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SEM AND EDX CHARACTERIZATION OF ANCIENT POTTERY

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The potentialities of scanning electron microscopy (SEM) along with energy dispersive X-ray (EDX) analysis in assessing the chemical and mineralogical composition of ancient pottery are investigated. The results of SEM and EDX analytical characterization of the Bronze Age pottery from different regions of Lithuania are presented. Six samples of historical ancient pottery from five different archaeological complexes (villages Stanaičiai, Turlojiškės, Žvainiai, Nikėlai, and Jurgaičiai) were analysed. It was concluded that investigated pottery samples from different districts of Lithuania showed different chemical and phase compositions, possibly due to the different fabrication conditions.

Keywords: Bronze Age, Lithuania, ancient pottery, archaeological ceramics, microstructural, morphology, and elemental composition

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1. Introduction

Pottery is the most numerous group of the Bronze Age finds. Pottery analysis reveals important information about the daily life as well as the ethnical and cultural aspects of the society of the period. Moreover, the physical-chemical characterization of pottery used in ancient times provides historical and technological information regarding its manufacture [1–3]. Thus, the knowledge of chemical and mineralogical compositions is mandatory in the characterization studies of pottery. The chemical composition mainly depends on the raw materials, as well as on the processing and depositional changes. The mineralogical composition depends on both the initial composition and the processing as minerals are the "fingerprints" of the stable and metastable solid phases formed during firing [4–8]. Therefore, careful characterization of ancient pottery is a very important task not only to archaeologists but to materials scientists and people working in the field of conservation chemistry as well [9–11].

Until quite recently Lithuanian archaeologists have been basically using the visual observation method to characterize the Bronze Age pottery. They described vessel shapes, surface decoration, ornamentation, temper in the clay body, thickness of the walls and base, etc. Such a visual observation of pottery is indispensable, but it is just the first step of investigation. A more detailed chemical and physical analysis of pottery is lacking. In the present study, attention has been focused on the characterization of pottery samples obtained from different regions of Lithuania using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The main aim of this study was to explore the potentialities of the above-mentioned methods of analysis in assessing the microstructural, chemical, and mineralogical composition of ancient pottery.

2. Experimental

The Bronze Age pottery samples found in different Lithuanian villages were chosen for the characterization. Six samples of historical ancient pottery from five different archaeological complexes (Stanaičiai, Turlojiškės, Žvainiai, Nikėlai, and Jurgaičiai) have been selected. Two different types of ceramics from Stanaičiai village (rough and flat) were analysed. The exact locations of the above mentioned archaeological complexes are presented in Fig. 1.

The morphology, microstructure, and elemental composition of all pottery samples were examined using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The measurements were recorded under vacuum in the specimen chamber of the scanning electron microscope EVO 50

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Fig. 1. Location of archaeological complexes of Stanaičiai, Turlojiškės, Žvainiai, Nikėlai, and Jurgaičiai villages (Lithuania).

(United Kingdom) equipped with the energy dispersive X-ray spectrometer (Oxford Instruments) and operating in secondary electron mode. The used accelerating voltage was 20 keV, and the working distance was 10 mm. The cation content was analysed using L, K lines.

3. Results and discussion

The measurement of the wavelength (or energy) of each characteristic X-ray that is emitted when electrons with several kilovolts of energy strike a solid specimen enabled us to find out which main elements are present in the pottery samples, i. e., to carry out a qualitative analysis [12]. The EDX spectra obtained for two samples from Stanaičiai village (rough and flat) are shown in Fig. 2. One can see that the main cations detected in both EDX spectra are silicon, aluminium, potassium, iron, and magnesium. The well resolved oxygen line is also seen in the spectra of both samples indicating the metal oxides to be the main crystalline phases in the Stanaičiai pottery. Moreover, from the EDX spectrum of the flat sample, phosphorus can also be detected in this ceramics. The EDX spectra of the historical pottery from archaeological complexes of Turlojiškės and Žvainiai are presented in Fig. 3. Despite the fact that

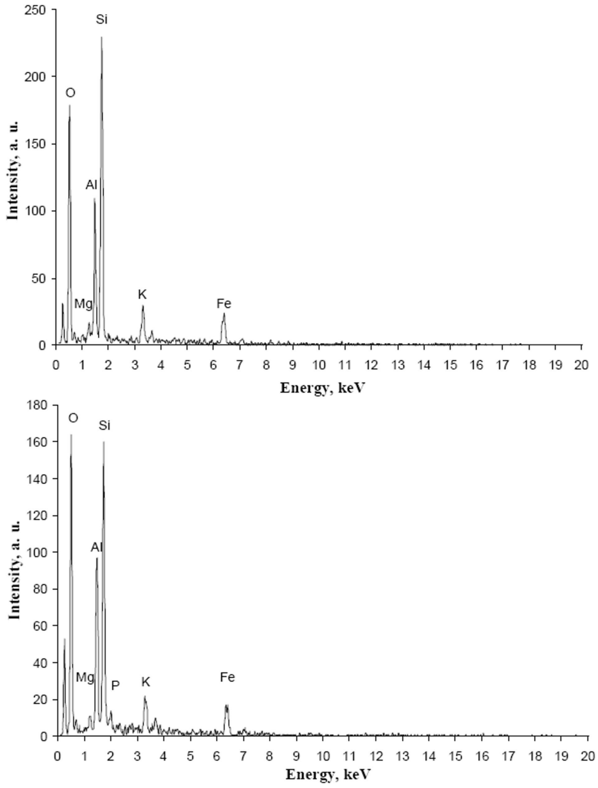

Fig. 2. Energy dispersive X-ray spectra of pottery samples from Stanaičiai village: rough sample (at the top) and flat sample (at the bottom).

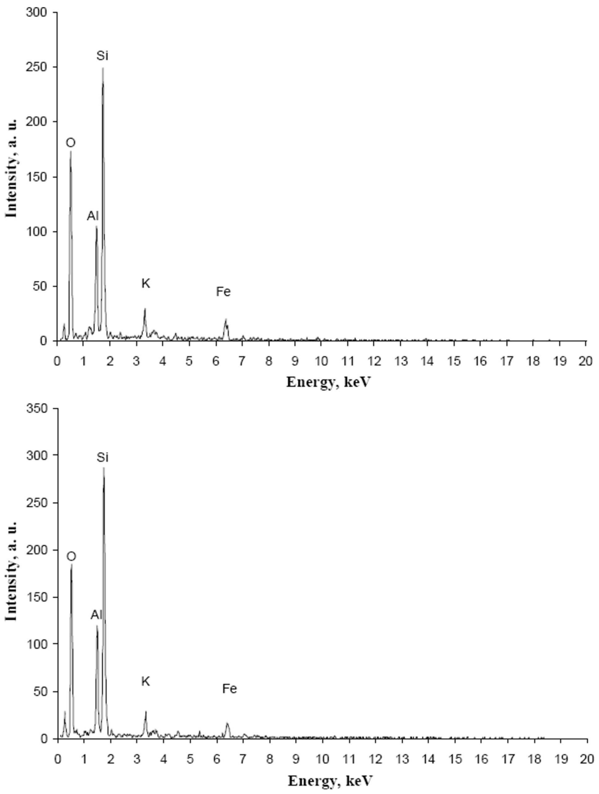

Fig. 3. Energy dispersive X-ray spectra of pottery samples from Turlojiškės (at the top) and Žvainiai (at the bottom) villages.

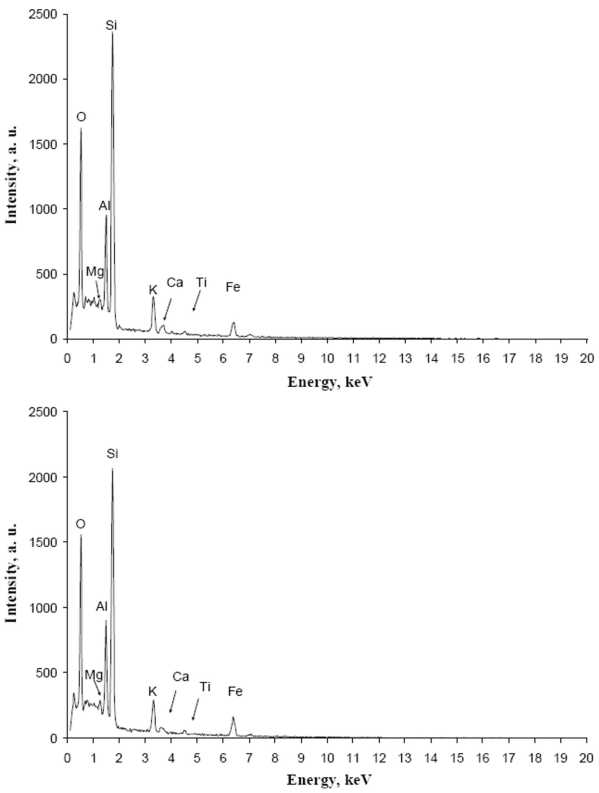

Fig. 4. Energy dispersive X-ray spectra of pottery samples from Nikėlai (at the top) and Jurgaičiai (at the bottom) villages.

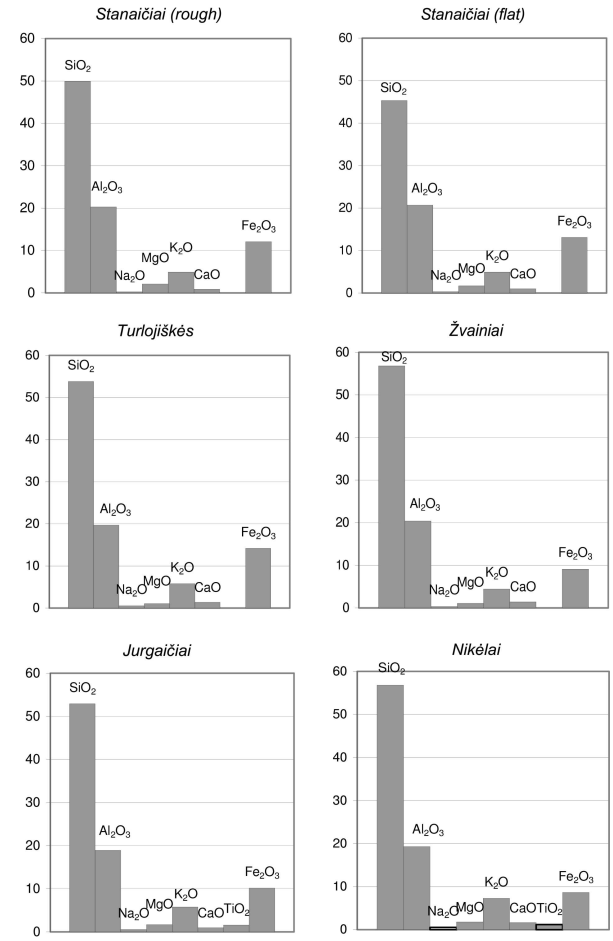

Fig. 5. Major oxides (%) found in the archaeological pottery samples.

villages Turlojiškės and Žvainiai are located in different regions of Lithuania (Southwest Lithuania and Northwest Lithuania, respectively) both EDX spectra are very similar, indicating the presence Si, Al, K, and Fe in the samples. These results suggest that the analysed pottery specimens have similar history in view of used raw materials or manufacture conditions. The possible shipping of pottery from one place to another could also be considered. The appearance of magnesium, calcium, and titanium along with Si, Al, K, and Fe in the EDX spectra of pottery samples from Nikėlai and Jurgaičiai is evident (Fig. 4). Again, these two spectra are almost identical. This is not surprising since both archaeological complexes are located at a walking distance from each other.

From data of qualitative analysis only the dominating elements in pottery samples were detected. The lower concentrations of other satellite elements could also be determined. Thus, using the scanning electron microscope we can obtain compositional information, however, a quantitative analysis of synthesized samples could be carried out as well. The measurement of the amount of X-rays of any type emitted per second could tell us how much of the element is present. The average metal ratios determined by energy dispersive X-ray analysis in the pottery samples and expressed as metal oxides [13] are summarized in Fig. 5. As can be seen, the silica, alumina, and iron oxide predominate in all ceramic samples. However, the determined low concentration of CaO in comparison with the K_2O amount was rather unexpected [3, 13].

Scanning electron microscopy was also employed for the investigation of specific surface morphological features of ancient pottery [14–16]. The micrographs obtained in secondary electron mode for two samples from Stanaičiai village (rough and flat) are shown in Fig. 6. As can be seen, the surface morphology of these two samples is quite different. These micrographs give a direct view on the densification, which is a very informative feature about the technology used [17]. For example, the image of a flat sample (Fig. 6, bottom) shows that the surface of pottery contains volumetric plate-like grains with pronounced formation of chips. This allows us to interpret that pottery was fired at relatively low temperatures. The SEM image of a rough sample from Stanaičiai (Fig. 6, top) shows the "molten" surface coated with spherically shaped particles. Such a microstructure is characteristic of the ceramics sintered at one time at high temperatures [18].

Figure 7 shows the surface features of the historical pottery from archaeological complexes of Turlojiškės and Žvainiai. Apparently, the surface morphology of these two pottery samples differs considerably in comparison with specimens excavated from the Stanaičiai archaeological complex. However, both samples from Turlojiškės and Žvainiai show a very similar microstructure. The micrographs from Turlojiškės and Žvainiai pottery samples reveal a broad distribution of agglomerates of fine particles, with a porous structure and size of <10 μm. The voids are large (tens of micrometres in size) with various arbitrary shapes. One can determine from the morphology observed that both specimens were fired using a multi-step technology.

Figure 8 shows the microstructure of the pottery samples from Nikėlai and Jurgaičiai. The elemental composition of these two ceramic samples was determined to be almost the same. However, the morphology of these two specimens was completely different. Individual micro-sized particles can be clearly seen on the surface of the pottery sample from Nikėlai (Fig. 8, top). It can also be seen that the Nikėlai solids are composed of grains with no regular shape. This observation suggests

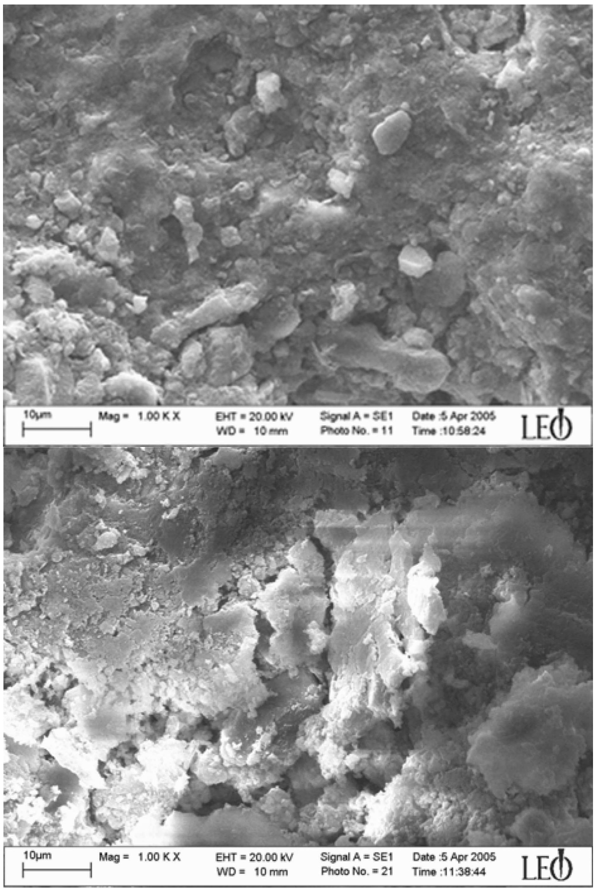

Fig. 6. Scanning electron micrographs of pottery samples from Stanaičiai village: rough sample (at the top) and flat sample (at the bottom).

that many grains have not dissolved completely in the body but have evolved from the outermost to transform into other phases. On the contrary, the "molten" and dense surface microstructure is observed for the pottery sample from the Jurgaičiai archaeological complex (see Fig. 8, bottom). It is apparent that the grains are completely dissolved in the body, which gives the formation of networks, maintaining a glassy-like outline with no internal porosity. Thus, the fabrication of pottery was performed at higher temperatures using one-step technology.

4. Conclusions

Ancient ceramic findings from five different archaeological complexes of Lithuania (Stanaičiai, Turlojiškės, Žvainiai, Nikėlai, and Jurgaičiai villages) have been studied by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. Based on the obtained experimentally composition and microstructure of archaeological ceramics, we interpret the most prominent characteristics of the technology applied to

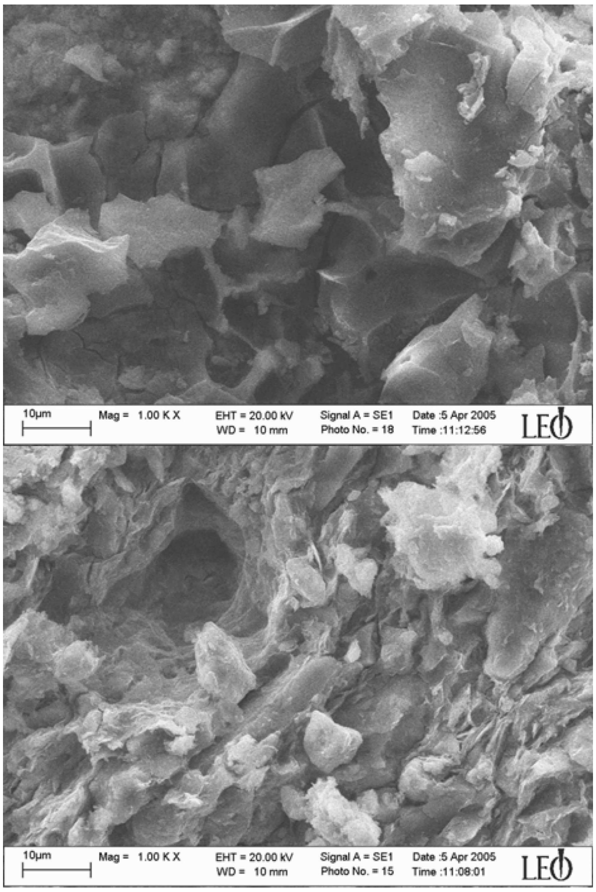

Fig. 7. Scanning electron micrographs of pottery samples from Turlojiškės (at the top) and Žvainiai (at the bottom) villages.

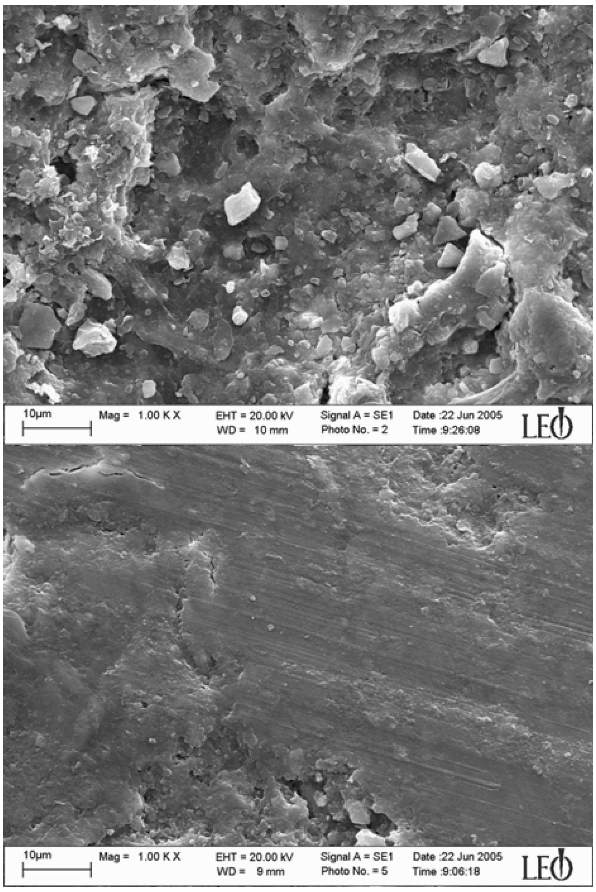

Fig. 8. Scanning electron micrographs of pottery samples from Nikėlai (at the top) and Jurgaičiai (at the bottom) villages.

produce the Bronze Age pottery found in different Lithuanian villages: silica- and alumina-rich raw materials, different firing temperatures for the body, one- or multi-step firing technologies. The obtained results have demonstrated that SEM and EDX analysis methods are indispensable tools of attaining information on some special technological features of ancient pottery.

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SENOVINĖS KERAMIKOS APIBŪDINIMAS SEM IR EDX METODAIS

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Santrauka

Skleidžiamosios elektroninės mikroskopijos (SEM) ir rentgeno spindulių dispersinės analizės (EDX) metodais buvo apibūdinti senovinės archeologinės keramikos pavyzdžiai. Apibūdintos skirtingų Lietuvos archeologinių radimviečių (Stanaičių, Turlojiškių, Žvainių, Nikėlų ir Jurgaičių) įvairios keraminės šukės. Nustatyta, kad skirtingose vietovėse rastos archeologinės keramikos paviršiaus ypatumai, cheminė bei fazinė sudėtis yra nevienodi. Tai gali būti susiję su keraminių dirbinių gamybos technologiniais ypatumais.