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

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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.

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

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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 Neolithicisation 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 γ-Fe_2O_3, and is an intermediate mineral between haematite (α-Fe_2O_3) and magnetite (Fe_3O_4). 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_o" 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_o" 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.