Experimental analyses by X-ray µ-CT for the study of the effects of firing temperature on the ceramic body morphology

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Aims

This work proposes a new analysis procedure by the use of X-ray Micro Computed Tomography (µ-CT) aiming to study the effects of firing conditions on the final features of ceramic materials in order to distinguish the influences of the production techniques.
Recent results on archaeological and art materials by the innovative and non-destructive X-ray µ-CT show promising results in Cultural Heritage field. This technique offers the advantages to provide information by images of the inner part of the object preserving its integrity [1]–[3].
Ceramics are complex objects, rich source of information and constitute a large part of the staple memory of past and present human activities. The study of this material is essential in order to thoroughly understand the materiality of historical events and their echo in the present. Archaeometric research on potteries are focused on studying their production techniques, provenance, age, usage and conservation state. In order to contribute in these issues, scientific analyses on ceramic materials, able to provide the characterisation of the chemical and morphological features of the artefacts which are connected to production aspects, are forcefully involved. Chemical and mineralogical composition, particle packing, porosity, microstructure, as well as morphology of ceramic matrix are correlated to native material composition and firing temperature [4], [5].
This research work presents the innovative results obtained investigating the physical properties, such as the total porosity (close and open porosity) of the ceramic materials by X-ray µ-CT. The investigation by means of µ-CT of micro-structural characteristics of ancient ceramics is of particular interest in archaeometry and a few works were found in literature aiming at determining production technology and use of pottery by studying the present inclusions [1], [6].
Laboratory-made raw ceramic materials and Early Medieval potteries coming from the archaeological site of Torcello, in the Venetian Lagoon, have been considered and analysed. The research was performed at first by studying the relationship between raw material composition, firing temperatures and the final chemical-physical features of raw ceramic samples *ad hoc* made in laboratory, following traditional methods and using three kinds of raw clay materials and different firing temperatures (between 400° and 1000°C). Subsequently, archaeological potteries from Torcello, one of the first settled islands on the northern Venetian lagoon, were selected as interesting case studies.
These samples were investigated by chemical, mineralogical and morphological points of view, with particular regard to the porosity of ceramic mixture, which was proved to have a key role to understand its structural parameters, material composition and firing temperature [7], [8].

Method

The lab-made ceramic samples and those coming from the archaeological site in Torcello island were scanned using the nano-CT scanner SkyScan 2011 device of the "Geomodel"

Research Centrum of Saint-Petersburg University with a beam energy of 50 kV, a current of 200 µA and performing a 180° rotation with a step size of 0,25°.
Elaboration and visualization of images were performed by CTvox and CTan programs, and the percentage of the voids as a function of pore size in the range between 1 to 100 µm of the analysed samples was calculated.
The chemical-mineralogical composition of ceramics was determined by Scanning Electron Microscope (SEM-EDX), X-ray Diffraction (XRD) and Fourier-Transform Infrared Spectroscopy (FT-IR) analyses. Furthermore, µ-CT investigation and results were compared and integrated with those obtained by traditional methods such as Mercury Intrusion Porosimetry (MIP), which provides information regarding the open porosity of meso and macro pores (pore size range between 0,003–20 µm), and SEM images for morphological and microstructural considerations.

Results

Archaeological potteries (1154_10, 1159_2, 1210_1 and 1151_5 samples) and the lab-made raw ceramics of three pastes (LS, S and G) at room-temperature (unfired, T0) and those fired at 400°C (T1), 700°C (T4), 900°C (T6) and 1000°C (T7), were analysed. Morphological and microstructural changes were quantified carrying on porosity studies by means of MIP and µ-CT.
Total porosity measured by µ-CT (Fig.1-2) of LS and G pastes, fired at different temperatures, increases at 700°C and decreases at 900°-1000°C. The reduction of total porosity at higher temperatures may be in accordance to the morphological observations made on the basis of SEM images (Fig.3), where the samples fired at high temperature (900° and 1000°C) have a more compact aspect than that one related to samples fired at lower temperature (400° and 700°C).
In the case of S samples, µ-CT results emphasizes the variations which occur in the matrix at 700°C and 1000°C, suggesting that the reactions of dehydroxilation of clay minerals and the beginning of silicate melting strongly affect the microstructure of the raw ceramic samples.
Archaeological samples as 1154_10 and 1159_2 exhibit lower total porosity than 1210_1 and 1151_5 sherds. These last two sherds with higher total porosity are those including secondary calcite, while the first two with lower total porosity include primary calcite, both detected by FT-IR investigations. As it is shown in Fig.4, MIP and µ-CT results seems to have opposite trends for the 1154_10, 1159_2, 1210_1 and 1151_5 samples. Probably the secondary calcite has been formed by precipitation process after burial period, suggesting that secondary calcite tends to reform in smaller pores. These consideration may explain the low open porosity calculated by MIP, which analyses meso and macro open pores, and the high total porosity obtained by µ-CT, which allows to investigate total porosity between 1 to 100 µm. The lower total porosity measured by tomographic analyses of 1154_10 and 1159_2 sherds are in agreement with the morphological observations which suggested higher densification stage and firing temperature (800-850°C).

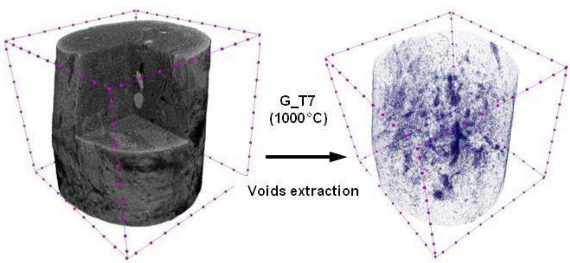

Figure 1: µ-CT viewings of a raw ceramic sample (G_T7, fired at 1000°C).

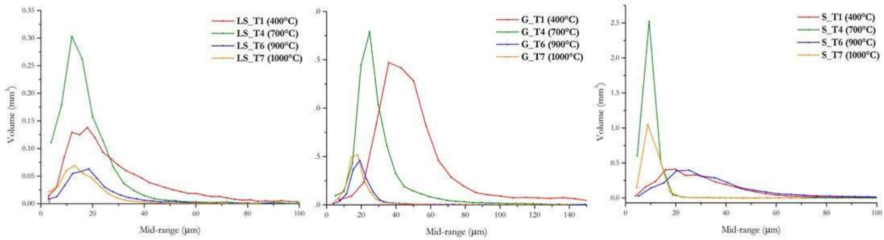

Figure 2: Pore volume vs pore radius calculated by µ-CT of lab-made raw ceramic specimens.

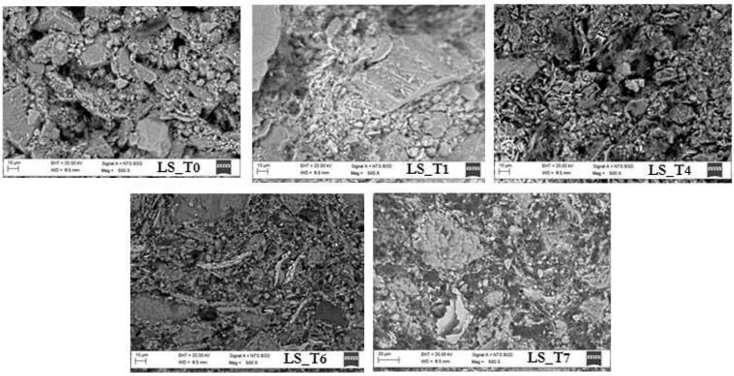

Figure 3: SEM micrographs of polished cross-sections of raw ceramic samples (LS) unfired and fired at different temperatures. SEM images show a more densification stage at higher temperatures.

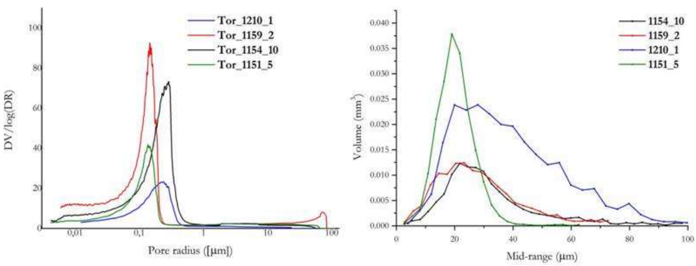

Figure 4: On the left: pore size distribution curves of open pores of the analysed sherds from Torcello measured by MIP. On the right: total pore volume vs pore radius calculated by µ-CT of selected Torcello samples.

Conclusion

The interesting and promising porosimetry results obtained by µ-CT are connected to both firing temperature and mineralogical composition of the potteries. Tomographic results brought out the different behaviour of the porosity considering both open and closed pores and greater

pore radius, opening new insights in considering the influence of the closed porosity that needs to be studied for a complete awareness of the ceramic material features.
The results obtained encourage the application of X-ray μ-CT allowing the implementation of the data obtained by MIP and SEM in a non-destructive way, offering the possibility of obtaining imaging of the microstructure and pore distribution and more specifically to investigate the role of close porosity on the material microstructure and the porosity behaviour during the firing processes.

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