Studying the production technology of a set of archaeological ceramic sherds through magnetic and spectrometric measurements

Deyan Lesigyarski¹, Anelia Nikolova¹, Boika Zlateva²,³

¹ National Institute of Geophysics, Geodesy, and Geography – Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 3, 1113 Sofia, Bulgaria; e-mails: dlesigyarski@geophys.bas.bg, anikolova@abv.bg
² Faculty of Chemistry and Pharmacy, Sofia University “St. Kliment Ohridski”, 1 James Bourchier Blvd., 1264 Sofia, Bulgaria
³ Centre of Archeometry with Laboratory of Conservation and Restoration, Sofia University “St. Kliment Ohridski”, 35 Galichitsa Str., 1264 Sofia, Bulgaria; e-mail: ahbz@chem.uni-sofia.bg

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Abstract. An interdisciplinary approach is applied to study a set of 50 archeological ceramic sherds dated to a broad period, from the Early Bronze Age to the Late Medieval in Bulgaria. The sherds originate from a single archeological site in the northwest part of the country, situated near the village of Tarnyane, Vidin District, and can be characterized both as local and import production. Using laboratory magnetic susceptibility measurements, as well as X-ray fluorescence, the elemental composition and maximum firing temperatures of the specimens are characterized. The results obtained are taken into account to draw conclusions about the clay used as well as the high-temperature technology applied for the production of the ceramic vessels referred to different periods and purposes (mainly kitchenware and tableware). This allows for shedding light on the technological skills of the societies that produced the studied specimens, especially for the earlier ages.


Keywords: archeometry, ceramics, magnetic susceptibility, X-ray fluorescence.

INTRODUCTION

Ceramic materials are the most common finds in the study of archeological sites. Usually, they include a rich variety of samples, depending on the economic and social conditions in which they were made. Due to their remarkably high resistance to the effects of the environment, they preserve to this day very valuable information about the social and technological development of past societies (Hein and Kilikoglou, 2017). In this regard, any information about the technology used to make the ceramic finds is extremely useful in the analysis of archeological data. Obtaining such information is the aim of the present case study. For that purpose, a set of 50 archeological ceramic sherds, as well as ten clay samples, have been analyzed by rock-magnetic and spectrometric methods. All of the specimens investigated were discovered at rescue archeological excavations in 2021 during the construction of the Vidin–Montana highway (northwestern Bulgaria). The site was located on the territory of Tarnyane Village, in the vicinity of the small Voynishka River. Head of the excavations was Dr. Elena Vasileva. An Early Bronze Age (EBA, about 2000 BCE) housing area, followed by later Iron Age (IA) structures, and a Late Medieval (LM, 15th–17th century CE) settlement and necropolis appeared during the excavations on an area of approxi-
mately 0.13 km². The ceramic sherds for this study are dated mainly to the EBA and LM periods. No entire vessels were analyzed.

From the very location of the ancient settlements, samples were taken from the loess-clay deposit of the site, and a total of ten structures (open pits) were sampled (one sample per structure). It should be noted that the content of the sand fraction in the tested clays is visibly high. These clay samples belong to different stratigraphic layers and were later analyzed by X-ray fluorescence (XRF) in order to check their elemental composition’s resemblance to that of the ceramic specimens’ clay matrix.

**METHODOLOGY**

The elemental composition of the studied samples was quantified, using X-ray fluorescence spectral analysis (XRF) on a Bruker Titan S1 portable instrument. The element determinations were carried out in the “Geochem Trace” mode of operation, with a duration of 1 min for each measurement. The concentrations of 24 chemical elements were determined: Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Ba, and Pb.

For the determination of the maximum firing temperatures ($T_{\text{max}}$), an experimental procedure was applied, involving stepwise heating of selected samples in a laboratory furnace in the range of 300 °C to 1100 °C (35 steps in total) and measuring their magnetic susceptibility $K$ (AGICO Kappabridge KLY-2 instrument) after cooling to room temperature at each step (Rasmussen et al., 2012). Mass-specific susceptibility ($c$) was then calculated by dividing $K$ to the sample’s weight. The sharp change in the $c$ values means that significant changes in the (magnetic) mineralogy occurred and, therefore, indicates the point at which the laboratory temperature exceeded the ancient firing temperature (Fig. 1). The approximate accuracy of this determination is in the range of 20 °C.

**RESULTS AND DISCUSSION**

The concentration values of some of the elements determined are summarized in Table 1. Compared to the raw clay materials analyzed, the pottery fragments show significantly lower Ca content, especially for those dated to the Middle BA, Late IA and Late Medieval. From a technological point of view, such a result should be expected. Calcium content up to 3–4% in the clay matrix serves as a flux during the high-temperature treatment and facilitates the formation of ceramic material of higher quality (Ceccarelli et al., 2014). A larger amount of CaCO$_3$, however, could cause cracks in the ceramic vessel due to the expansive gas evaporations and, therefore, washing the excess calcareous amount of the raw clay during its initial preparation for pottery production was a preferred procedure among ancient potters.

Statistical treatment of the data obtained by XRF analysis was performed in order to separate the specimens produced by the clay material analyzed or by different clay types and, with a great probability, in separate production centers. Results obtained by cluster analysis (Ward’s method, Statistica 10 software) show the distribution of the samples in four clusters, where significant parts of the EBA fragments, Late Medieval fragments, and clay sam-

![Fig. 1. Examples of the maximum firing temperature determinations using mass-specific magnetic susceptibility measurements.](image)

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samples are separated into three clusters: 80%, 60%, and 90% of the specimens, respectively. Thus, it appears that most of the ceramic fragments referred to the different periods are actually made of clay material that does not match the elemental composition of the sampled clay deposit.

Summary information on the investigated fragments and the experimentally determined maximum firing temperatures ($T_{\text{max}}$) is presented in Table 2. For each fragment, a specific value of $T_{\text{max}}$ was determined, and in the last column of Table 2 is the interval between the lowest and the highest values, which includes the remaining $T_{\text{max}}$ determined for the corresponding group of fragments.

According to the values obtained, the average $T_{\text{max}}$ is higher for medieval pottery, especially concerning the glazed tableware. The trend towards an increase in the determined maximum firing temperatures for the nearer-to-modern finds was also observed in earlier experimental studies of ceramic artifacts performed at the Laboratory of Paleomagnetism (Kostadinova-Avramova et al., 2018). On the other hand, the medieval values have a more inhomogeneous distribution compared to those obtained for the earlier (Bronze Age) vessels. This may be a sign by which the two groups of samples with different dates can be distinguished.

**CONCLUSION**

Applying both magnetic and spectrometric measurements appeared very useful when studying the provenance and production technology of archaeological pottery artifacts. That way, in this case study, it is possible to use the analytical data to distinguish between pottery production dated to the Early Bronze and Late Medieval ages. It can be concluded that medieval pottery was produced by applying higher firing temperatures, especially for the glazed vessels. However, there is no clear evidence that any of the examined ceramics were produced in situ, using clay from the sampled locality.

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