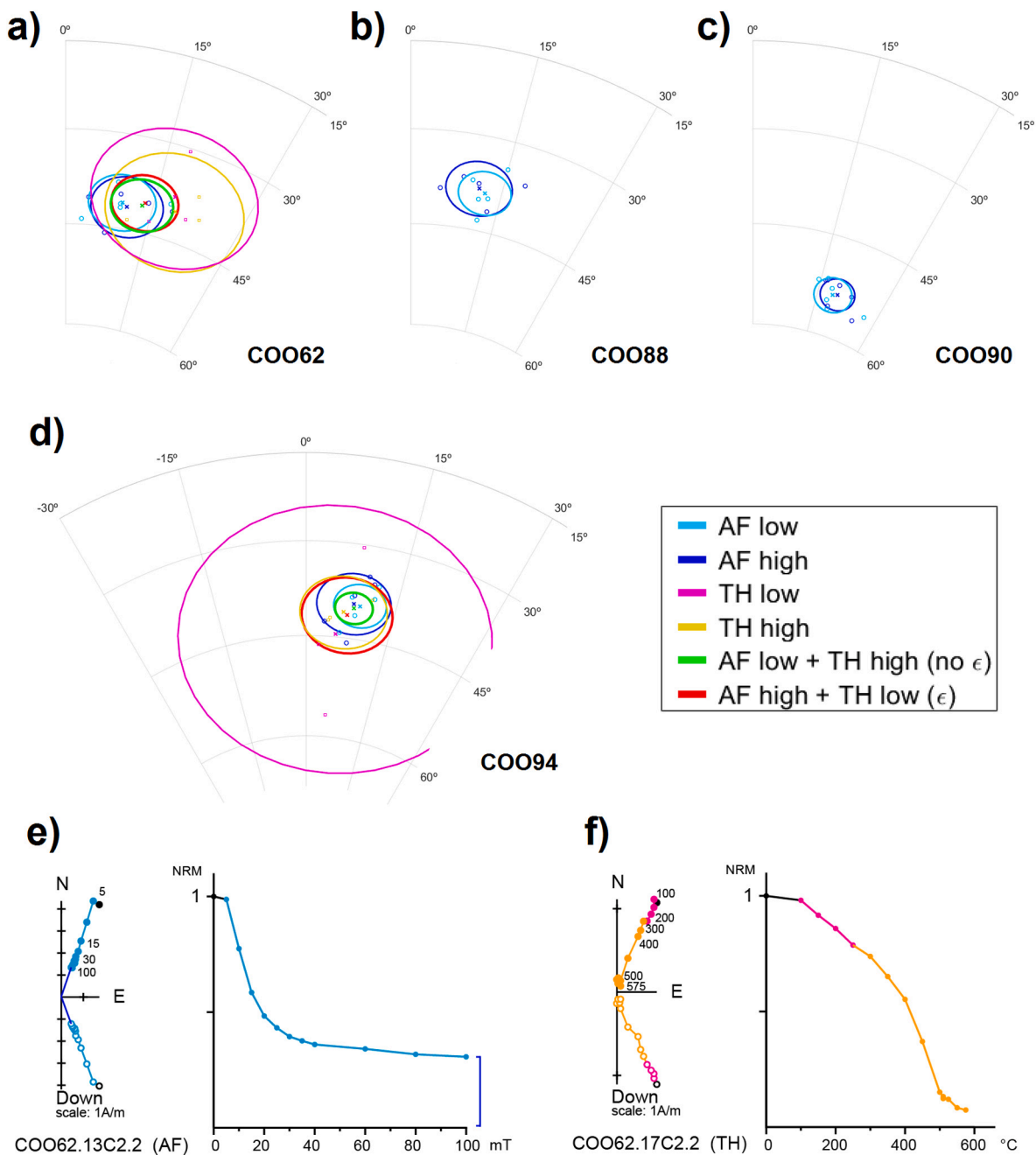


Fig. 3. Panels a–d: comparison between directions calculated from different intervals (see text for details) of alternating field (AF) and thermal Thellier-type (TH) demagnetizations. Specimen (open dots) and mean values (crosses) with α_{95} limit (circles) are represented. Where both AF and TH directions are available, also two joint mean and α_{95} are plotted for the ϵ -Fe₂O₃ (AF high and TH low) and the other magnetic phases (AF low and TH high). Panels e–f: examples of Zijderveld diagrams for AF and thermal demagnetizations as a function of the coercive field and temperature respectively. The same color legend is used throughout the figure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(Gich et al., 2005; Machala et al., 2011). It is a magnetically hard phase that does not reach saturation even at 5 T (Lopez-Sanchez et al., 2016b). Two magnetic populations were clearly noticed in the derivative of the hysteresis curve displayed in Fig. 5d (dark green line), which exhibited a well-defined peak at 0.19 T (H_{c1}) and two bumps at around 2.23 T (H_{c2}). These features reveal the heterogeneity of the particle size distribution obtained, since only the ϵ -Fe₂O₃ particles > 30 nm in size have a coercive field of ~2 T (Ohkoshi et al., 2015). Coercivities below this particle size are significantly reduced and the magnetic hysteresis loop obtained results in a combination of magnetic responses coming from the different particle sizes (Ohkoshi et al., 2015). The contribution to the H_{c1} coercivity population of traces of maghemite present below

the detection limits of XRD and CRS, cannot be excluded due to its high saturation magnetization (60–80 A m² kg⁻¹, Cornell and Schwertmann, 2003). However, the coercivity values of maghemite are typically confined below 64 mT (Cornell and Schwertmann, 2003) and, therefore, the soft magnetic population (H_{c1}) could be attributed to other magnetic minority phase or ϵ -Fe₂O₃ uniquely.

Next, the reliability of synthetic ϵ -Fe₂O₃ (EPSsyn) as a palaeomagnetic marker was studied by imparting a TRM along the sample Z axis. Due to the epoxy resin in which the synthetic ϵ -Fe₂O₃ particles were embedded, this experiment could not be extended to temperatures higher than 235 °C. Above this temperature, the epoxy resin can combust and the sample destroyed. After TRM acquisition, EPSsyn exhibited

Table 2

Mean directions calculated from different intervals of AF and thermal demagnetizations. N, number of specimens considered in the mean; D_m , mean declination; I_m , mean inclination; α_{95} , semiangle of confidence at 95%; k, precision parameter; orig, origin of demagnetization plot.

ϵ -Fe ₂ O ₃ (AF high or thermal low)						Other magnetic phases (AF low or thermal high)					
Interval	N	D_m (°)	I_m (°)	α_{95} (°)	k	Interval	N	D_m (°)	I_m (°)	α_{95} (°)	k
COO62											
AF (100 mT - orig)	5	10.7	41.5	4.7	264	AF (5–100 mT)	5	9.7	41.0	4.4	306
TH (100 - 200 °C)	3	18.0	38.2	10.9	130	TH (200–575 °C)	3	18.8	40.3	9.1	184
AF + TH	8	13.5	40.4	4.3	164	AF + TH	8	13.1	40.8	4.1	187
COO88											
AF (100 mT - orig)	5	11.2	38.5	4.3	322	AF (5–100 mT)	5	12.3	39.1	3.4	503
COO90											
AF (100 mT - orig)	6	19.5	53.6	2.4	804	AF (5–100 mT)	6	18.5	53.8	2.6	670
COO94											
AF (100 mT - orig)	5	8.0	39.6	4.8	256	AF (5–100 mT)	5	9.0	39.8	3.4	510
TH (100–200 °C)	3	5.4	44.6	20.7	37	TH (200–575 °C)	3	6.4	41.1	5.7	476
AF + TH	8	7.1	41.5	5.9	89	AF + TH	8	8.1	40.3	2.4	513

The colors in the table correspond to those indicated in the Fig. 3.

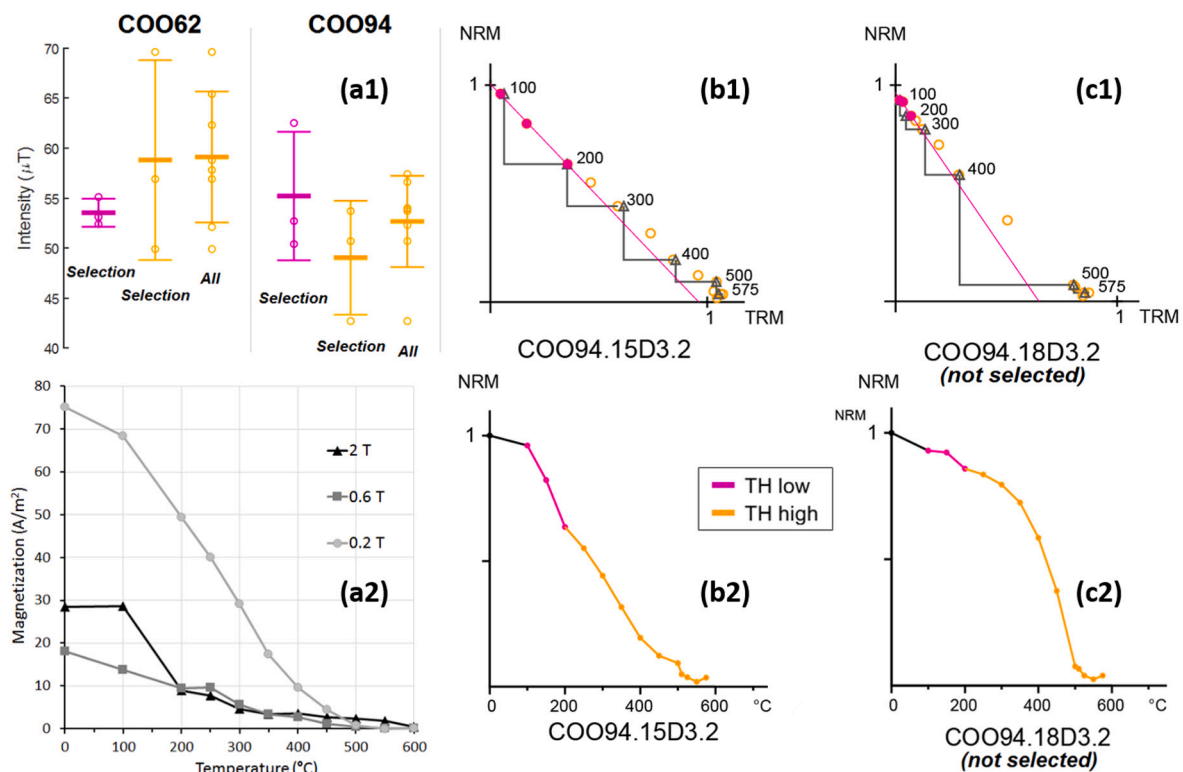


Fig. 4. (a1) Comparison between palaeointensity values obtained from the ϵ -Fe₂O₃ phase (100 °C to 200–250 °C, magenta line) and from the other magnetic phases (200–250 °C to 575 °C, orange line). Specimen (open dots) and mean values (thick marks) with 1 standard deviation (error bars) are plotted. (a2) Lowrie test from a COO94 specimen. An important amount of ϵ -Fe₂O₃ is detected. (b1–2) Arai plot and unblocking temperature spectrum from a specimen accepted for palaeointensity determination by Molina-Cardin et al. (2018). (c1, 2) Arai plot and unblocking temperature spectrum from a specimen rejected by Molina-Cardin et al. (2018) because of the small fraction of NRM associated with ϵ -Fe₂O₃.

Table 3

Mean palaeointensity values derived from different intervals of temperature in TH demagnetizations. T1, T2, temperature interval; N, number of specimens considered in the mean calculation; F, palaeointensity estimation (includes corrections for 2nd component and anisotropy); σ_F , standard deviation.

ϵ -Fe ₂ O ₃ (TH low)				Other magnetic phases (TH high)			
Interval	N	F (μT)	σ_F (μT)	Interval	N	F (μT)	σ_F (μT)
COO62							
TH (100–200 °C)	3	53.5	1.4	TH (200–575 °C)	3	58.8	10.0
				(all specimens)	8	59.1	6.5
COO94							
TH (100–200 °C)	3	55.2	6.4	TH (200–575 °C)	3	49.0	5.7
				(all specimens)	8	52.7	4.6

The colors in the table correspond to those indicated in the Fig. 4.

a remanence (hereby denoted NRM) intensity of 0.03 A m^{-1} and a magnetic susceptibility of 4.22×10^{-4} . Stepwise thermal demagnetization of the TRM showed that the sample started to demagnetize at 215 °C and lost around 50% of its remanence by 235 °C (Fig. 6c). This temperature is in agreement with the unblocking temperature of ϵ -Fe₂O₃ (Popovici et al., 2004). Although the sample is not completely demagnetized at 235 °C, it yielded a direction that is parallel to the applied field (Fig. 6a).

The remaining 50% of the remanence could not be thermally demagnetized and carried a direction that was slightly offset from the sample Z axis (Fig. 6a). Since demagnetization only reached 235 °C,

some of this remanence may be associated with ϵ -Fe₂O₃ above its blocking temperature of around 240 °C (Popovici et al., 2004) or to another magnetic phase. Furthermore, any hematite present in the sample that carries a remanence associated with the sample synthesis will not be fully demagnetized. This may also explain why the undemagnetized component carries a different direction.

In terms of palaeointensity, the EPSsyn sample yielded an Arai plot with a linear trend from 215 °C up to 235 °C and that passed all pTRM checks. As a result, a good quality palaeointensity determination could be made (Fig. 6b), which gave a value of $(62.7 \pm 3.1) \mu\text{T}$. The anisotropy of the TRM ellipsoid was determined at 230 °C, giving rise to a

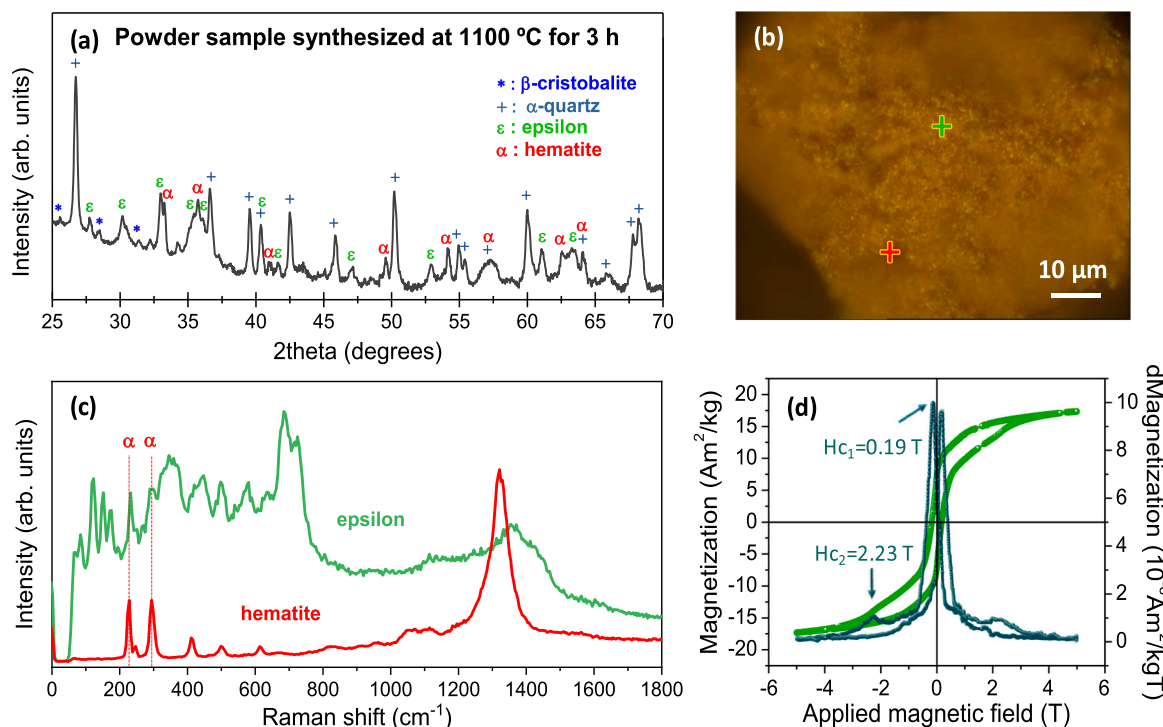


Fig. 5. Structural and magnetic characterization of the powder sample synthesized at 1100 °C for 3 h: (a) XRD pattern, (b) optical micrograph and (c) Raman spectra obtained at 300 K from particle aggregates acquired in ϵ -Fe₂O₃-rich and hematite-rich regions. The green and red crosses of figure b represent the points where the Raman spectra were acquired; (d) Magnetic hysteresis loop and its derivative obtained at 300 K under a maximum applied magnetic field of 5 T. $H_{c1,2}$ indicates the coercivities of the observed magnetic populations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

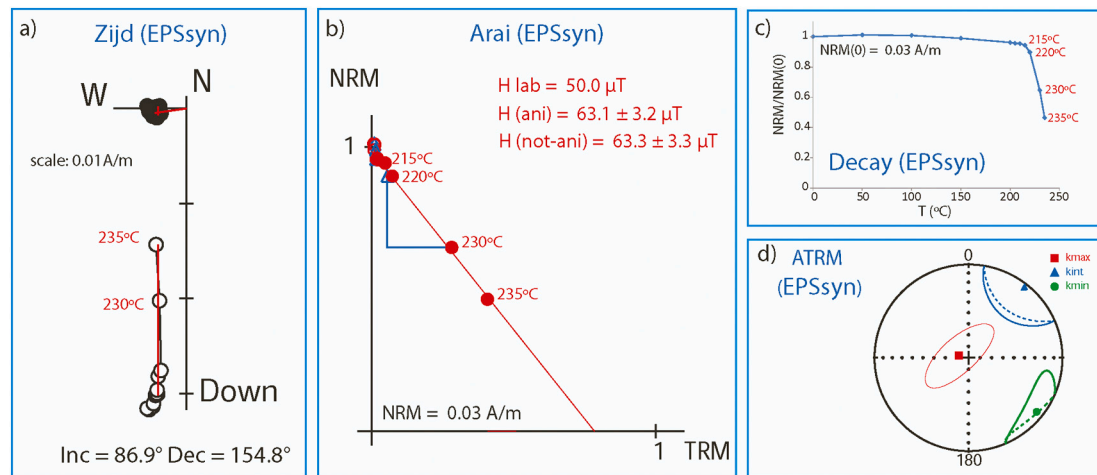


Fig. 6. (a) Orthogonal vector projection of the remanent magnetization during stepwise thermal demagnetization, (b) Arai plot of remanent magnetization remaining (NRM) against thermoremanence acquired (TRM) and palaeointensity determinations (H_{lab} = applied field, $H_{(ani)}/H_{(not-ani)}$ = palaeointensity determination with/without anisotropy correction), (c) remanent magnetization decay curve (NRM_0 = intensity after acquisition of original laboratory-imparted TRM), and (d) anisotropy of thermoremanence (ATRM) ellipsoid calculated at 230 °C.

Jelinek anisotropy factor $P_J = 1.34$, a shape parameter $T = 0.09$, a lination $L = 1.14$ and a foliation $F = 1.17$. All these values lead to a neutral isotropic shape of the thermoremanence ellipsoid (Fig. 6d). After ATRM correction the palaeointensity was found to be $(62.1 \pm 3.0 \mu T)$. Finally, the effect of the second undermagnetized component has also been corrected, giving rise to values of $(63.3 \pm 3.3) \mu T$ and $(63.1 \pm 3.2) \mu T$ before and after ATRM correction.

All of the palaeointensity determinations are higher than the 50 μT field applied during the original TRM acquisition. This difference may be because the ATRM ellipsoid was determined at 230 °C, when only 50% of the NRM is lost. It is more commonly performed in the 60–70% demagnetization range (Chauvin et al., 2000) and the constraint of using epoxy resin could have affected the calculation of the ATRM ellipsoid (Fig. 6d).

6. Discussion

Synthetic routes to grow $\epsilon\text{-Fe}_2\text{O}_3$ are mostly based on the sol-gel method (Gich et al., 2005, 2006; Ohkoshi et al., 2007, 2015, 2017; Tadic et al., 2008, 2017, 2020; Namai and Ohkoshi, 2011, 2018; Nikolic et al., 2017a, 2017b; Wang et al., 2017; Ma et al., 2019, 2020). The iron oxide precursor micelles are embedded in a mesoporous silica matrix to reduce the atomic diffusion and to promote metastable phases when the densification step is carried out at high temperatures in an oxidizing atmosphere (Popovici et al., 2004; Tucek et al., 2010; Machala et al., 2011). These synthetic conditions are subjected to specific molar relations of the chemical precursors employed and several iron oxide polymorphs can be obtained as a function of temperature. In this scenario, $\epsilon\text{-Fe}_2\text{O}_3$ formation requires temperatures above 900 °C, maghemite starts at lower temperatures (> 600 °C) and hematite usually begins above 1100 °C (Ohkoshi et al., 2015).

Broadly speaking, the formation of different iron III oxides (maghemite, $\epsilon\text{-Fe}_2\text{O}_3$ and hematite) in archaeological materials might depend on the temperature reached in the kilns and the aggregation state between particles present in the baked clays. In the case of the COO62.5 sample, the top region might have reached 1200 °C (Tite, 1969) and the temperature in the interior decreased gradually (intermediate and bottom regions). However, nature cannot offer a control over mesoporous matrixes or molar relations of the precursors to achieve single-phase samples. In this sense, archaeological samples would be expected to contain different regions with various concentrations of iron oxide precursor particles. This configuration could result in several

polymorphs upon heating. An evident example is observed in Fig. 2g where $\epsilon\text{-Fe}_2\text{O}_3$ phase, maghemite and hematite (Fig. 2g) are found in regions relatively close to each other. This shows that, along with temperature, particle aggregation also plays an important role in controlling iron oxide formation. A representative scheme of this approach is illustrated in Fig. 7.

On the outermost sample surface facing the heat source, reducing conditions produced by combustion can favour the formation of chemically stable magnetite (Fig. 2a–d). This oxide can be easily mistaken for maghemite because it holds important structural and magnetic analogies (Cornell and Schwertmann, 2003). Using CRS, the two phases can be distinguished, even if cation substitution modifies the shape of their Raman spectra (Fig. 2). Below the most superficial zone a non-reactive environment is expected. Only atomic diffusion between different minerals is produced at high temperatures, which are already oxidized. As a consequence, the occurrence of maghemite is expected to be more prevalent inside the baked clay than magnetite. This is what is observed in the COO samples. This highlights that the selection of the part of the sample used for archaeomagnetic studies is crucial in determining the type of remanence carrier.

In terms of directional studies, $\epsilon\text{-Fe}_2\text{O}_3$ carries the same direction as the other remanence-bearing minerals in the COO samples (Fig. 3, Table 2). This is supported by the experiments carried out on the synthetic EPSsyn sample, which acquired a TRM parallel to the applied magnetic field (Fig. 6). $\epsilon\text{-Fe}_2\text{O}_3$ is thermally stable over the temperature range reached in the TH experiments. For the COO samples, palaeointensity determinations made over the 200–300 °C range were indistinguishable from those made over the rest of the demagnetizing temperature range (Fig. 4, Table 3). Previous studies have also obtained reliable palaeointensities from similar archaeological materials containing $\epsilon\text{-Fe}_2\text{O}_3$ (Donadini et al., 2007; McIntosh et al., 2011; Kostadinova-Avramova et al., 2019). The EPSsyn sample supports these observations, in that it acquires a TRM parallel to the applied magnetic field and yields a linear Arai plot (Fig. 6). However, the resulting palaeointensity determination is not in agreement with the applied field. The sample is thermally demagnetized more easily than it is magnetized and there is an overestimation of the determined palaeointensity. Interestingly, McIntosh et al. (2011) also observed this demagnetization behaviour in AF demagnetization and IRM magnetization experiments in natural samples.

Although $\epsilon\text{-Fe}_2\text{O}_3$ can lead to linear behaviour in the TH experiment, no further firm conclusions can be drawn from the synthetic sample. The main limitation of the experimental results is related to the

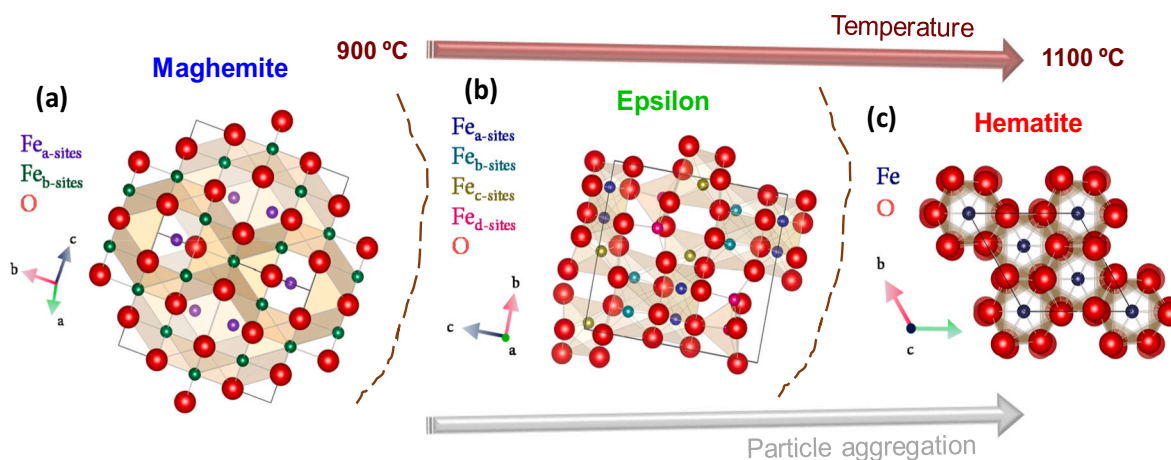


Fig. 7. Illustration of the most thermodynamically stable iron III oxide polymorphs, taking into account temperature and particle aggregation: (a) maghemite, (b) ϵ - Fe_2O_3 and (c) hematite crystalline structures. For maghemite (figure a), ferric ions occupy two non-equivalent positions, a-sites (octahedral coordination) and b-sites (tetrahedral coordination) (Machala et al., 2011). In the case of ϵ - Fe_2O_3 phase (figure b), ferric ions occupy two distorted octahedral positions ($\text{Fe}_{\text{a-sites}}$ and $\text{Fe}_{\text{b-sites}}$), one regular octahedral ($\text{Fe}_{\text{c-sites}}$) and one tetrahedral ($\text{Fe}_{\text{d-sites}}$) (Tronc et al., 1998; Zboril et al., 2002; Machala et al., 2011; Ohkoshi and Tokoro, 2013). For hematite (Figure c), the Fe atoms possess a single cationic position in octahedral coordination (Zboril et al., 2002; Machala et al., 2011). The positions of the Fe atoms are displayed with different color in each polymorph. In contrast, for clarity, the positions of the O atoms are shown in red in the three crystalline structure representations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

maximum temperature imposed by the epoxy resin, which has a melting point close to 235 °C. After thermal demagnetization to 235 °C, around 50% of the remanence remained and the source of this second component has yet to be confirmed. It is possible that it is related to a part of the ϵ - Fe_2O_3 remanence that has not yet been demagnetized, along with a hematite or other magnetic phase contribution. Both of these minerals may have acquired a remanence during the synthesis process and only part if it was remagnetized during the first TRM acquisition.

In COO samples, magnetic experiments and Raman data confirm the presence of ϵ - Fe_2O_3 . In these archaeological materials, a ferromagnetic fraction is frequently demagnetized along with the ϵ - Fe_2O_3 phase (Molina-Cardin et al., 2018). Furthermore, viscous components or other unstable magnetic phases may be present at low temperatures, masking the contribution of ϵ - Fe_2O_3 . Additional experiments are still needed to ensure that synthetic ϵ - Fe_2O_3 provides trustworthy palaeointensity estimations. What has been demonstrated, both by the study carried out on the synthetic sample (EPSsyn) and by the reevaluation of the data from archaeological samples (COO), is that ϵ - Fe_2O_3 phase adequately records the direction of the palaeofield.

7. Conclusions

An increased understanding is being achieved concerning the thermal and environmental conditions controlling the formation of epsilon iron oxide in natural and archaeological contexts. In this study, structural and magnetic studies have been carried out in baked clays coming from an Islamic pottery complex in Córdoba, Spain. The results revealed through this work establish the specific conditions where it could be predicted the emplacement of the ϵ - Fe_2O_3 phase in combustion structures.

The temperatures in the kiln probably reached 1200 °C. The formation of different iron oxides can be observed in the baked clay interior due to the successive activation of the kiln over time and the aggregation state between particles. From CRS experiments, the formation of magnetite + hematite is detected in the superficial region closest to the heat source (0 cm in depth profile), maghemite + ϵ - Fe_2O_3 + hematite in the intermediate region (from 1 cm to 3 cm in depth), and maghemite + hematite in the bottom region (from 4 cm to 6 cm). The magnetic properties reveal the presence of each iron oxide at particular points within the clay, except for hematite, that is

magnetically undetectable due to its reduced saturation magnetization compared to the other phases. ϵ - Fe_2O_3 is formed preferentially within the intermediate region, with maximum concentrations occurring at 2 cm in depth in the specific case studied. If the ϵ - Fe_2O_3 formation temperature in synthetic samples is above 900 °C, these archaeological findings are confirmed as combustion structures that have experienced high temperatures in the intermediate region, and higher in the top region.

The reevaluation of previous archaeomagnetic results was performed taking into account the thermal range which ϵ - Fe_2O_3 could have an important influence (below 250 °C). The results obtained confirm that it adequately records the direction of the past geomagnetic field. Statistically, palaeointensity studies are not entirely conclusive, probably due to the low quantity of ϵ - Fe_2O_3 present in the samples.

Furthermore, the viability of carrying out palaeomagnetic studies on this polymorph was investigated by synthesizing samples rich in ϵ - Fe_2O_3 phase and simulating the conditions found in archaeological samples. This work is the first palaeomagnetic experiment carried on a synthetic ϵ - Fe_2O_3 sample in which a stable thermoremanent magnetization is recorded. A reliable direction was obtained, along with a linear Arai plots that yielded a palaeointensity that was slightly larger as the applied magnetic field.

CRediT authorship contribution statement

J. López-Sánchez: Conceptualization, Project administration, Investigation, Writing - original draft, Writing - review & editing, Formal analysis. **A. Palencia-Ortas:** Writing - original draft, Writing - review & editing, Formal analysis. **A. del Campo:** Investigation. **G. McIntosh:** Writing - original draft, Writing - review & editing, Formal analysis. **M. Kovacheva:** Writing - original draft, Writing - review & editing, Formal analysis. **F. Martín-Hernández:** Writing - original draft, Writing - review & editing, Formal analysis. **N. Carmona:** Investigation, Writing - original draft, Writing - review & editing, Formal analysis. **O. Rodríguez de la Fuente:** Writing - original draft, Writing - review & editing, Formal analysis. **P. Marín:** Writing - original draft, Writing - review & editing, Formal analysis. **A. Molina-Cardin:** Investigation, Writing - original draft, Writing - review & editing, Formal analysis. **M.L. Osete:** Conceptualization, Project administration, Writing - original draft, Writing - review & editing, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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