Study of manufacturing technology in historical materials bymeans of reproductions: the case of the mediaeval *carreaux de pavement* from the Iberian Peninsula

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Tiebas Castle (Navarra, Spain) was built in the mid-13th century as a sign of ostentation and power for the newly crowned Teobaldo II of Navarre. The castle was designed following the canons and luxuries of the French court to which Teobaldo II belonged as Count of Champagne. One of these luxuries was tiling the castle floors with decorated glazed ceramics, called *carreaux de pavement*. This type of mediaeval tiles reached its maximum diffusion in France and England between the 12th and 14th centuries.

The manufacturing technique of these tiles has been unknown until now. Through experimental archaeology, replicas were made and simultaneously analysed together with the original archaeological samples found in the Castle. To achieve compatibility with the elemental and mineral composition of the original samples, a local decalcification clay was used as raw material for the replicas. Additionally, they were constructed using similar thicknesses (1 cm and 2,5 cm) as the archaeological samples. The replicas were fired at different temperatures (700, 800, 850, 900, 950, 1000 and 1100 ºC) and times (1, 3, 6, 24, 48, 72 hours). The analytical techniques used were the following: acid digestion, colorimetry, compressive tests, Fourier transform infrared spectroscopy (FT-IR), X-ray fluorescence (XRF) and X-ray diffraction (XRD).

One of the key variables used to follow the changes produced during the firing processes was the hematite crystal size. Sintering and internal reduction of porosity during firing led to resistance to attacks by aqua regia (3 HCl + HNO_3) to generally soluble elements at low pH, e.g. Fe. The results of hematite crystal size and %SiO_2 and %Fe_2O_3 of the solid residue (after the acid attack) were used to build an empirical model that determined the firing time and temperature of the archaeological samples. Some mineralogical phases were also useful to confirm the firing temperature range like the absence of mullite and cristobalite, high temperature phases (≥1000 ºC) or illite, low temperature phase (≤850 ºC).

Our study concluded that the firing time of the archaeological samples was higher than 24 hours and the firing temperature range was between 875 and 950 ºC. The results not only allow us to estimate a narrow range of firing temperatures, but also serve as a basis for future investigations on the manufacturing technology of the upper layers (engobe and glaze) of these types of ceramics.

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Introduction

Tiebas Castle (Navarra, Spain) was built in the mid-13th century as a sign of ostentation and power for the newly crowned Teobaldo II of Navarra. The castle was designed following the canons and luxuries of the French court to which Teobaldo II belonged as Count of Champagne. One of these luxuries was tiling Castle floors with decorated glazed ceramics, called *carreaux de pavement*. This type of mediaeval tiles reached its maximum diffusion in France and England between the 12th and 14th centuries.

The manufacturing technique of these tiles has been unknown until now. Through experimental archaeology, *replicas* were made and simultaneously analysed together with the original archaeological samples found in the Castle. To achieve compatibility with the elemental and mineral composition of the original samples, a local decalcification clay was used as raw material for the *replicas*. Additionally, they were constructed using similar thicknesses (1 cm and 2.5 cm) as the archaeological tiles. The *replicas* were fired at different temperatures (700, 800, 850, 900, 950, 1000 and 1100 ºC) and times (1, 3, 6, 24, 48, 72 hours). The techniques used were the following: acid digestion, colorimetry, compressive tests, Fourier transform infrared spectroscopy (FT-IR), X-ray fluorescence (XRF) and X-ray diffraction (XRD).

Once all the *replica* samples were analyzed, the analytical variables that increased or decreased proportionally with firing temperature and time were considered. The results of them were modeled and the archaeological samples results were extrapolated on the model to obtain the firing conditions of *carreaux de pavement* manufacturing method (**Fig. 1**).

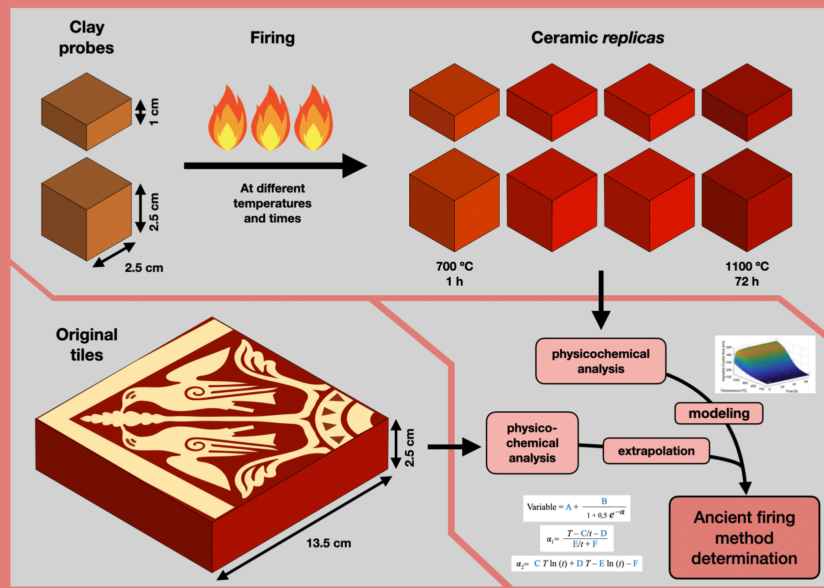

Fig. 1. Schematic summary of the manufacturing method determinaton.

Changes in mineral phases

The changes of the mineral phases in the paste were especially revealing since some phases were formed or destroyed depending on the firing times and temperatures. Some phases were very useful to establish a firing temperature range in the archaeological samples: the absence of mullite and cristobalite, high temperature phases (≥1000 ºC) and the absence of illite, low temperature phase (≤850 ºC). One of the key variables used to follow the changes during the firing was the crystal size of hematite (**Fig. 2**). It was selected since its growth with temperature allows it to be traceable within the range used (700 – 1100 ºC).

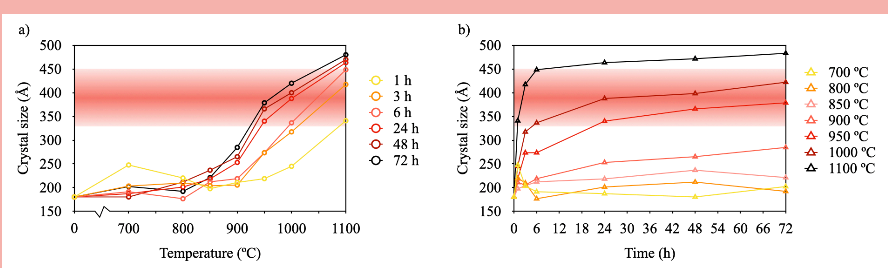

Fig. 2. Crystal size of hematite (2θ = 33.3º) depending on (a) firing temperatures and (b) firing times.

Sintering and resistance to acid attack

Sintering and internal reduction of porosity during firing increased the resistance to *aqua regia* (3 HCl + HNO_3) attacks, so those elements generally soluble at low pH, like Fe or K oxides, are retained in the undigested solid. **Fig. 3** shows how the red color (produced by hematite) of the samples was maintained before and after the acid attack, in those samples heated at high times and temperatures. On the contrary, in those heated for short times or at low temperatures was not maintained.

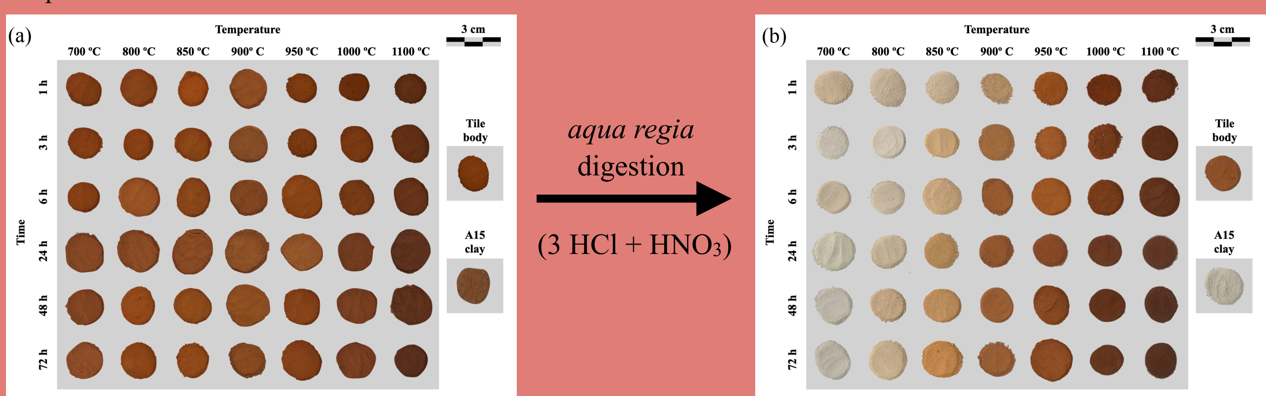

Fig. 3. Images of the *replica* powder samples before (a) and after (b) acid digestion. Images of the archaeological tile residue (M4) and the clay (A15) before (a) and after (b) acid digestion.

Modeling and extrapolation

The results of hematite crystal size (HCS) and $\%SiO_2$ and $\%Fe_2O_3$ of the solid residue (after the acid attack) of *replica* samples were used to build empirical models considering their firing conditions **(Fig. 4a)**. The extrapolation of the respective data of the archaeological samples in the models allowed to obtain a relationship of the firing time and temperature used in Middle Age (**Fig. 4b**). The models of these three variables (HCS, $\%SiO_2$ and $\%Fe_2O_3$) were defined by the following equations:

$$\text{Variable} = A + \frac{B}{1 + 0{,}5\, e^{-\alpha}} \quad \text{where} \quad \alpha_1 = \frac{T - C/t - D}{E/t + F} \quad \text{for HCS}$$

$$\text{and} \quad \alpha_2 = C\,T \ln(t) + D\,T - E \ln(t) - F \quad \text{for } \%SiO_2 \text{ and } \%Fe_2O_3.$$

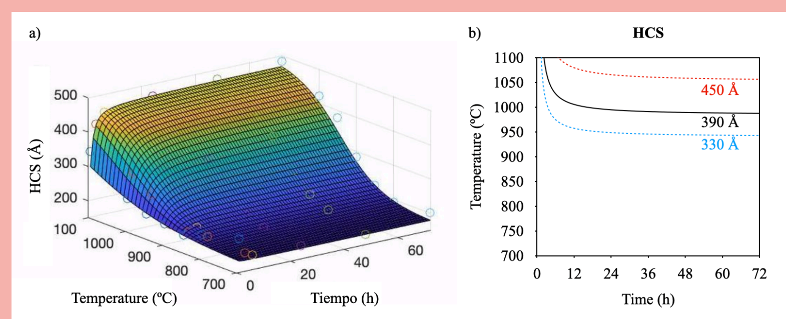

Fig. 4. a: Experimental model obtained from *replica* samples for hematite crystal size (HCS). b: Temperature-time curves obtained for HCS results. In red, maximum values; in blue, minimum values; and in black, mean values.

Conclusions

Our study concluded that the firing time of the archaeological samples (paste) was higher than 24 hours and the firing temperature range was between 875 and 950 ºC. The results not only allow us to estimate a narrow range of firing temperatures, but also serve as a basis for future investigations on the manufacturing technology of the upper layers (engobe and glaze) of these types of ceramics.

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