

# Clays from the Bay of Naples (Italy): New insight on ancient and traditional ceramics

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## Abstract

The features of two clayey raw materials from the Bay of Naples and their fired products were investigated via minero-petrographic and physical techniques.

Clay preparation and firing dynamics were performed following a process similar to that performed by ancient and traditional potters. A high-CaO marine clay from Ischia was mixed with different amounts of volcanic temper in order to replicate most common ware. These mixtures show a fair mechanical resistance starting from relatively low firing temperatures (>850 °C). The addition of temper resulted in different technological characteristics. A low-CaO weathered pyroclastics from the Sorrento Peninsula was prepared to simulate heat resistant and refractory ceramics. Fired products are characterised by a less resistant ceramic body up to 1000 °C compared to Ischia ceramics. Despite worse strength these ceramics show a porous structure, yielding better refractory performances.

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## 1. Introduction

The objective of this study is to understand the technological potential of two different types of clayey raw materials for manufacturing ceramics, with particular attention to archaeological pottery and traditional technologies. Experimental firing was performed with two raw materials from the Bay of Naples area, which were selected from among a set of already characterised samples from the Campania region.<sup>1</sup> Our attention was focused on the Bay of Naples because the area is renowned for its rich archaeological record and for the presence of attested pottery production centres (e.g., Ischia, Cuma, Pompeii, Neapolis).<sup>1–7</sup> The two clays come from two different sites on the bay, the island of Ischia and the Sorrento Peninsula respectively,

and they are characterised by their different geological origin and minero-petrological composition. In particular, we considered the calcium oxide (CaO) concentration as a key feature, since it provides peculiar technological properties to the end-products.<sup>8–11</sup>

The raw material collected in the island of Ischia is a high-CaO clay (hereafter *HCC*; CaO > 6 wt.% after Maniatis and Tite<sup>9</sup>) and, despite the volcanic nature of the island, it is a marine sediment now outcropping at approximately 600 m above sea level following the Mt. Epomeo resurgence.<sup>12</sup> The historical and archaeological importance of Ischia is well known. The island is considered to be one of the first and most important production sites for pottery in the Bay of Naples, especially in the Hellenistic period, and its clay was most likely exported to supply the workshop on the coast in the Graeco-Roman period.<sup>2,3,7,13</sup> Pottery production on the island of Ischia and exportation of raw material as well are documented from the 16th to the 19th century A.D.<sup>14</sup>

The raw material from the Sorrento Peninsula is a low-CaO clay (hereafter *LCC*; CaO < 6 wt.%) deriving from weathered

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pyroclastic deposits. This raw material is currently exploited by a traditional ceramic workshop in Maiano, a small village of Sant'Agello (Naples), to produce bricks, mainly used to build wood-burning ovens and renowned for their refractory properties.<sup>1</sup>

In order to optimise the experimental procedures, the mix design and the ceramic test pieces were fired at different temperatures under oxidising conditions. Clay bodies were prepared according to the results from previous studies on Campanian wares (e.g., use of volcanic temper and its amount for specific ceramic classes),<sup>5,6</sup> as well as the knowledge of today's traditional craftsmen.

The Ischia clay was used either in the condition in which it was found or mixed with different percentages in weight of volcanic temper from the Campi Flegrei.

The clay body containing 0% or 10% of temper replicated the characteristics of fine ware,<sup>4,7,11,15,16</sup> 20% of temper was added to roughly simulate most common ware, amphorae, or bricks,<sup>4,15</sup> while 30% of temper was used to obtain coarse ware and bricks.<sup>5,6,15,17,18</sup>

The Sorrento clay was used to replicate heat resistant ceramics products (e.g., cookware) and refractory bricks, as this raw material has features suitable for this kind of product, namely low-CaO composition and high coarse grain content.<sup>19</sup>

The ceramic test pieces were analysed via mineralogical methods to obtain useful data for the interpretation of ancient ceramics in terms of technology and provenance, as well as to improve the existing knowledge on traditional ceramic manufacturing.

## 2. Experimental procedure

Ceramic test pieces were prepared using two clayey materials from the island of Ischia (IS; UTM coordinates: 33 T 408,283 mE 4,509,355 mN) and from the Sorrento Peninsula (SO; UTM coordinates: 33 T 449,430 mE 4,497,255 mN). Major details concerning their geological context are provided elsewhere.<sup>1</sup>

The volcanic beach sand used as temper (AQM; UTM coordinates: 33 T 419,359 mE 4,516,746 mN) in IS mixtures was sampled from the beach of *Acquamorta* in Monte di Procida (Campi Flegrei).

The grain size of clayey raw materials was determined by a wet method using standard sieves,<sup>20</sup> for the determination of the >74  $\mu\text{m}$  fraction (No. 200 ASTM sieve). The passing fraction was complementarily analysed by means of a sedimentation technique,<sup>21</sup> allowing the evaluation of the <2  $\mu\text{m}$  (clay fraction). The grain size of the temper was evaluated via a dry sieving method.<sup>22</sup> The Atterberg limits<sup>23–25</sup>: liquid limit ( $w_L$ ), plastic limit ( $w_P$ ), shrinkage limit ( $w_S$ ), and plasticity index ( $PI = w_P - w_L$ ), were also estimated to define the critical values of water controlling the different rheological stages of clayey sediments. The organic matter content was determined on pre-dried samples (overnight at 110 °C) through a loss on ignition technique, consisting of heating at 450 °C over 72 h in a muffle furnace.<sup>26</sup>

Four types of clay bodies were prepared with the clays from Ischia. The first type was prepared without any temper addition (IS), while the other three types were clay/temper mixtures prepared with 10% (IS-A), 20% (IS-B), and 30% (IS-C) in weight of temper. Weathered pyroclastics from Sorrento (SO) were prepared without any temper addition, owing to the natural abundance of coarse inclusions.

The clay bodies were prepared with extreme accuracy, leaving the clays in water for several hours until a semi-liquid consistency was obtained. Successively, the samples were dried until the proper plasticity was achieved. After that, the right amount of temper (10%, 20%, or 30% of clay dry weight) was added and the clay bodies were accurately kneaded to eliminate air excess. Samples were fashioned in a wooden mould (32 cm  $\times$  24 cm  $\times$  4 cm) and cut with a metal wire to obtain eight raw bricks (12 cm  $\times$  8 cm  $\times$  4 cm) per type of paste. Accurate drying of raw bricks was achieved in laboratory after 10 days under controlled thermo-hygrometric conditions ( $T = 25^\circ\text{C}$ ,  $HR = 50\%$ ).

Firing was performed under an oxidising atmosphere in an electric muffle furnace (Nabertherm HTCT 08/16) equipped with an electronic controller (Nabertherm P330). Control of the correct calibration of the firing temperature of the kiln was performed via the pyrometric cones (Orton type) method.<sup>27</sup> The firing process was reproduced to be similar to that which is currently performed by traditional potters from the Sant'Agello workshop, who use a wood-firing cycle of approximately 7–8 h. A slow initial heating rate ( $1.5^\circ\text{C min}^{-1}$ ), followed by a higher heating rate ( $3^\circ\text{C min}^{-1}$ ) starting at 200 °C to the maximum  $T$ , was followed by a soaking time of 90 min and then by a cooling according to the free drift of the switched off kiln. The bricks were quickly immersed in water after firing to set free from  $\text{Ca}(\text{OH})_2$  or CaO excess if present.<sup>28</sup>

Mineralogical analyses of the raw materials (clays and temper) and fired ceramics were carried out by means of X-ray powder diffraction (XRPD). A McCrone Micronising Mill was used to obtain a very fine powder ( $\sim 10 \mu\text{m}$ ).<sup>29</sup> The data were acquired with a PANalytical X'Pert PRO 3040/60 PW diffractometer (CuK $\alpha$  radiation, 40 kV, 40 mA, scanning interval 4–80° 2 $\theta$ , equivalent step size 0.017° 2 $\theta$ , equivalent counting time 120 s per step, RTMS X'Celerator detector). Identification of the clay phases was performed on oriented aggregates on fraction below 2  $\mu\text{m}$ . The data were obtained with a Philips PW 1710 diffractometer (CuK $\alpha$  radiation, 30 kV, 40 mA, scanning interval 3–35° 2 $\theta$ , step size 0.020° 2 $\theta$ , counting time 2 s per step) on air-dried samples and after thermo-chemical treatments (ethylene glycol solvation, 550 °C heating). A relative percentage of mixed layer phyllosilicates and the statistical layer ordering variable (Reichweite;  $R$ ) was also estimated according to Moore and Reynolds,<sup>30</sup> meaning that the mixed layer minerals may be randomly distributed ( $R = 0$ ) or ordered ( $R \geq 1$ ).

X-ray fluorescence spectrometry (XRF, PANalytical Axios instrument) allowed us to obtain chemical analyses of major oxides (wt.% of  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ) and trace elements (ppm of Rb, Sr, Y, Zr, Nb, Ba, Cr, Ni, Sc, V) of the raw materials and ceramics (detection

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