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Characterization of elemental and firing-dependent properties of Phlegrean ceramics by non-destructive ED-XRF and NMR techniques

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ABSTRACT

A combination of energy dispersive X-ray fluorescence (ED-XRF) and 2D proton nuclear magnetic resonance (^{1}H NMR) relaxometry was employed for the characterization of two groups of similar ceramic fragments from the high-medieval production of the Phlegrean area (Miseno and Cuma, Southern Italy). Both methods are based on the use of non-destructive and portable instruments. This approach allows to correlate complementary microstructural features of ceramics, both dependent and independent of the firing technique.

The ED-XRF analysis has shown up the degree of elemental homogeneity of these two ceramic populations and has lead to reasonable hypotheses about continuity in raw clay source utilization and manufacturing methods over the time period of this Phlegrean ceramic production (VI–XIII centuries A.D.), which have proven coherent with literature data.

The NMR investigation has allowed to reveal the structural differences among findings, concerning pore space topology and the magnetic attributes of pore walls. Such differences have been associated to the peculiar interplay between temperature and duration of firing and have proven in step with the temperature assignments provided by archaeologists.

This way the usefulness of the proposed methodology for the characterization of the microstructural fingerprint of ancient ceramics has been clearly shown and reliable conclusions about the technological evolution of and the mutual influence between the investigated ceramic productions have been drawn.

1. Introduction

Archaeological ceramic findings are among the most versatile material testimonies of ancient human cultures, since the microstructure of ceramic sherds inherently keeps trace of the provenance of raw clay and of technical–stylistic abilities at the time and place of the associated pottery production (Velde and Druc, 1999).

Hence, characterizing ancient ceramics has the meaning to improve the understanding of the history and cultural background of ancient civilizations in terms of manufacturing activities, trade pathways, life continuity and logistic importance of archaeological sites (Tite, 1999, 2008).

The possible combinations of the various microstructural parameters in ceramics, such as size distribution of grains and pores and elemental and mineralogical composition, are actually innumerable and result from a complex interplay among source clay materials, temper additives, manipulation procedures, kiln atmosphere and time–temperature relation during firing (Barsoum, 2003).

In addiction, a significant source of ambiguity in assigning firing-temperature reference values to pot sherds arises from the actual possibility of reaching the same effective thermal conditions, as well as of producing the same structural effects on the final objects, by means of different choices of heating rate, peak temperature and soaking time. This makes it more appropriate to talk about "equivalent firing temperatures" (Gosselain, 1992; Livingstone Smith, 2001). The scientific investigation of ancient ceramics requires as many as possible microstructural factors to be taken into account and a common practice is to adopt multi-technical, and thus time-consuming, laboratory approaches, which not always ensure the feasibility of *in situ* measurements or even the full safety of artworks.

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The aim of this paper is to illustrate the efficiency of a non-destructive and on-site methodology, which combines the different analytical capabilities of ED-XRF (Karydas et al., 2005) and 2D proton NMR relaxometry (Casieri et al., 2009) for the characterization of ancient ceramics.

ED-XRF analysis investigates the elemental signature of pottery, which is mostly influenced by the composition of raw clay materials. Several studies (Kilikoglou et al., 1988; Cogswell et al., 1996) have shown that the bulk elemental concentrations are firing-independent, except for those volatile compounds released during the thermal decomposition of clays, such as water vapor and CO_2 (Toledo et al., 2004). Therefore, the elemental characterization of ancient ceramics may give information about source clay materials, manufacturing recipes and fabric types (Tite, 2008). Moreover, it proves helpful for a suitable selection of model clay materials and for the geochemical characterization of archaeological sites by a study of local ceramic productions.

In this work, elemental analyses have been carried out by a mobile X-ray spectrometer, which permits on-site measurements with due respect of the material integrity of samples (Felici et al., 2006).

Somewhat complementary to the atomic properties explored by XRF is the physical information about porous materials provided by ^{1}H NMR relaxometry, which measures the nuclear magnetization decay for hydrogen nuclei of water confined in the porous system. In fact, proton relaxation yields information about the pore space properties, such as open porosity, interconnectivity and size distribution of pores, and about the magnetic attributes associated to elements and minerals at pore walls (Watson and Chang, 1997). Undoubtedly, porous, as well as magnetic, characteristics of ancient artefacts depend on the initial properties of the unfired clay paste, but they are both strongly modified by the firing process (Barsoum, 2003; Nodari et al., 2007).

Unlike the single-exponential time decay of longitudinal and transverse nuclear magnetization for bulk water (Callaghan, 1991), governed by single values of spin–lattice (T_{1B}) and spin–spin (T_{2B}) relaxation times, respectively, water confined in a porous medium experiences more complicated magnetic nuclear interactions. These are due to the presence of electronic spins of paramagnetic species at fluid/solid boundaries and to the confining structure itself, which hinders the molecular motion of spins.

Within a single pore, as well as in a mono-dispersed porous system (with a surface-to-volume ratio *S/V*), the biphasic fast exchange model leads to the simple expression $1/T_{1,2} = (1/T_{1,2B}) + \rho_{1,2}(S/V)$ for both relaxation rates (Brownstein and Tarr, 1979). The macroscopic surface relaxivity $\rho_{1,2}$, proportional to the surface relaxation rate ($T_{1,2S^{-1}}$), depends on the strength of solid/liquid interactions at pore walls, while $T_{1,2B^{-1}}$ can usually be neglected. In real poly-dispersed water-saturated porous systems, where pores can exhibit various sizes and/or interconnection degrees, many different decay modes govern the time evolution of nuclear magnetization: in this case, an Inverse Laplace Transform is usually performed to obtain a distribution of relaxation times (AA. VV., 1989; Watson and Chang, 1997).

Neglecting relaxation mechanisms other than pure surface effects, both T_1- and T_2-distributions may be interpreted in terms of the *V/S*-distribution for pores. However, the correspondence between T_2- and *V/S*-profiles can be compromised, in the presence of magnetic field gradients, by molecular diffusion, which contributes to spin dephasing. The greater the magnitude of local field inhomogeneities and the longer the spin evolution time of NMR experiments, the stronger the T_2-shortening effects due to secular relaxation contributions (Gillis and Koenig, 1987; Anand and Hirasaki, 2008). The sources of field inhomogeneity can be instrumental and/or intrinsic to the sample, such as those due to susceptibility constrasts at solid/liquid interfaces and at sharp discontinuities in the pore system, as well as to significant concentrations of para- and/or ferromagnetic centers at pore surfaces (Bryar et al., 2000). The latter circumstance is typical of earthenware rich in iron, which, being the most reactive element in ceramics, undergoes many firing-induced mineralogical transformations that strongly modify its magnetic features (Keating and Knight, 2007, 2008; Keating et al., 2008). Moreover, red ceramics, such as the archaeological samples discussed in this work, owe their color to the presence of hematite (Fe_2O_3), which forms by oxidizing firings at temperatures above 750 °C and exhibits the highest magnetic susceptibility among all pure Fe(III)-oxides. Therefore, not only pore space properties, but also the magnetic characteristics of iron minerals are strongly dependent of the firing history of ceramics.

In order to resolve and concurrently link these two firing-dependent features of ceramics, the NMR characterization of archaeological items was performed by means of T_1–T_2 correlation measurements (Ernst et al., 1987), which allow observing both T_1 and T_2 relaxation in one single experiment. The so-obtained two-dimensional probability density function $P(T_1,T_2)$ assigns a specific couple (T_1,T_2) of relaxation times to each spin population; thus, $P(T_1,T_2)$ correlates the *S/V*-dependence of T_1 and T_2 to the magnetic susceptibility effects that influence T_2 (Casieri et al., 2009). The NMR investigation was carried out by a portable NMR surface probe, which, unlike conventional NMR spectrometers, requires no sort of constriction on the volume or on the shape of samples (Blümich et al., 2008).

To test the validity of non-destructive ED-XRF and 2D NMR relaxometry for the investigation of ancient ceramics, we selected well-characterized ceramic specimens coming from the archaeological sites of Cuma and Miseno (Southern Italy). The chronological and stylistic classifications of these ceramics were previously determined by archaeologists, who also investigated the physical and petrographic characteristics of fragments by means of standard analytical procedures (De Rossi, 2004; Botti et al., 2006).

The article by Casieri et al. (2009) has shown the usefulness of two-dimensional NMR correlation maps in identifying reference ceramics materials for the estimation of firing temperature in some Miseno samples. The temperature assignment has proven coherent with the archaeological dating and with neutron scattering results obtained by Botti et al. (2006), so showing the validity of this method.

On the basis of this earlier work, we now aim at checking whether the combination of the ED-XRF compositional analysis with the T_1–T_2 NMR characterization of firing-dependent properties of well-characterized specimens is able to provide a valid description of their manufacturing signature.

2. The archaeological context

During these last years, the ancient cities of Miseno and Cuma in the Phlegrean area (Naples, Italy) have been interested by archaeological investigations aimed at clarifying the life continuity and the strategic importance of the Byzantine Duchy of Naples (Fig. 1).

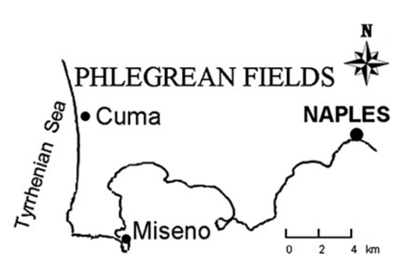

Fig. 1. The Phlegrean Fields area and the location of Cuma and Miseno.