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FT-IR spectroscopic analysis to study the firing processes of prehistoric ceramics

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ABSTRACT

In this work, we present a FT-IR absorbance investigation on prehistoric ceramics with the aim of characterizing the phase transformations that occur during the cooking processes. The measurements were performed on several potteries belonging to the Middle Bronze Age excavated in the Catania hinterland (Sicily, Southern Italy). Based on the macroscopic observation, the samples may be distinguished on coarse and fine ceramics, and the petrographic study showed a strongly heterogeneous structure and composition. The results were compared with the data obtained by means of X-ray diffraction (XRD) and with the microscopic qualitative observations of the birefringence of the groundmass. The whole set of the data showed a firing temperature in the 800–900 °C range. The simultaneous presence in several samples of calcite and clay minerals and of new-formed Ca-silicates should be indicative of a quite primitive technological firing process with strong temperature variation inside the kiln.

1. Introduction

One of the most frequent questions in archaeometric research of potteries concerns the determination of the firing technology [1–3]. It is well known, in fact, that the firing temperature, together with the composition of clayey sediments, is the main parameter conditioning the mineralogical assemblage and the reorganisation of the structure of the ceramics. Therefore the identification of the mineral phases is a powerful tool for the semi-quantitative determination of the maximum temperature reached [4–11].

These information about the technology are particularly important for the study of prehistoric industry, since they permit to trace the evolution of knowledge. In particular, the Middle Bronze Age in Sicily (XV–XIII century BC) represents a crucial moment in the evolution of pottery production. In this period, in fact, a deep technological breakthrough happens, that overcomes the experimentalism of the previous period and gradually directs the production of ceramic to a standard that will remain unchanged until the Greek colonization.

The development of more advanced furnaces, able to cook pottery at higher temperature, the conscious addiction of temper and the control of the oxygen's activity in the oven in order to influence the firing conditions, together with the related colors of surfaces are some of the most prominent technical achievements. At the same time, a deeper knowledge of the natural territory determined a new accuracy in the selection of clays and new shaping techniques, with rudimental versions of potter's wheel.

However, the insufficiency of specific archaeometric studies [12–17] represented until now a serious interpretative handicap for archaeologists. In particular, the lack of interdisciplinary studies determined a significant delay in the research of the prehistoric Sicily.

Here, we present an FT-IR absorbance study performed on an important ceramic group from the Middle Bronze Age (15th–13th century BC), excavated in "Grotte di Marineo" near Licodia Eubea (Catania), together with an "ancillary" petrographic analysis. The whole set of results showed some new aspects of pottery production for this period, setting some points regarding the technological knowledge of the primitive populations as far as pottery firing is concerned.

2. Experimental details

2.1. Materials

The site of Grotte di Marineo, excavated by the Soprintendenza ai Beni Culturali e Ambientali of Catania in 1988 and 1989 [18–20], is composed by four natural caves continuously occupied from Neolithic (6th millennium BC) to Late Bronze Age (end of 2nd millennium BC). This settlement flourished during Middle Bronze Age (Thapsos culture, 15th–13th century BC), with the development of a large troglodytic village, including distinct residential, funerary, cultic and productive spaces [21].

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The most important evidence for this period is represented by pottery of Thapsos type and in particular by a group of 230 diagnostic specimens, belonging to all the three chronological subphases of the Thapsos culture (Thapsos I: 1440/1420–1400/1380 BC; Thapsos II: 1400/1380–1310/1300 BC; Thapsos III: 1310/1300–1270/1250 BC), recently object of a comprehensive analysis [21,22].

From the macroscopic observation of the abundance and granulometry of inclusions, three main types of potteries were distinguished:

(a) With fine inclusions (<0.25 mm), representing the 22% of entire sampling, mostly cups.
(b) With medium-fine inclusions (0.25–1 mm), prevalently recognized in the cups, mugs and bowls and representing the 48% of the sampling.
(c) With coarse inclusions (>1 mm) observable in the basins and jars specimens, representing the 30% of the sampling.

From a technological point of view, the specimens exhibit common features of the typical Thapsos produced all over Sicily in Middle Bronze Age. Pottery is handmade, and fired in reducing conditions. The paste is generally colored from reddish gray (2.5 YR 6/1) to gray (7.5 YR 5/1). The ceramics are quite brittle, as testified by several repair holes, and by sporadic voids on the surface (present in the 5% of the samples).

Black blotches (present in the 50% of the samples) and over burning are the most typical features of this period of the prehistoric pottery technology, characterized by continuous experiments in order to set proper standards.

As can be observed in several other Italian prehistoric contexts [23], some specimens of the studied Grotte di Marineo's pottery (see Fig. 1), basically belonging to open vessels, have inner part of the rim overburned. This evidence suggests their firing upside down in a furnace with lower firing chamber. Again, in some cases is even possible to distinguish large black spots with vertical pattern that can be related to the use of open kiln or single chamber oven. Sometimes all the surfaces of the vessel were burned, getting an uniform black color. In these cases, all the surfaces were burnished in order produce a kind of rough *bucchero* ware.

Fig. 1. Selection of specimens from Grotta di Marineo with black spotted surfaces.

2.2. Methods

FT-IR measurements were performed by using a BOMEM DA8 FT-IR spectrometer. The experimental set-up was equipped with a Globar lamp source, a KBr beamsplitter, and a DTGS/MIR detector, that spanned a spectral range from 450 cm^{-1} to 4000 cm^{-1}. In such a configuration it was possible to use a resolution of 4 cm^{-1}. From each shard, about 2 mg of material was drawn from non-significant parts of the ceramic body, in order to avoid damages that could affect the integrity and artistic content of the object. The samplings were powdered, dispersed in a caesium iodide (CsI) matrix, transparent in the investigated frequency range, and reduced in pellets. The measurements were performed in transmission configuration and in dry atmosphere to avoid unwanted dirty contributions. Due to the complexity of the experimental FT-IR absorbance profiles, the spectra of the samples were initially compared with those of standard minerals and clays (Sadtler database "Minerals and Clays") for a reliable assignment of the bands.

The results were compared with the semi-quantitative mineralogical composition obtained by previous X-ray diffraction (XRD) measurements. The firing temperatures were also estimated by the qualitative optical microscopic (OM) observations of the groundmass birefringence.

3. Results and discussion

Firstly, we performed a petrographic analysis of all samples, in order to classify them into different fabrics. From that, the studied ceramics were subdivided into six fabrics on the basis of mineralogical and structural characteristics and according to the petrographic classification of Whitbread [24]. In this work, particular attention has been focused on the groundmass birefringence observed under crossed polars (close to the significance of optical activity *sensu* [24]). Low or absent birefringence is, in many cases, indicative of the achievement of high firing temperature when the reaction brings to modifications of the original mineralogical association of the groundmass (mainly clay minerals and calcite) and to the formation of cryptocrystalline new phases (anorthite, diopside, wollastonite and gehlenite).

The studied potteries may be subdivided into six fabrics: (i) the fabric A (samples 1B, 1B1, 1B2), characterized by limestone inclusions and fossil rich groundmass and present high birefringence; (ii) fabric B samples (2B2, 1A, 2B), having volcanic glass inclusions, fossil poor groundmass and low or absent birefringence; (iii) fabric C ceramics (1C, 1C1), characterized by the presence of volcanic glass and quartz inclusions, non fossiliferous groundmass and low or absent birefringence; (iv) fabric D (2A, 2C3), with dominant volcanic glass and limestone inclusions, fossiliferous groundmass and medium birefringence; (v) fabric E (2C1, 3B, 1A1, 1A2, 1D, 2B4, 2D, 3B1) characterized by volcanic glass, volcanic rocks and grog inclusions, fossiliferous groundmass and high birefringence except sample 3B1; (vi) fabric F (1D1, 2A1, 2A2, 2A3, 2B1, 2B3, 2C, 2C2, 2D1, 3A, 3A1, 3A3, 3A2), with volcanic glass, volcanic rocks ± plagioclase and pyroxenes inclusions, fossiliferous groundmass and low or absent birefringence with exceptions of the sample 3A1.

The FT-IR analysis was used with the aim to determine, through the mineralogical composition, the firing temperature, taking into consideration that all the examined potteries have CaO abundance higher than 6 wt.% [22] and according to Maniatis and Tite [25] are produced with calcareous clay sediments.

The obtained information were compared and if necessary integrated with those obtained by means of X-ray diffraction (XRD). The mineralogical associations of all the studied potteries are reported in Table 1 together with the birefringence of the groundmass and the esteemed firing temperature.