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MULTI-METHOD ANALYSIS OF BRONZE AGE CERAMICS FROM SATU-MARE COUNTY, ROMANIA

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ABSTRACT Bronze Age settlements have been discovered in the region of river Eriu, Satu Mare County, Romania. This study includes the archaeometric examination of eight ceramic artifacts dated from Early to Middle Bronze Age, representing the Otomani culture. The used methods were petrography, scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR) and thermal analysis (thermal gravimetric analysis - TGA and differential scanning calorimetry - DSC). The study of archaeological ceramics needs an interdisciplinary approach, where the scientific research can have an important role in supporting the archaeological study. Our aim was to support by scientific methods the archaeological assumptions, which describe the culture, their knowledge and opportunities. For this purpose we wanted to select the most appropriate measuring methods and how can the measuring results complete each other for a complex description of the culture. Therefore, the evaluation methodology of the measurement data was given an increased importance. The selection of the samples depended on archaeological background, therefore the samples allowed a case study for the testing of the measuring methods. The mineral-petrographic analysis included the approximation of firing temperature, identification of potential raw material sources, similarity between samples and the determination of the technology used. Additional objective was the establishment of usability for the testing methods to have accurate measurements. Loam from the region was also analyzed and compared with the results of the ceramic samples.

Keywords: *ancient ceramics, physical and mineralogical analyses, reference loam, Bronze Age, Otomani culture, Romania*

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INTRODUCTION

The excavated ceramic artifacts represent the culture of Carei in the second millenium B.C. The settlement concatenation named Bobald established a culturally varied society which entailed numerous finding collections. In this North-Romanian region could evolve an unified ceramic direction.

The first human settling on the plain of Carei was in the late neoliticum. Later in the third part of the early Bronze Age the Sanislau group dominated the region. In the middle Bronze Age the settlement concatenation of Bobald developed its own culture without secedeing from the Otomani culture. The middle Bronze Age can be divided into three parts, each of them note another developing stage in the Otomani culture (*Fig.1).*

The existing settlement concatenations had a central and more, smaller settlements which were located in form of a satellite ring. In case of Carei-Bobald five ancient settlements together with the central settlement created a concatenation with representative pottery and bronze culture.

The characteristics of the artifacts can be determined by proper evaluation of the measurement results, but these are not always precise, depending on the method used or on the fact that the properties of the clay depend on several factors between the moment of manufacturing and measuring, like usage, burial, excavation, cleaning and storage, which appear as critical effects.

Due to this fact it is important to reduce the available measuring methods for more accurate results. It is also important the comparative study of the local, reference loam with the artefacts, since they can form the basis for the determination of composition and helps also in the reconstruction of the technology used. This permits the closer examination of the culture from Bronze Age.

Figure 1. The map of excavation locations in Satu Mare County (Berveni, Capleni, Carei, Tiream, Andrid and Pir). The settlement Sanislau represents source the cultural influence in this region besides the Otomani culture.

RESULTS AND DISCUSSION

The aim of the study was to use the results of different measuring methods to scientifically describe the given culture from Bronze Age. This means a wider data set but in the same time more valid information. The information received from one of the measurements complete or form the basis of evaluation in case of another measured data.

Besides the supplement of the archaeological background we also wanted to test the usability of the methods to find the necessary and sufficient information amount for future measurements.

Petrography

A significant similarity was observed in the color of the samples varying shades of gray to black, referring to reductive firing conditions. The only exception was represented by sample no. 12 with a sandwich structure of black interior and lighter outer layers. This layered texture suggested a short-term firing, where the oxygen diffusion was insufficient to unify the color.

The matrix is considered relatively homogenous, however iron aggregates can be also found in some cases. It can be also observed the presence of ceramoclasts in each sample, which makes up 2-3 % of the matrix. The 1 mm thin layer on the outer wall indicates subsequent modification, not an alteration-taking place during firing process.

According to the granulometry, samples can be divided in two categories, medium-fine-grained and coarse-grained ceramics with the maximum particle of 1-2 mm. Based on the ratio between crystalline vs. amorphous phases in the matrix, two fabric types can be defined: microcrystalline and microcrystalline to microcrystalline - amorphous The characteristic of the matrix and also the dominant presence of illite, kaolinite and montmorillonite confirmed a lower firing temperature than 900°C.

The crystalloclasts are represented by quartz, micas (muscovite and biotite) [1], iron oxide (hematite) and plagioclase as part of the feldspar group (albite, anorthite), epidote, garnet and zircon [2], [3], [4]. The calcite, which is present on the fissures, also suggests that the firing temperature didn't exceed 850-900°C.

The porosity had limited values varying between the pore size of 0.5 x 1.5 and 2.0 x 3.0 mm. This could be observed in case of long, elongated pores, which extended parallel with one another, as in the case of the secondary, irregular pores.

The oval shape of the pores and the parallel position of the mica also reflected the production technology, which in this case was plastic squeezing. The specific properties of the samples can be seen on *Table 1.*

Table 1. The results of the SEM, XRD and petrography analysis:

Sample No.	Estimated Firing Temperature (°C)		Composition
	SEM	XRD	Petrography
1.	700-900	700-850	Crystalloclasts (quartz, micas) Ceramoclasts in a microcrystalline matrix
2.	~ 900	700-850	Microcrystalline matrix with carbonate and quartzite litoclasts Crystalloclasts (garnets, zircon, micas)
3.	~ 700	750-850	Microcrystalline matrix with ceramoclasts Aggregates of iron oxides-hydroxides Crystalloclasts (feldspar, quartz, micas)
4.	700-900	700-850	Microcrystalline matrix with ceramoclasts Carbonatic litoclast Crystalloclasts (quartz, micas)
5.	< 900	700-900	Crystalloclasts (quartz) Ceramoclasts
6.	700-900	700-900	Microcrystalline matrix Secondary calcite on the wall Carbonatic litoclast Crystalloclasts (quartz, micas)
11.	700-900	750-900	Crystalloclasts (quartz) Ceramoclasts
12.	700-900	750-900	Microcrystalline matrix with iron oxide-hydroxide aggregatess Crystalloclasts (feldspars, quartz, micas)

SEM/EDX

EDX analysis

Due to the examination it was ascertained the composition of the reference loam and all of the artifacts.

The composition varied from sample to sample; even so the main chemical elements were silicon, aluminum and oxygen. The additional components also didn't show significant variety, which increased the probability of raw materials from the same region.

The composition of the reference loam was compared with the ceramic artifacts. The widest similarity showed sample no. 3 which refers not only to the components but also to the weight percentage values. This result sustained the usage of similar raw materials in this case. Due to this where only one measurement was possible sample no. 3 was analyzed.

SEM analysis

The first case is the reference loam fired at 300°C (*Fig. 2; letter a*) the rough grains, sharp particles such as lumpy texture was representative and no sign of softening appeared.

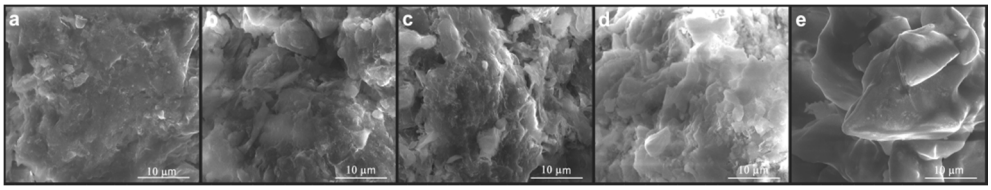

Figure 2. The SEM images of reference loam fired at 300°C (a), 500°C (b), 700°C (c), 900°C (d) and 1100°C (e).

Firing the reference loam at 500°C (*Fig. 2; letter b*) no considerable external changes appeared similar as above.

Firing the loam at 700 (*Fig. 2; letter c*) and 900°C (*Fig. 2; letter d*) it could be seen that the increase of the temperature still didn't affect significantly the surface of the particles, however, the grains started to stick together and the individual particles started to form larger ones.

The most remarkable change was observed by firing the reference loam at 1100°C (*Fig. 2; letter e*): it could be seen that the interface was completely changed, the particles were merged and the surface was softened.

The firing temperature estimation was based on the 2000- and 4000-fold magnification images, which were compared to the images made on the reference loam. The samples no. 1, 4, 6, 11 and 12 the estimated firing temperature range was 700-900°C. In case of sample no. 2 and 5 the temperature trends to 900°C while at sample no. 3 this value is 700°C [5].

As an overview: the determination of the firing temperature was difficult in the interval 300-900°C which can be attributed to several factors like the point wise analysis and the powdered form of the artifacts.

On the other hand, the morphological changes were hardly detectable under 1100°C as it was in case of reference loam. Although the effect of increasing firing temperature was plain, the estimation of firing temperature was difficult; therefore the interval was wider, which can be seen in *Table 1*.

XRD analysis

XRD analysis of reference loam

Through the XRD analysis the phase transitions during firing and the representative stability intervals for the components were studied.

The evaluation of the diffractograms was made by program Match 1.9a. Therefore it was detected the mineralogical composition, in addition, the program enabled the weight percent proportion of the samples by a semi-quantitative analysis based on the ratio of intensities.

Quantitatively the most relevant mineral was quartz, which appears as α-quartz and turns into β-quartz at 573°C [6], respectively appears as α-cristobalite. As a component of feldspars anorthite is also present in significant quantities. As part of the same mineral group microcline and albite appeared as well. Kaolinite and illite, the representatives of the clay mineral group were present in varying degrees. In addition the presence of many other minerals was detected despite their low intensities or due to the concurrence of peaks.

The possible components confirmed the presence of the elements presented by EDX analysis. The main elements were oxygen, aluminum, carbon and calcium, which appear as the spectra's main components forming quartz and anorthite.

Changes can be observed during the rising of temperature by the disappearance or formation of phases depending on temperature.

At 300°C and 500°C due to the low temperature the main component was α-quartz marked in the black part of the columns on *Fig. 3*. As the firing temperature was higher the rate of the quartz increased as well, which could be attributed to the decomposition of other phases at lower temperatures.

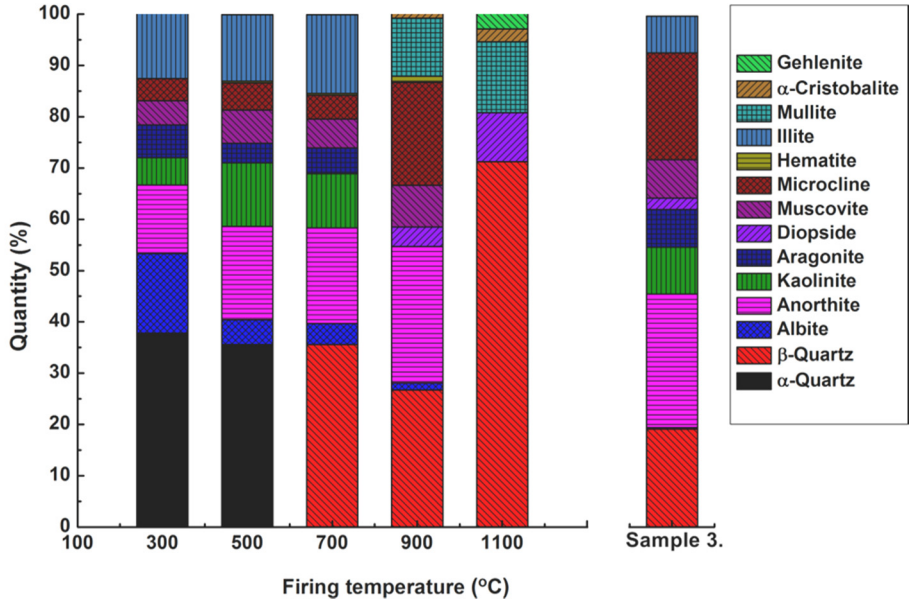

Figure 3. The mineralogical composition of reference loam fired at different temperatures by the semi-quantitative analysis of the program used.

The representatives of the plagioclase group, namely anorthite, and albite, microcline were also present at all firing temperatures, excluding 1100°C. In this wide temperature range these phases were stable [7], [8], [9]. Moreover their proportion was still growing compared to the other phases [10], [11], [12], [13]. Mica was thermally stable up to 500°C [14], but its presence was demonstrated in case of 700 and 900°C as well which could be attributed to a form of muscovite which was stable below 1100°C. The aragonite belonging to the carbonates group it wasn't stable at higher temperatures: it started its decomposition into CaO and CO_2. The studies revealed the presence of aragonite up to 700°C, above this temperature it wasn't demonstrable. The presence of the feldspars and carbonates increases the plasticity of the material, resulting the decreasing of the sintering temperature and a compact product below 1100°C [15].The kaolinite decomposes to meta-kaolinite around 550°C and forms Al-Si spinel above 925°C, at 1100°C forms mullite and cristobalite. This phase transition can be followed on *Fig. 3*. The kaolinite appeared above 550°C due to the fact that the presence of kaolinite and meta-kaolinite couldn't be distinguished. Since the temperature scale was wide, it couldn't be observed the transformation of meta-kaolinite into spinel.

In addition the participation of the mullite and α-cristobalite denoted the phase transition.

Illite was stable until 750°C, at higher temperature starts its decomposition and ends around 950-1000°C in oxidizing atmosphere, it ends around 850°C in reductive atmosphere, which may result new phases like diopside, anorthite. The formation of new phases brings in the decrease of the amount of illite and the increase of the amount of new phases at higher temperatures [7], [15].The presence of gehlenite and diopside was observed at 900 and 1100°C, with an increasing proportion. The larger the quantity of CaO is, the higher is the amount of minerals with calcium content, meaning diopside, anorthite and gehlenite [15].

Minerals diopside and mullite are able to take in Fe^{3+} ions due to their crystal structure. Therefore the formation of free iron-oxide (hematite in our case) is not necessary [15]. Nevertheless hematite appeared in small amount at 900 and at 1100°C, which can be attributed to the former fact.

XRD analysis of the artifacts

The estimation of firing temperature of the ceramic artifacts was based on searching for discontinuities in any physical property that can be linked to a specific temperature interval. The description of the culture was performed by more measuring methods. The firing temperature was deduced from XRD results and mineralogical analysis [16].

The type of the clay mineral and the structural changes due to firing were studied by FT-IR and also by SEM as methods for the confirmation of firing temperature. The XRD was used basically for the identification of minerals [17].

The X-ray patterns of the samples were evaluated similarly to the case of reference loam. Based on the weight percentage by the program Match 1.9a and mineral stability it was made a comparison between the reference loam and sample results to estimate their firing temperature.

The mineralogical composition of the samples is presented in *Table 2*. The main components of the ceramic artifacts belong to the silicates group and it was also significant the presence of oxides and carbonates [18]. The representatives of the silicate group were the clay minerals (mainly illite and kaolinite), micas and feldspars.

Table 2. The mineralogical composition of samples according to the interpretation of the X-ray patterns

Sample No.	1.	2.	3.	4.	5.	6.	11.	12.
Illite	×	×	×	×	×	×	×	
Kaolinite	×	×	×	×	×	×		×
Montmorillonite	×	×	×	×			×	×
Muscovite			×	×	×	×	×	×
Biotite				×		×	×	×
Anorthite	×	×	×	×	×	×	×	×
Microcline	×	×	×	×	×	×	×	×
Albite			×	×	×	×	×	×
Mullite								
Diopside			×	×	×	×		×
Epidote				×				
Zircon				×		×		×
Quartz	×	×	×	×	×	×	×	×
Hematite	×	×		×	×			
Aragonite	×	×	×	×	×	×		×

Considering the weight percent proportion of the appeared elements, no wide variation was observed. The slight variations in the composition of ceramics can be attributed to the slight difference in raw materials or due to the prolonged or repeated exposure to heat, in addition could have differed in the speed of heating.

Compared to the artifacts in case of reference loam couldn't be detected more of the minerals, like epidote, zircon, biotite and montmorillonite. Due to their absence they weren't used for the estimation of firing temperature.

Sample no. 1 contained anorthite and microcline, whom presence supported the firing temperature below 1000°C.

The large amount of illite suggested that this temperature could not exceed immoderately 750°C and it was less than 900°C. The absence of mullite and the amount of carbonates alluded to the firing temperature less than 850-900°C.

Similarly to the latter case, sample no. 2 contained anortite and microcline indicating the firing temperature below 1000°C. The presence of illite, kaolinite (meta-kaolinite) and the absence of mullite, diopside also suggested 900°C as upper limit. The dominance of anorthite compared to illite marked the beginning of decomposition at 700-750°C.

In case of sample no. 3 the reappearence of anorthite, microcline and muscovite meant a firing temperature below 1000°C. This value was changed to 850-900°C by the presence of illite, kaolinite (meta-kaolinite) and carbonates because at this level it started their decomposition.

The diopside in samples no. 4, 5 and 6 indicated a firing temperature above 750°C. The upper limit was 850-900°C shown by the feldspars, muscovite, carbonates, illite and kaolinite.

In the sample no. 11 the illite and anorthite suggested a firing temperature at 700-750°C, the upper limit marked by the illite, feldspar and muscovite as 900°C.

In case of sample no. 12 the absence of illite and mullite, the appearence of diopside, anorthite, feldspar and muscovite clearly assumed a temperature above 750°C and below 900°C.

FT-IR analysis

The FT-IR spectroscopy was used in case of reference loam fired at different temperatures and also on sample no. 3.

The appeared bands sustained the presence of silicates, carbonates and oxides (mainly quartz and iron-oxide). The broadening of the spectral lines can be attributed to the overlapping of the peaks.

The dominant mineral was quartz, which made an appearance at 796-798 cm^{-1}, 778-780 cm^{-1} and 692-694 cm^{-1} wave number values [19], [20]. The clay minerals were identified and differentiated from each other at 3432 cm^{-1} (montmorillonite) and 1033-1038 cm^{-1} (kaolinite) [20], [21]. The peak at 3432 cm^{-1} can be also attributed to absorbed water molecules derived from the measurements or the burial of the samples [22].

The presence of iron-oxides (hematite) was indicated by the peaks at wave numbers between 519-527 cm^{-1} and 469-472 cm^{-1} which also supports the conception of firing temperature above 600°C [20]. Several bands indicated

the feldspars in the samples, the shoulder at 552-563 cm^{-1} (microcline), the peaks at 479 cm^{-1} and between 429-435 cm^{-1} (anorthite and albite) wave numbers [20].

The strong peaks of the silicates (kaolinite) could be easily identified being centered between 1033 and 1038 cm^{-1} wave numbers due to the Si-O bond vibrations [20].

Organic matter was detected by a shoulder at 2957-2958 cm^{-1} and the wave numbers 2923-2924 cm^{-1} and 2848-2853 cm^{-1}, whom presence could be attributed to subsequent burial or rehydratation during use. This theory was based on their showing in case of samples fired above 800°C where the organic materials aren't supposed to be present [19].

The carbonates were present by the wave numbers at 875 and 712 cm^{-1}, which implied to a lower firing temperature or to a post-burial of the samples [20].

The Si-O-Al deformation vibrations at 519-527 cm^{-1} were attributable to the aluminum remained in the octahedral sheet [20]. This bond indicated the iron-oxides (hematite) which were formed by the substitution of aluminium with iron during the firing process around 600°C [18], [21], [22], [23].

DSC and TGA analysis

The thermal gravimetric analysis and differential scanning calorimetry are basic methods for monitoring the physical and chemical transformations in ceramics. The method can be used in the estimation of thermal- and decomposition properties. In addition it is useful to follow the changes in weight of samples.

The evaluation of the TGA and DSC curves of the sample no. 3 showed the loss of adsorbed water in the interval 40-140°C by two endothermic peaks, which could be also identified on the TGA curve by a significant weight loss.

The next endothermic peak around 280°C was attributed to the organic matters remained in the samples. The endothermic peak between temperatures 400-600°C denoted the dehydroxilation of clay minerals by the loss of hydroxyl groups in kaolinite and illite. While illite retained its distorted structure, kaolinite decomposed into meta-kaolinite.

Calcium-carbonates decomposed into calcium-oxide and carbon-dioxide in the range of 600-800°C, which indicated a remarkable weight loss on the TGA curves. In the same time appeared a strong endothermic peak on the DSC curve.

Subsequently, around 900°C it started the shrinkage of the ceramic body. In addition at this temperature level other processes may also occur resulting by the crystallization of other minerals.

The reference clay measured in natural form was characterized by less clear curves. The place of the peaks was similar to the case of sample no.3, the peaks were in the same temperature range only slight differences appeared [24].

It is a question whether the exothermic peaks in both cases around 950°C are the signs of the crystallization of new minerals or just simply measuring failures [25]. The answer needs the repetition of the measurements, which is now a future plan.

CONCLUSIONS

The comparison of the ceramic samples with the reference loam denoted a large advantage not only in the definition of the simple properties but also in the estimation of firing temperatures resulting in more accurate assessment. By firing the reference loam at different temperatures the physical and chemical changes and transformations could be detected.

As a first conclusion, the chemical composition of the reference loam was similar to those used by ancient potters, which was not only confirmed by EDX but also by XRD analysis. Due to the similarity the loam could be used as reference in further evaluations.

As a second result of our investigation we concluded that XRD was the most convenient method for estimating the firing temperature. With the proper evaluation of the diffractograms the phase composition could be detected, which referred to the temperature of the furnace. In each case a firing temperature interval was given according to the phase composition.

The further conclusions were that the SEM investigations as an auxiliary measuring method confirmed the firing temperature intervals from the XRD analysis, although the method was less reliable by detecting only visually the changes in morphology.

Also DSC and TGA measurements provided simple and reliable complementary results referring to the study of the physical and chemical processes, which occur at firing, the most relevant changes were the transformations like the decomposition of hydroxyls or the carbonate decomposition.

As a supplementary method, FT-IR was used to confirm the presence of minerals by the corresponding bonds on the spectra. By this method the peaks of the silicates (mainly clay minerals), carbonates and quartz were identified.

The petrographic studies not only made it possible the analysis of texture but also provided information about mineral composition to complement the firing temperature and technology estimation and also the comparison of samples.

EXPERIMENTAL SECTION

Sample preparation and analytical techniques

For the purpose of archaeological study eight ceramic fragments were selected from the excavations in Satu Mare County, three of them stem from Carei and the rest from surrounding settlements, which can be seen on *Fig. 1*. Loam from the excavation deposit founded in Carei was also analyzed.

The sample preparation of the ceramic depended on the method used. The reference loam was fired at different temperatures, 300, 500, 700, 900 and 1100^{o}C for two hours. This permitted to follow the compositional changes in the material during firing. The upper limit of the firing temperature was 1100^{o}C, although Bronze Age technology might not reach such high temperatures, but it was representative regarding the phase transitions in the material.

The petrographic study consisted of two parts, the macroscopic examination made by Nikon SMZ 645 stereo microscope and the type used for microscopic study was Nikon Eclipse E200.

Scanning electron microscopy was coupled with energy-dispersive X-ray analyzer (spot size of 10 μm). This method allowed the analysis of the ceramic powder.

Scanning electron microscopy was performed by Philips XL30 ESEM-FEG device. The SEM images of the reference loam fired at different temperatures were used to reveal the changes in morphology. These were studied on the 2000-fold, 4000-fold and also on the 8000-fold enlarged surface.

X-ray powder diffraction patterns were measured by diffractometer Shimadzu XRD 600 with Cu-Kα radiation.

Fourier-transformed infrared spectroscopy was carried out by Jasco FT-IR 615, the samples were measured in form of KaBr pellets (300 mg KaBr mixed with fine powder of 1-1.2 mg sample). The spectra were obtained in the range of 4000–400 cm^{-1}.

The thermal gravimetric analyses were performed on a SDT Q600 (V20.9 Build 20) instrument.

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