Revealing the mediaeval lead-glazing manufacturing technique of the *carreaux de pavement* from Tiebas (Navarra, Spain)

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Lead-based compounds have been used as glazes in ceramics since ancient times. In this communication, the glazed tiles of the Castle of Tiebas (Spain) were studied. These specific type of tiles, known as *carreaux de pavement*, were a stylistic import from northern France, presented on the same pavement as monochromatic tiles (without decoration) or dichromatic tiles (decorated). Dichromatic tiles can be identified by their three-layered body: a top layer covered by a thin layer of lead glaze with colour; a middle layer, also known as *engobe*, consisting of a thin paste composed of clay or lime; and a bottom layer, which is also the thickest, named paste and made up of reddish clay. Monochrome tiles have only two layers: paste and glaze.

In order to identify the lead–glazing manufacturing technique employed during the Middle Ages, replicas have been studied under different experimental conditions. Both, replicas and archaeological samples were analysed and compared to estimate the original manufacturing conditions. As a base for the replicas, prismatic probes of decalcified clay (simulating the body) or kaolin (simulating the engobe) were used, with dimensions of 2 x 2 cm and 1 cm thick. Different amounts of lead-based compounds (PbS, Pb_0, $PbCO_3$ and PbO) were applied by brush to the surface of these probes: in quantities of 20, 30 and 40 mg/cm_2. Replica samples were fired at different times (12, 24 and 48 hours) and temperatures (850, 900 and 950 ºC). The analytical techniques used were the following: colorimetry, image analysis (IA), optical microscopy (OM), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, X-ray fluorescence (XRF), X-ray diffraction (XRD) and Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM-EDS).

Of all the lead-based compounds applied, $PbCO_3$ and PbO are the only ones that produced a good glaze on the paste and *engobe*. To determine the glazing conditions (quantity of Pb applied in mg/cm^2 and firing temperature and time) used in the original mediaeval samples, the following variables were especially relevant: the glazed surface composition (%Pb and %Si); the intensity ratio between lead $L\alpha$ and $M\alpha$ lines in the XRF spectra, the glass-covered surface (%) of each probe (obtained by IA) and the thickness of the glaze.

Key words: lead-glaze, experimental archaeology, mediaeval pottery, archaeometry, glazing Technology

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Introduction

Lead-based compounds have been used as glazes in ceramics since ancient times [1]. In this communication, the glazed tiles of the Castle of Tiebas (Spain) were studied [2]. These specific type of tiles, known as *carreaux de pavement*, were a stylistic import from northern France [3,4]. Dichromatic tiles can be identified by their three-layered body: a top layer covered by a thin layer of lead glaze with colour; a middle layer, also known as *engobe*, consisting of a thin paste composed of clay or lime; and a bottom layer, which is also the thickest, named paste and made up of reddish clay. Monochrome tiles have only two layers: paste and glaze.

In order to identify the lead–glazing manufacturing technique employed during the Middle Ages, replicas have been studied under different experimental conditions (**Fig. 1**). Both, replicas and archaeological samples were analysed and compared to estimate the original manufacturing conditions. As a base for the replicas, prismatic probes of decalcified clay (simulating the body) or kaolin (simulating the *engobe*) were used, with dimensions of 2 x 2 cm and 1 cm thick. Different amounts of lead-based compounds (PbS, Pb^0, $PbCO_3$ and PbO) were applied by brush to the surface of these probes: in quantities of 20, 30 and 40 mg/cm². Following the results of previous research [5,6], replica samples were fired at different times (12, 24 and 48 hours) and temperatures (850, 900 and 950 ºC).

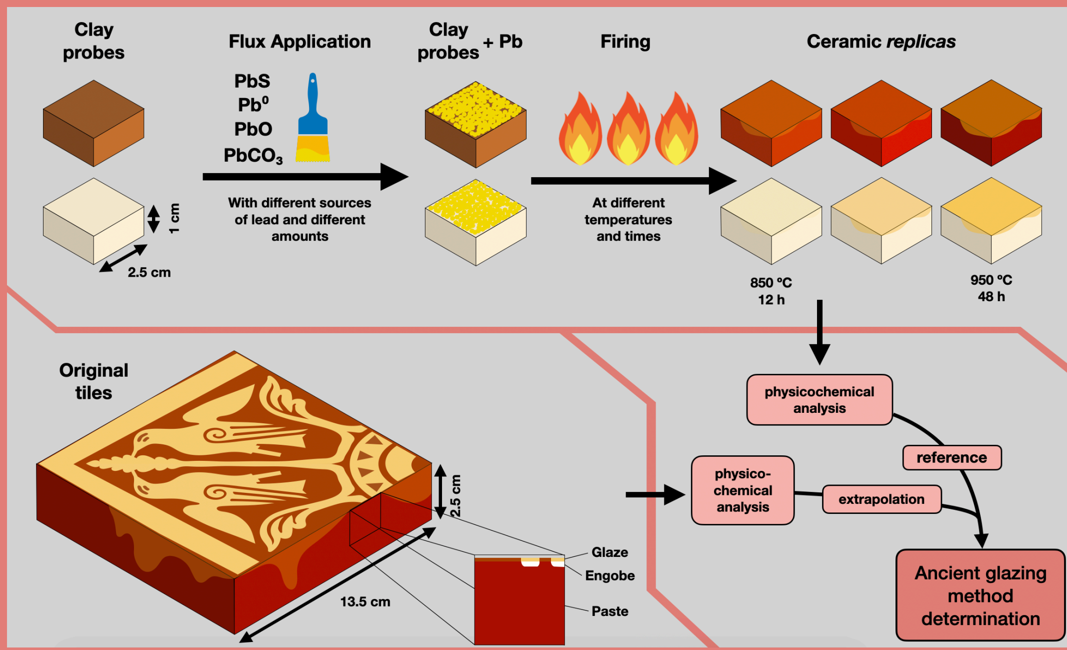

Fig. 1. Scheme of the glazing method determinaton through experimental archeology.

What source of lead was used in the glaze?

According to Tite M. *et al.* (1998) the flux used in lead transparent glazes could be galena (PbS), metallic lead (Pb^0), cerussite ($PbCO_3$) or massicot (PbO) [1]. To evaluate them as fluxes, they were applied on clay and kaolin replicas and fired at high temperature. The results were satisfactory in the case of cerussite and massicot (**Fig. 2**). On the other hand, galena only turned out to be a good flux on clay replicas, but not on kaolin ones. In the case of metallic Pb, a small surface well was obtained in both specimens, not corresponding to what was observed in the archaeological tiles.

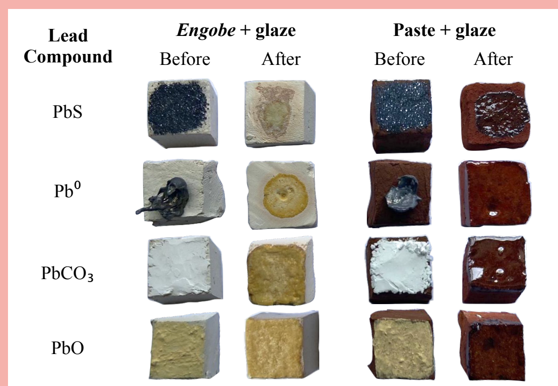

Fig. 2. Replicas of engobe and glaze with different lead-based fluxes before and after firing.

Was the lead-based compound used by itself or mixed with silica?

Tite M. *et al.* (1998) describes two methods for preparing the flux in ancient times: the use of the lead-based compound by itself; and the use of a mixture of the lead-based compound mixed with silica or a siliceous clay [1]. To determine which method was used in the *carreaux de pavement* of Tiebas Castle, the unslipped surface areas were analyzed by XRF. The results of **Fig. 3a** show how Pb content (from the flux) is inversely proportional to that of Si, Al and Fe (from the paste). Likewise, Si amount (**Fig. 3b**) is directly proportional to that of Al and Fe, corroborating that the Si only could come from the paste and not from a mixture of silica and flux.

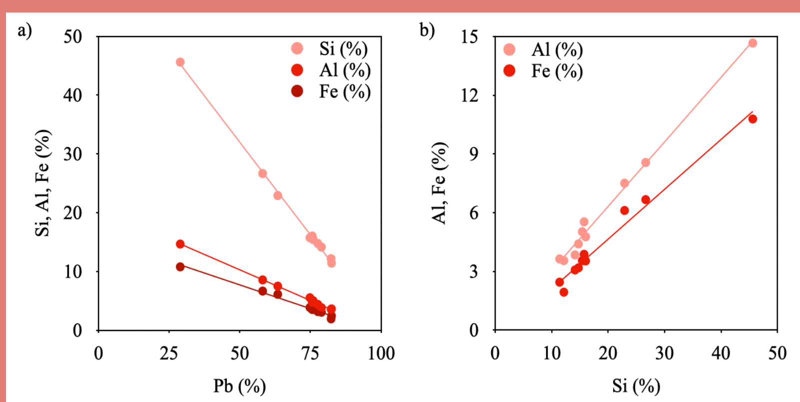

Fig. 3. Normalized composition (Pb, Si, Al and Fe) of the glazed surface of the archaeological samples.

How were the firing conditions?

Firing temperature and time favor the melting of the flux and its diffusion towards the paste or engobe. This increase in lead penetration can be followed by the Lα and Mα line intensities of lead in the XRF spectrum. In **Fig. 4**b-c it is observed how the Lα /Mα ratio increases with firing time and temperature. In archaeological samples the Lα/Mα ratio values are high and equivalent to high firing temperatures (950 ºC) and long times (>24 h).

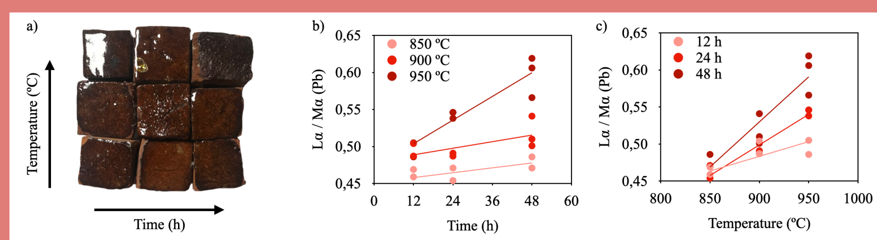

Fig. 4. Clay (a) replicas. Evolution of the intensity ratio between lead Lα and Mα lines in the XRF spectra with firing times and temperatures in clay replicas (b,c).

High firing temperature and time also favor the formation of new mineral phases and the destruction of previous ones. The most notable are the formation and disspareance of lead silicoaluminates (**Fig. 5**b-c): with increasing temperature $PbAl_2Si_2O_8$ (lead feldspar) is formed while $PbAl_2SiO_6$ and $Pb_6Al_2Si_6O_{21}$ dissapear [7]. In archaeological samples only was detected $PbAl_2Si_2O_8$, showing that firing temperature must been higher than 900 ºC.

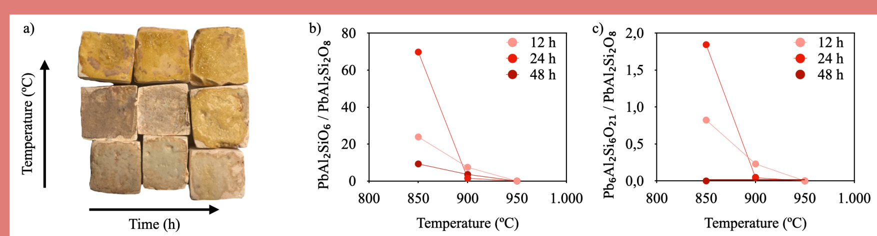

Fig. 5. Engobe (a) replicas. Evolution of the XRD counts ratios with firing temperature in engobe replicas: $PbAl_2SiO_6$ (2θ=34.3, PDF 30-0689) and $PbAl_2Si_2O_8$ (2θ=13.6, PDF 25-0428); $Pb_6Al_2Si_6O_{21}$ (2θ=10.8, PDF 32-0506) and $PbAl_2Si_2O_8$ (b,c).

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