

## Red ochre decorations in Spanish Neolithic ceramics: a mineralogical and technological study

J. Capel<sup>a,\*</sup>, F. Huertas<sup>b</sup>, A. Pozzuoli<sup>c</sup>, J. Linares<sup>b</sup>

<sup>a</sup> *Departamento de Prehistoria y Arqueología, Universidad de Granada, Campus de Cartuja, 18071 Granada, Spain*

<sup>b</sup> *Estación Experimental del Zaidín, CSIC, Profesor Albareda 1, 18008 Granada, Spain*

<sup>c</sup> *Dipartimento di Geofisica e Vulcanologia, Università degli Studi di Napoli 'Federico II', Largo S. Marcellino 10, 80138 Napoli, Italy*

Received 18 October 2004; received in revised form 28 November 2005; accepted 15 December 2005

### Abstract

Some Neolithic ceramics from south-eastern Spain have red to brown external decorations called “almagras” (red ochre). The pigment layer is essentially composed of a mixture of clay and iron oxides: haematite (red) and maghemite (brown). It is suggested that maghemite was formed during the firing process of ceramic in a reducing atmosphere. Several laboratory tests have been carried out to obtain maghemite by adding charcoal or pinewood sawdust to similar ceramic pastes. In fact, maghemite was formed, even when the piece was simply covered with pinewood sawdust before firing. The diverse original red colours are due to variations in iron oxide (or calcite) content and to redox conditions in the firing procedure. Brown- coloured ceramics owe their colour to maghemite and must be considered as a “fabrication defect”, due to the position of the ceramic piece in a zone where a reducing atmosphere prevailed in the course of firing.

© 2006 Elsevier Ltd. All rights reserved.

*Keywords:* Neolithic; Ceramic; Red ochre decorations; Spain; Archeometry; Experimental study

### 1. Introduction

The red ceramics called “a la almagra” (red ochre) first came to attention in the Iberian Peninsula following observations made in the 1930s in some areas of Andalusia. This ceramic, one of the most characteristic types found in several Andalusian archaeological settings, is very little studied; it has an unclear chronology and relationships with other Mediterranean scenarios are not well established [2,3,17,18].

Two different techniques of red ochre decorations can be distinguished from direct observation: a first type has a red (intense red to orange) external colour, adhering very well to the ceramic surface, as if it were an opaque enamel. A second type, considered as painted ceramic, is less firm and very friable.

With regards to the origin of these red ochre ceramics, Martínez-Santa Olalla [11] suggests a Near East provenance, with an important focus in the Anatolian and northern Syrian

zones. The first indication comes from the early Ugaritic, dating from between 2400 and 2300 BC. From these localities it probably migrated to Cyprus, where abundant material is found in the Erimi, Kirokhitia and Vounous settlements, with the red ochre ceramics overlapping the painted ceramics, which were eventually replaced by the new imported type.

Arribas [1] connects this red ceramic with the “Diana style” of Lipari (final phase of the Neolithic of Lipari) on account of its colouration and fabrication technique, although the shapes are very different. Muñoz [15] establishes another parallelism with the ceramics associated to the Ancient Neolithic of Tessalia (V–IV millennium). They are monochrome reds, but they also exhibit different shapes. Likewise, the authors treat in their work the existing problems of the origin and chronology raised by red ochre ceramics in Neolithic Andalusia [2,3,16–19].

The red ochre ceramics described as characteristic of the Andalusian settings of the western zone of Spain, especially the Cordoba caves, expanded to Portugal and eastern Andalusia, with very important locations in Malaga and Granada

\* Corresponding author.

*E-mail address:* [jcapel@ugr.es](mailto:jcapel@ugr.es) (J. Capel).

provinces. In the case of Cueva de la Carigüela (Piñar, Granada), a specific site with very well preserved stratigraphic sequences, the time frame is from the middle of the Vth millennium, for deep strata, to the second half of the IVth millennium for the beds with red ochre ceramics [3,17,21]. At present, the debate concerning the moment of the appearance of ceramics with red ochre decoration extends to the process of Neolithisation in the Andalusian region [2,5,10,18]. The questions are to know how societies evolved from the Epipaleolithic to the Neolithic and whether it was an external process coming from the Mediterranean Spanish zone and thence towards Andalusia or, on the contrary, a zone of different penetration was involved. In spite of the great importance assumed by ceramics with red ochre decoration in understanding the Neolithic period of Andalusia, the number of studies carried out is scanty [3,7,20]. A late influence can be recorded in the Valencia region, where this ceramic type is however of borderline importance [5,10,18]. The archaeological problems that this type of ceramics raise will be the subject of another article.

The first analytical studies carried out on Neolithic ceramics from southern Spain [7,19] show, among other interesting questions, that the ceramics with red ochre decorations contain two types of iron minerals: haematite and maghemite. The presence of maghemite affords a stimulating problem due to the fact that this phase is scarce in nature. The study of the genesis of maghemite is important however to understand the technology employed to produce such decorations, especially the peculiar formation conditions of maghemite.

From the mineralogical point of view, maghemite is an iron oxide, belonging to the spinels group. It corresponds to the polymorphic variety  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and is an intermediate mineral between haematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>). It can be said that maghemite is nothing but haematite with a small amount of ferrous iron. This fact causes the appearance of an octahedral void in its crystalline structure, needed to establish the electrical neutrality. For instance, a typical maghemite contains 21.5 iron atoms for each 32 oxygen atoms instead of the 24 iron atoms of the normal magnetite unit cell. The presence of ferrous iron increases the “*a*<sub>o</sub>” crystallographic parameter of maghemite [27,29].

On the other hand, maghemite can incorporate in its crystalline structure small amounts of aluminium. In this case the temperature of transformation to haematite increases [29], and the “*a*<sub>o</sub>” crystallographic parameter of maghemite decreases [24].

Both maghemite and magnetite are transformed to haematite by heat. The conversion temperature ranges from over 400 °C for maghemites of small size, to 600–800 °C for well-crystallised ones. For similar sizes, the higher the transformation temperature, the higher is the ferrous iron content [6]. The transformation of maghemite to haematite is exothermic [25].

Maghemite can develop from the oxidation of pre-existing magnetite. In soils, maghemite usually forms by heating (bush fires, undergrowth and forest fires) of iron oxihydroxides (goethite, lepidocrocite, ferrihydrite) in the presence of organic

matter. In such cases maghemite is poorly crystallised and can show isomorphic aluminium replacement [24,25,28].

In line with these statements, the themes this paper is intended to develop are as follows:

- To study pieces of Neolithic ceramics with red ochre decorations to identify and quantify the constituent iron minerals of such decorations.
- To analyse residues of red minerals found at some Neolithic sites to determine if maghemite was one of the components. Negative results in this respect would signify that maghemite had to form during the firing process of the ceramics. This being the case, laboratory tests were to be carried out to establish the possible conditions of maghemite formation in Neolithic workshops.

## 2. The samples

The samples studied belong to three types: (a) red (“almagras”) and red-grey-brown (“engobes”) coatings or decorations from original Neolithic ceramics; (b) iron ore fragments (haematite), found in vessels in some archaeological settlements; (c) artificial mixtures of clay and iron oxides with or without carbonaceous or organic matter used in laboratory experiments [20].

The specimens of archaeological ceramics were selected from ten Neolithic settlements in caves from the Granada province, SE Spain, (Fig. 1) located at:

- Alfacar: Cueva de las Majolicas.
- Alhama: Cueva del Agua, Cueva de los Molinos, Cueva de la Mujer, Sima del Conejo.
- Iznalloz: Cueva del Agua de Prado Negro.
- Güalchos: Cueva de las Campanas.
- Moclín: Cueva de Malalmuerzo.
- Pinos Puente: La Molaina. (seasonal inhabited place)
- Piñar: Cueva de la Carigüela.

The painted surface was carefully erased with a cutter, avoiding damage to the original ceramic substratum, to make sure that the powder obtained was representative of the decoration only. This powder was ground to pass through a sieve of 200 mesh ASTM.

In Cueva del Agua (Alhama) and in Carigüela (Piñar), vessels containing fragments of red iron ores (“almagra”: haematites) were found. These pigments were used to elaborate the original decorations.

A clay sediment from Gabia (near the city of Granada) was used to make the experimental ceramics. This clay has a mineralogical composition similar to that of the average Neolithic ceramics of the Granada province, according to Navarrete et al. [20]. The relevant data are listed in Table 1.

As additional materials to produce a reducing atmosphere during firing, powder of active carbon (Merck) and pinewood sawdust (<1 mm fraction) were used.



Fig. 1. Location of Neolithic sites, Granada, SE Spain. 1. Cueva de la Carigüela, 2. Cueva de Malalmuerzo, 3. Los Castillejos, 4. Cueva del Coquino, 5. La Molaina, 6. Sima del Conejo, 7. Cueva del Capitan.

**3. Methods**

X-Ray diffraction patterns were obtained with a Philips 1710 diffractometer, using a Co tube with a graphite monochromator.

A semi-quantitative mineralogical evaluation was obtained according to the method developed by Barahona [4].

Haematite has two principal X-ray reflections. One at 0.269 nm with maximum (100) intensity, and another one at 0.251 nm with less intensity (over 75). Maghemite has its diagnostic reflection at 0.251 nm. So, there is a coincidence of both minerals in this last peak. According to Schwertmann and

Heinemann [26], it is possible to deduce the presence and to quantify the amount of maghemite by means of the variation in the 0.269–0.251 peaks ratio. When maghemite is present, this ratio is less than that corresponding to haematite alone. The measurements of the peak reflections at 0.269 and 0.251 nm present certain problems due to the tendency to very broad peaks in some cases. So, these ratios of areas are liable to a possible error of measurement.

The chemical analysis of acid-dissolved iron oxides was carried out by UV-VIS spectroscopy using *o*-phenantroline as a coloured reactive. The amount of iron as haematite was deduced from these values.

Independently of the original Neolithic decorations, three series of experimental ceramics were analysed. The methodology for these procedures was as follows:

- “A” series: The proportion of components is shown in Table 2. From each mixture, eight pieces (dimensions: 1 × 1 × 0.5 cm) were prepared, in order to be moulded with water and, finally, heated in a crucible to temperatures from 300 to 1000 °C, after drying at room

Table 1  
Mineralogical composition of clay used in the experimental ceramics

Sample	Phyllosilicates	Quartz	Calcite	Dolomite	K-Feldspar	Plagioclase
Gabia	60	24	11	5	0	0
Neol. Ceram.	61	23	11	0	2	2

Gabia: Clay sediment from the locality of Gabia (near to Granada, Spain). Neolithic ceramics = Average composition of original Neolithic ceramics from Granada province, Spain. After Navarrete et al. [20].

Table 2  
Mixtures for experimental ceramics. “A” Series (weight %)

Clay	Coal	Iron oxide
80	0	20
77	4	19
74	7.5	18.5
71	11	18
69	14	17

Clay: clay sediment from Gabia. See Table 1.

temperature. Each temperature was maintained in the kiln during 2 h (samples: 302, 303, ... ,402, 403, ..., 1006).

- “B” series: A piece made from 8 g of clay, 2 g of iron oxide and 1 g of pine sawdust was prepared and moulded with water all together. Once dry at room temperature, the piece was heated in a crucible for 2 h to 450 °C. The time elapsed to reach this temperature was 6 h. From this piece five horizontal slides were cut from top to bottom (samples: B-1 to B-5).
- “C” series: A piece similar to that of “B” series (without sawdust in the ceramics mass) was heated in a crucible also at 450 °C, but immersed and covered in pine sawdust. From this piece, three horizontal slides were cut from top to bottom (samples: C-1 to C-3).

## 4. Results and discussion

### 4.1. Original red ochre Neolithic decorations: mineralogical composition

The results of the mineralogical analysis by X-ray diffraction are reported in Table 3. In this table, the Fe<sub>2</sub>O<sub>3</sub> content of the samples, obtained by acid dissolution, is also shown.

Table 3  
Mineralogical composition and Iron content of original Neolithic decorations in ceramics from caves

Sample	Hematite	Maghemite	Phyllosilicates	Quartz	Plagioclase	K-feldspar	Calcite	Fe <sub>2</sub> O <sub>3</sub>	Locality
HA-4	77	0	14	3	0	0	6	76.92	C.Agua-Alhama
HM-2	60	0	8	4	0	0	28	59.61	C.Molinos-Alhama
PC-7	73	0	8	2	0	0	17	72.84	C.Carigüela-Piñar
PC-8	87	0	0	2	0	0	11	87.05	C.Carigüela-Piñar
PC-9	90	0	7	3	0	0	0	89.56	C.Carigüela-Piñar
FM-1	14	6	73	4	1	1	1	22.18	Majolicas-Alfacar
HA-1	29	0	49	16	0	0	6	28.68	C.Agua-Alhama
HA-2	39	0	47	8	0	0	6	39.2	C.Agua-Alhama
HA-3	7	0	63	26	2	2	0	8.42	C.Agua-Alhama
HM-1	10	0	67	14	0	0	9	9.18	C.Molinos-Alhama
HU-1	5	4	56	31	1	0	3	9.23	C.Mujer-Alhama
HU-2	32	0	52	12	0	0	4	32.42	C.Mujer-Alhama
HC-1	9	0	61	22	8	0	0	9.05	Sima Conejo-Alhama
IP-1	8	3	54	29	6	0	0	11.48	Prado Negro-Iznalloz
GC-1	17	11	18	14	0	0	41	28	C.Campanas-Güalchos
MM-1	12	14	45	16	3	0	10	27.2	C.Malalmuerzo-Moclín
PM-1	5	0	14	7	0	0	74	5.24	Pob.Molaina-Pinos Puente
PC-1	7	4	73	11	4	0	1	11.11	C.Carigüela-Piñar
PC-2	16	10	48	17	2	0	7	26.39	C.Carigüela-Piñar
PC-3	0	15	44	20	5	0	16	16.01	C.Carigüela-Piñar
PC-4	20	13	49	15	2	0	1	32.65	C.Carigüela-Piñar
PC-5	0	6	53	35	0	6	0	6.97	C.Carigüela-Piñar
PC-6	2	31	44	10	0	0	13	33.58	C.Carigüela-Piñar

The first five samples correspond to small pieces of “pure” iron oxides (samples HA-4, HM-2, PC-7 and PC-9) found in two vessels from the Neolithic deposits of Cueva de la Carigüela and Cueva del Agua. It is possible moreover to observe that they contain haematite, in addition to phyllosilicates, quartz and calcite. That is to say, the “pure” iron oxides contain non-ferrous impurities. The important fact is that they do not contain maghemite, which indicates that this had to form during the production process of the ceramic piece with the Neolithic methodology. In the study conducted by Middleton [14] on ceramics painted with haematite, proceeding from the archaeological contexts of the Bronze Age, it is demonstrated that the initial composition of the iron ore used in the production of these paintings is haematite with impurities of clay, quartz and calcite [12,13].

In the samples with reddish or reddish-grey decorations there is to be remarked the variability in the contents of phyllosilicates and haematite. The quantity of phyllosilicates in such decorations is always higher than those containing the “pure” iron oxides, which means that the decorations must have resulted from a mixture of haematite and clay. The presence, in some instances, of maghemite is to be viewed as a consequence of the firing process, since it does not exist, as already stated, in the original haematite. Probably a suspension of iron oxide and clay in water was used as the painting matter, the clay acting as a vehicle for the oxide, improving its dispersion in water, and furnishing the proper viscosity for the mixture to be spread on the ceramic surface.

With the aim of proving whether a particular type of clay was employed to produce the above mixture, the mineralogical analyses have been recalculated, discounting the quantity of iron phases contributed by the “pure” haematite. The results appear in Table 4a,b, with reference to the ceramic decorations

Table 4  
Mineralogical composition of Neolithic red ochre decorations. Recalculated composition without iron phases. Locality: (a) Alhama and (b) Piñar

Sample	Phyllosilicates	Quartz	Plagioclase + K-feldspar	Calcite
(a) Locality: Alhama				
HA-1	70	24	0	6
HA-2	80	14	0	6
HA-3	68	28	4	0
HU-1	61	34	1	4
HU-2	78	19	0	3
HC-1	66	25	9	0
HM-1	74	16	0	0
Mean value	71	23	2	4
Average Neolithic ceramic <sup>a</sup>	70	23	3	4
(b) Locality: Piñar				
PC-1	71	24	5	1
PC-2	65	23	3	9
PC-3	53	24	6	17
PC-4	75	22	3	–
PC-5	57	37	6	–
PC-6	82	18	–	–
Mean value	67	25	4	6
Average Neolithic ceramics <sup>b</sup>	62	30	2	6

<sup>a</sup> Ceramics matrix from Alhama zone, Spain. After Navarrete et al. [20].

<sup>b</sup> Ceramics matrix from Piñar zone, Spain. After Navarrete et al. [20].

from Alhama (Cueva del Agua) and Piñar (Carigüela), including in each case the mean mineralogical composition of the Neolithic ceramics drawn from the work by Navarrete et al. [20]. It can be observed that the mean value of the clay employed in the mixture matches very well the local mean value of the relevant zones. It is possible, therefore, to state that the clay employed was in each case the one locally available, which appears as rather obvious. In connection with such results it becomes feasible to calculate with the following procedure, in every instance, the relative amounts of clay and “pure” iron oxide used to produce the decorating paint: by discounting from the mineralogical analysis of each paint sample the components corresponding to the iron oxide from the relevant localities, the remaining mineral phases must correspond to the clay that was employed.

For instance, in the specimen HA-1 from the Cueva del Agua de Alhama, there exists 29% of Fe<sub>2</sub>O<sub>3</sub>, and given that the iron oxide is not pure, these 29 g of Fe<sub>2</sub>O<sub>3</sub> must be accompanied by 5 g of phyllosilicates, 2 g of quartz and 7 g of calcite, in agreement with the mineralogical composition of the iron mineral (specimen HA-4, Table 3). All these mineralogical phases were contributed by the “pure” iron oxide and they sum up to a total of 49 g. It is consequently to be inferred that the mixture was composed of 43 g “pure” iron and 57 g local clay.

The results of this calculation have been displayed in Table 5a,b, and it is to be noted that the agreement between the calculated and the observed values is very high. However,

it has been possible to carry out such calculations only with respect to the ceramics originating from the outcrops where “pure” iron minerals have been found. The calculations do not have to lead one to assume that the people who produced this type of ceramic employed a system of “weights and measures” in manufacturing their vessels, but they would rather imply the existence of a work technique sufficiently precise and properly mastered to attain the intended final result.

According to Table 3, two groups of samples can be recognised, the first with a content of Fe<sub>2</sub>O<sub>3</sub> about 5–10%, the other of over 30%. The observed variability in the modal values can be interpreted as proof of the technological skill possessed by the various communities, as previously indicated. The decorations in the first group exhibit a lighter reddish colour (they contain a lower amount of red iron oxide) than those in the second group (with a larger content of the same oxide). Such mineralogical classification agrees very well with the visual evaluation that led to the archaeological classification of the first as “pale red ochre”, and the second as “red ochre”.

Therefore, the following samples can be classified, from the mineralogical standpoint, as “red ochre” *sensu stricto*:

- Sample HA-1 and HA-2 from Cueva del Agua de Alhama.
- Sample HU-2 from Cueva de la Mujer.
- Sample PC-2, PC-4 and PC-6 from Cueva de la Carigüela.

Conversely, the following samples can be classified, as “pale red ochre”:

- Sample HA-3 from Cueva del Agua de Alhama.
- Sample HU-1 from Cueva de la Mujer.
- Sample HC-1 from Sima del Conejo.
- Sample HM-1 from Cueva de los Molinos
- Sample PC-1, PC-3 and PC-5 from Cueva de la Carigüela.

Other possible aspects to be considered are the thickness of the paint cover, the colour firmness and the variations that in some samples tend toward the dark grey or brown. Such characteristics are a function of the clay and haematite content, and of the presence of maghemite. The latter has a dark-brown-grey reddish colour and produces brown tones. Thus, if the maghemite is produced under reducing conditions, the type of atmosphere in the kiln can prove a determining factor in the final colour of the ceramic piece. On the other side, the presence of calcite (specimens GC-1, PC-3, PC-6 and PM-1) tends to lighten the tones [22]. Finally, in the case of more diluted paints, the ceramic’s own colour can influence the final aspect of the decoration.

The samples archaeologically classified as “engobes” are those with a larger proportion of maghemite. Therefore their colour being browner, they had to be fired in a reducing atmosphere, as will be discussed below. It can be suggested that the “engobes” might represent “defective pieces” in some kiln batches, since in the same level of strata we find ceramics of good decorative quality together with these of bad quality. Besides the study of all the ceramics has demonstrated the equality in the process of manufacture and of firing [20]. It sounds

Table 5  
Calculation of red ocher and clay original mixtures. Locality: (a) Alhama and (b) Pinar

Sample	Phyllosilicates	Quartz	Plagioclase	K-Feldspar	Calcite	Fe <sub>2</sub> O <sub>3</sub>		%
(a) Locality: Alhama								
HA-1	5	2	—	—	7	29	Red ocher contribution	43
HA-1	40	13	1	1	2	—	Clay contribution	57
HA-1	45	15	1	1	9	29	Calculated value	100
HA-1	49	16	—	—	6	29	Observed value	100
HA-2	6	2	—	—	10	39	Red ocher contribution	57
HA-2	30	10	1	—	2	—	Clay contribution	43
HA-2	36	12	1	—	12	39	Calculated value	100
HA-2	47	8	—	—	6	39	Observed value	100
HA-3	1	1	—	—	1	7	Red ocher contribution	10
HA-3	63	20	2	1	4	—	Clay contribution	90
HA-3	64	21	2	1	5	7	Calculated value	100
HA-3	63	26	2	2	—	7	Observed value	100
HU-1	1	1	—	—	2	9	Red ocher contribution	13
HU-1	61	20	2	1	3	—	Clay contribution	87
HU-1	62	21	2	1	5	9	Calculated value	100
HU-1	56	31	1	—	3	9	Observed value	100
HU-2	5	2	—	—	8	32	Red ocher contribution	47
HU-2	38	12	1	1	2	—	Clay contribution	53
HU-2	43	14	1	—	10	32	Calculated value	100
HU-2	52	12	—	—	4	32	Observed value	100
HC-1	1	1	—	—	2	9	Red ocher contribution	13
HC-1	61	20	2	1	3	—	Clay contribution	87
HC-1	62	21	2	1	5	9	Observed value	100
HC-1	61	22	8	—	—	9	Observed value	100
HM-1	2	1	—	—	2	10	Red ocher contribution	13
HM-1	59	20	2	1	3	—	Clay contribution	85
HM-1	61	21	2	1	5	10	Calculated value	100
HM-1	67	14	—	—	9	10	Observed value	100
(b) Locality: Piñar								
PC-1	1	—	—	—	1	11	Red ocher contribution	13
PC-1	54	26	1	1	5	—	Clay contribution	87
PC-1	55	26	1	1	6	11	Calculated value	100
PC-1	63	11	4	—	4	11	Observed value	100
PC-2	2	1	—	—	3	26	Red ocher contribution	32
PC-2	42	20	1	1	4	—	Clay contribution	68
PC-2	44	21	1	1	7	26	Calculated value	100
PC-2	48	17	2	—	7	26	Observed value	100
PC-3	1	—	—	—	2	16	Red ocher contribution	19
PC-3	50	24	—	1	5	—	Clay contribution	81
PC-3	51	24	—	1	7	16	Calculated value	100
PC-3	44	20	5	—	15	16	Observed value	100
PC-4	2	1	—	—	4	33	Red ocher contribution	40
PC-4	49	17	1	1	4	—	Clay contribution	60
PC-4	37	18	1	1	8	33	Calculated value	100
PC-4	39	15	2	—	1	33	Observed value	100
PC-5	—	—	—	—	1	7	Red ocher contribution	8
PC-5	57	28	1	1	5	—	Clay contribution	92
PC-5	57	28	1	1	6	7	Calculated value	100
PC-5	53	35	—	6	—	7	Observed value	100
PC-6	2	1	—	—	4	34	Red ocher contribution	41
PC-6	37	16	1	1	4	—	Clay contribution	50
PC-6	39	17	1	1	8	34	Observed value	100
PC-6	44	10	—	—	12	34	Observed value	100

HA = Cueva del Agua (Alhama); HU = Cueva de la Mujer (Alhama); HC = Sima del Conejo (Alhama); HM = Cueva de Los Molinos (Alhama).  
PC = Cueva de la Carigiuela (Piñar).

illogical that they were intentionally obtained through the transformation of an enticing bright red colour into one consisting of dark shades of brown.

#### 4.2. Experimental ceramics: “clay–red ochre–charcoal” system (“A” series)

Mixtures of clay, haematite and charcoal were moulded with water and, in line with the methodological indications, 40 test samples were prepared. Successively, these were put in a crucible and were fired in a kiln at 450 °C.

From the X-ray diffraction study of the test samples the data assembled in Table 6 were obtained. The ratio of areas of the peaks at 0.269 and 0.251 nm can serve to show the presence of maghemite in addition to haematite. It is important to consider that the first reflection corresponds to haematite only, while the second one is common to both minerals. Therefore a reduction of the said ratio with respect to the theoretical initial value will indicate the presence of maghemite, and will moreover allow its quantification.

Now then, the different “pure” iron oxides (haematite) exhibit rather variable values in the ratio of areas of the 0.269 and 0.251 reflections. Normally, such values are quite high with respect to the theoretical ratio of 1.33 [6], depending on the site and also within the same site. These variations must be a consequence of the differences in individual particle sizes and of the replacements by ferrous iron and aluminium. Therefore, to perform calculations on the possible presence of maghemite it is necessary to start from the values of the haematite utilised from each site. Practically, to elaborate the samples of this “A” series, some haematites possessing a ratio of areas of 1.46 have been utilised. In Table 6 the said ratio of areas and the possible maghemite contents have been presented. The difficulty of measuring the areas of the peaks in order to calculate the haematite/maghemite ratio has been already mentioned. In the present case, it is even more difficult due to the amorphous character of charcoal. Probably during the firing process this charcoal can change to graphite, essentially amorphous, whose combustion temperature is high. Because of all this, the values in Table 6 have to be taken only as an expression of tendencies. It will be remembered (see Table 1) for example, that specimen 302 corresponds to a mixture of clay and haematite, without charcoal, heated to 300 °C, while specimen 303 corresponds to a mixture of clay, haematite, and 4% charcoal, heated to 300 °C, and so on.

It can be observed that in Table 6 the values of the mentioned ratio of areas are closer to the initial value at low firing temperatures. As temperature is increased, there exists a tendency for the ratio of areas to decrease, which corresponds to the formation of maghemite, as indicated in Table 6. The small observed variations in each temperature series must correspond to homogeneity problems in the specimen and to difficulties of measurement of the areas.

Two important facts must be taken into consideration: first, that the higher the initial charcoal content, the greater the maghemite quantity that shows up; and second, that this mineral persists even at high temperatures. The appearance of

Table 6

Experimental ceramics. “Clay–Red Ocher–Coal” system. “A” series. X-Ray parameters

Sample	0.269/0.251	%Hematite relative	%Maghemite relative
302	1.56	100	—
303	1.44	100	—
304	1.60	100	—
305	1.54	100	—
306	1.62	100	—
Mean	1.54	100	—
402	1.43	99	1
403	1.45	10	—
404	1.27	91	9
405	1.57	100	—
496	1.36	95	5
Mean	1.41	95	5
502	1.37	96	4
503	1.28	91	9
504	1.17	86	14
505	1.43	99	1
506	1.24	89	11
Mean	1.30	94	6
602	1.43	99	1
603	1.30	92	8
604	1.41	98	2
605	1.36	96	4
606	1.28	91	9
Mean	1.36	95	5
702	1.15	85	15
703	1.18	86	14
704	1.58	100	—
705	1.44	100	—
706	1.22	88	12
Mean	1.31	100	—
802	1.18	86	14
803	1.21	88	12
804	1.19	87	13
805	1.19	87	13
806	1.26	90	10
Mean	1.22	88	12
902	1.40	97	3
903	1.34	94	6
904	1.12	83	17
905	1.11	82	18
906	1.23	89	11
Mean	1.23	89	11
1002	1.12	83	17
1003	1.34	94	6
1004	1.25	90	10
1005	1.08	81	19
1006	1.21	88	12
Mean	1.21	87	13

maghemite seems to indicate that it forms above 300 °C, a fact which appears normal, since with the increase of the charcoal content the presence of oxygen during the combustion is negatively affected, and the conditions can be generated to create the necessary environment apt to reduce a small quantity of ferric ions to ferrous ions and thus produce maghemite. The increase and persistency of maghemite at high temperatures can be due to the fact that the ferrous ion, formed at lower temperatures, cannot oxidise due to alterations in the porosity of the fired piece, meaning that a balanced exit of gases cannot be achieved. Probably it is a matter of meta-stable systems that could disappear with much longer firing times. Another possibility which would be conducive to the formation of maghemite is based on the fact that phyllosilicates are destructed, as previously hinted to, by deshydroxylation at such high temperatures (starting from 500 °C). The ferrous ions of the silicate structures can, with the unburned carbonaceous matter, aid the formation of maghemite. The probable graphitisation of charcoal also must be considered. The newly formed graphite can persist at high temperatures: in this kind of “closed” system its preservation appears to extend up to 1000 °C.

Finally, if the average values obtained from the areas of the peaks for each temperature are examined, it is possible to infer that the ratio of areas considered clearly decreases with temperature, even when there is no charcoal - which seems to indicate that there is an effect, proper to the clay, that with the generation of iron oxides during its destruction by deshydroxylation, can lead to the formation of maghemite, as indicated before.

To ensure that we were not dealing with a question strictly connected to the thermal behaviour of haematite, an additional experiment was devised. Two “pure” iron oxides, from two sites in Alhama, were submitted to heating from 300 ° to 1000 °C. The obtained values for the ratio of areas of the peaks at 0.269 and 0.251 nm show that there are no evident heat effects on the ratio of areas. At any rate, a very slight tendency to increase appears to be detectable, the opposite of what can be observed when firing is carried out in the presence of charcoal. The single most evident question is that, in such case, the haematite reflections tend to become more acute, which shows that its size and crystallinity improve with heat.

As a consequence, the firing at 450 °C of clay, iron oxides and charcoal mixtures is conducive to the formation of maghemite in small quantities, and gives way to the colouration of the mass in the brown-grey-reddish hues typical of this mineral.

#### 4.3. Experimental ceramics: “clay–red ochre–sawdust” system: “B” series

The next step was to consider that a factual confirmation could result from the use of sawdust as the reducing matter. In this way more reducing elements—nitrogen, hydrogen, sulphur, typical of lignite derivatives of wood—would be introduced in the system, approaching in a better way the possible methodology of Neolithic craftsmen, who were compelled to use straw, bushes, wood splinters, etc. It was also

hoped that, with this system, higher quantities of maghemite could be obtained.

In this series, as indicated in the methodology, mixtures of clay, iron oxide and pinewood sawdust were employed. The inclusion of sawdust in the mixture was to ensure that the contact between the reducing gases and haematite would be very high, on a par with charcoal in the previous series of tests. The mixture was moulded with water, left to dry, coated with sawdust and then fired in a crucible at 450 °C. This temperature was selected on account of being that of combustion of organic matter.

Table 7 shows the data obtained from different roundels cut horizontally from the fired piece, as has been described. The colour change is striking. The most superficial roundel, being more oxidised, has a red-brown-grey colour; shifting all the way to a dark brown with the gradual lowering of the cuts towards more reduced areas (bottom of the crucible). The ratio of areas of the 0.269 to 0.251 peaks, and the percentage of maghemite perfectly agree with such colour changes. In the upper zone (B-1), oxidised haematite prevails, whereas in the lower zone (B-5), reduced maghemite maintains a high concentration.

If such results are compared with those of Table 6 corresponding to the previous series, a greater formation of maghemite is observed, making up to 62% in relative quantity compared to haematite, with a dark-brown mass colour. It follows that the presence of sawdust in the ceramic mass led to the formation of maghemite. Sawdust produced a reducing environment motivating the conversion of part of haematite to maghemite. Nevertheless, even if the test sample was covered with sawdust, the surface part, in contact with air, exhibited a reddish hue and contained less maghemite because it is a less reducing zone. Probably, the position of the piece in the kiln, its being more or less close to the openings, the firing time without removal of the cover, the type of plant (fresh or dry) utilised, represented important factors in the production of highly variable redox environments in the Neolithic kilns, above all if one considers that the type of kiln utilised consisted of a pit dug in the ground, above which the ceramic was placed, overlaid by the vegetal fuel. The temperatures reached by this type of kiln ranges between 600 and 800 °C [8,9,23].

For these reasons, and to progress a step further, a mixture of clay and iron oxide only was prepared, to execute the following series of tests. The pinewood sawdust was utilised to

Table 7  
Experimental ceramics. “Cay- Red Ocher-Sawdust” systems. “B” series

Sample	0.269/0.251	%Hematite relative	%Maghemite relative	Colour
B-1(top)	1.15	86	14	Brown red
B-2	1.13	83	17	Brown reddish
B-3	0.73	59	41	Brown
B-4	0.65	54	46	Brown
B-5 (bottom)	0.43	38	62	Dark brown

0.269/0.251 = Ratio of peak areas at 0.269 and 0.251 nm.



surround the piece inside the crucible, without mixing it in the ceramic mass.

#### 4.4. Experimental ceramics: “clay–red ochre–(sawdust)” system: “C” series

The mixture of clay and haematite was moulded with water and dried at ambient temperature. Then the mould was introduced in a crucible and entirely surrounded and covered with sawdust. Firing temperature, as in the previous set of tests, was kept at 450 °C.

The results of mineralogical analysis have been gathered in Table 8. Specimens C-1 and C-3 are the upper and lower roundels, respectively. A very important variation in the ratio of areas of the reference peaks (0.269 and 0.251) can be observed. This way, up to 72% of maghemite comes into formation, which represents an absolute value of 11%, considering the quantity of iron oxide initially present. The colour also was in full agreement with mineralogy. In the same way, specimen C-3, the one with the higher maghemite quantity, exhibited a dark-brown colour.

In Neolithic times, the firing of pieces had to be carried out using as a heat source bushes, straw, branches and trunks of trees. Such material was sufficient to create an atmosphere capable of reducing, in some zones, part of the haematite in the paints to maghemite. This reducing ambient was something certainly undesirable for the Neolithic craftsmen. They had to look for a more oxidising atmosphere, aiming to preserve the red colour of their haematite-based paints.

The last question to be dealt with is whether the newly formed maghemite is stable at high temperatures.

To clarify this point, part of specimen C-3, the one with the highest quantity of maghemite, was submitted to a firing temperature of 700 °C for the duration of 2 h. The result is very clear. The colour shifts from dark-brown to red-brown and the percentage of maghemite drops in a significant way. It can be suggested that if the temperature is increased (and probably also the firing time) maghemite undergoes destruction, on condition that the kiln atmosphere stays oxidising.

These data clearly offer evidence that maghemite can form without necessarily including in the ceramic matrix any kind of organic matter, although a reducing atmosphere is indispensable in the kiln.

Finally, and as a general rule in this work, there is no trace of aluminium substitution in maghemite, according to the X-ray diagrams.

Table 8  
Experimental ceramics. “Clay-Red ochre-(Sawdust)” system. “C” series

Sample	0.269/0.251	%Hematite relative	%Maghemite relative	Colour
C-1 (top)	1.17	86	14	Brown red
C-2	0.60	51	49	Brown
C-3 (Bottom)	0.30	28	72	Dark brown
C-3 (Heated 700 °C)	1.33	94	6	Brown red

0.269/0.251 = Ratio of peak areas at 0.269 and 0.251 nm.

## 5. Conclusions

Based on the complex of experiments and the data obtained, some criteria can be established that characterise the ceramics decorated with red iron oxide.

- The red paint used for decorating the ceramics was a mixture of local clay and a red iron oxide (haematite).
- The mixture was used in variable proportions depending on the required hue: the brighter the tone of red desired, the higher the red iron oxide contents had to be.
- There exist two types of preferred mixtures of clay and iron oxide: one with a small quantity of red iron oxide (about 5–10%) and another around 30%.
- With the mixture of clay and iron oxide a suspension was prepared, which was used to paint the outer surface of the ceramic once it had dried, and before it was fired.
- The final colour of the decoration was related to the reducing or oxidising atmosphere in the kiln, which abetted or hindered, respectively, the formation of maghemite. The higher the percentage of maghemite, the darker brown the resulting colour. The rather common appearance of ceramics with this mineral phase is to be interpreted as a “fabrication defect” of the piece, since—beyond the will and control of the craftsmen—the initial red colour shifted to assume grey or brown tonalities due to the reducing ambience prevailing in some parts of the kiln.

## Acknowledgements

The specimens of Neolithic ceramic, collected in the course of several archaeological excavations, were made available for this study by Prof. Maria Soledad Navarrete of the Department of Prehistory, Granada University, Spain. Many thanks are due to Dr Angelo Pesce for his valuable comments and for improving the English text. This work is dedicated to the memory of Mr Juan Rodriguez-Robledo, our X-ray master technician, who died recently.

## References

- [1] A. Arribas, Le neolithique ancien de la Peninsule Iberique. (II Atlantic Colloque of Neolithic, Groningen, 1966), *Paleohistoria* XII (1967) 11–16.
- [2] M.D. Asquerino Fernández, Periodización y Cronología del Neolítico Andaluz. (Simposios de Prehistoria “Cueva de Nerja” II La problemática del Neolítico en Andalucía), Fundación Cueva de Nerja, 2004, pp. 17–25.
- [3] P. Atoche Peña, La cerámica a la almagra en las cuevas de Andalucía Oriental (Su encuadre en el Neolítico de Granada y Málaga), Resúmenes Ph.D. Thesis, La Laguna, 1987.
- [4] E. Barahona, Arcillas de ladrillería de la provincia de Granada: Evaluación de algunos ensayos de materias primas, Ph.D. Thesis, Universidad de Granada, Granada, 1974.
- [5] J. Bernabeu, Indigenismo y migracionismo. Aspectos de la neolitización en la fachada oriental de la Península Ibérica, *Trabajos de Prehistoria* 53 (1996) 37–54.
- [6] G. Brown, Associated minerals, in: G.W. Brindley, G. Brown (Eds.), *Crystal structures of clay minerals and their X-ray identification*, Miner. Soc. London, London, 1980, pp. 361–410.

- [7] J. Capel, M.S. Navarrete, E. Reyes, Aplicación de métodos analíticos al estudio de cerámicas a la almagra, *Actas Congreso Nacional Arqueología, Murcia*, 1983, pp. 95–104.
- [8] A. Gibson, A. Woods, *Prehistoric Pottery for the Archaeologist*, Leicester University Press, Leicester, 1997, pp. 46–59.
- [9] M. Licka, Résultats d'expériences relatives a la cuisson de la céramique préhistorique dans différents types de structures de cuisson et de fours: première étape, in: T. Hackens, Schvoerer (Eds.), *Datation-Characterisation des céramiques Anciennes*, 10, 1984, pp. 210–213 PACT.
- [10] B. Martí, J. Cabanilles, J. Bernabeu, El Neolítico de l'Est i el Sud Peninsular, *Cota Zero* 7 (1991) 58–67.
- [11] F. Martínez Santa-Olalla, La fecha de la cerámica a la almagra en el Neolítico Hispano-Mauritano, *Cuadernos de Historia Primitiva del Hombre* III (1948) 95–106.
- [12] A. Masson, Les ocres et la petroarchéologie. L'aspect taphonomique, *Revue d'Archéométrie* 10 (1986) 87–93.
- [13] B. Michel, J. Weiss, R. Wessicken, M. Maggetti, Analyses mineralogique, chimique et technologique d'engobes argileux, *Revue d'Archéométrie* 11 (1987) 63–75.
- [14] A.P. Middleton, Technological investigation of the coatings on some haemetite-coated pottery from southern England, *Archaeometry* 29 (1987) 250–261.
- [15] A.M. Muñoz, Estado actual de la investigación sobre el neolítico español, *Pyrenae* 6 (1970) 13–28.
- [16] A.M. Muñoz Amilibia, El proceso de cambio en el neolítico andaluz. Evolución y difusión, (Simposios de Prehistoria "Cueva de Nerja" II La problemática del Neolítico en Andalucía), *Fundación Cueva de Nerja*, 2004, pp. 115–118.
- [17] M.S. Navarrete, La cultura de las cuevas con cerámica decorada en Andalucía Oriental, *Cuadernos de Prehistoria de la Universidad de Granada, Serie Monográfica, I*, 1976.
- [18] M.S. Navarrete Enciso, Significación cultural y cronológica de la cerámica cardial en Andalucía (Simposios de Prehistoria "Cueva de Nerja" II La problemática del Neolítico en Andalucía), *Fundación Cueva de Nerja*, 2004, pp. 26–34.
- [19] M.S. Navarrete, J. Capel, Algunas consideraciones sobre la cerámica a la almagra del neolítico andaluz, *Cuadernos de Prehistoria de la Universidad de Granada*, 1980, Serie Monográfica 5, pp. 15–35.
- [20] M.S. Navarrete, J. Capel, J. Linares, F. Huertas, E. Reyes, Cerámicas Neolíticas de la provincia de Granada. Materias primas y técnicas de manufacturación, *Monografías Arte y Arqueología*, Universidad de Granada, Granada, 1991.
- [21] M. Pellicer, El Neolítico y el Bronce de la Cueva de la Carigüela de Piñar (Granada), *Trabajos de Prehistoria XV* (1964).
- [22] J. Petrus, R. Iberg, Mineralogical changes during firing of calcium-rich brick clays, *Ceramic Bulletin* 57 (5) (1978) 503–505, 509.
- [23] P.M. Rice, *Pottery Analysis. A Sourcebook*, The University of Chicago Press, Chicago, 1987, pp. 152–158.
- [24] U. Schwertmann, Iron oxides, in: J.B. Dixon, S.B. Weed (Eds.), *Mineral in Soil Environments*, second ed., Soil Sci. Soc. Amer, Madison, 1989, pp. 379–438.
- [25] U. Schwertmann, R.M. Cornell, *Iron Oxides in the Laboratory*, VCH, Weinheim, 1991, pp. 12–48.
- [26] U. Schwertmann, B. Heinemann, Über das vorkommen und die Eutstehung von Maghemit in nordwest deutschen Böden, *Neues Jahrbuch Mineral Monatsh* (1959) 174–181.
- [27] J.W. Stucki, B.A. Goodman, U. Schwertmann, *Iron in Soils and Clay Mineral*, D. Reidel Pub. Co, Dordrecht, 1988.
- [28] R.M. Taylor, The influence of chloride concentration on the oxidation of Fe(II) chloride. I. Effect of (Cl)/(Fe) on the formation of maghemite, *Clays and Clay Minerals* 32 (1984) 167–174.
- [29] R.M. Taylor, Non-silicate oxides and hydroxides, in: A.C.D. Newman (Ed.), *Chemistry of Clays and Clay Minerals*, Mineralogical Society Monograph 6, Longman Sci. Tech, London, 1987, pp. 129–201.