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XRD and SEM characterization of archaeological findings excavated in Lithuania

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In this article the results of an analytical characterization of archaeological pottery and amber samples from different regions of Lithuania are presented. The samples of ancient pottery and amber from villages *Benaičiai* (West Lithuania) and *Turlojiškės* (South Lithuania) were characterized by powder X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). It was concluded that the investigated pottery samples from the Western and Southern Lithuania showed different morphology and phase composition, possibly due to different fabrication conditions. However, the morphology of the archaeological amber samples excavated in different complexes was almost identical. The XRD results showed that a small amount of quartz is trapped inside amber.

Key words: archaeological findings, Western and Southern Lithuania, pottery, amber, analytical characterization

INTRODUCTION

Pottery and amber are the most numerous groups of Bronze Age finds. Pottery and amber analysis reveals important information about the daily life and ethnical and cultural aspects of the society of a certain period. Therefore, pottery studies are crucial for the reproduction of the lifestyle of society during a particular period [1–6]. It is well known that the production processes of antique ceramics can be derived together with changes in the manufacturing techniques. In this respect, maximum heating temperature, the duration of firing and kiln redox atmosphere are important factors helping to understand the transformations [7, 8]. Contemporary literature on amber deals predominantly with its botanical significance, identification and provenance of different inclusions (insects, plant species, etc.) [9–11]. However, the literature speaks about the prevention of amber deterioration, especially by the environmental control. Therefore, careful characterization of ancient pottery and amber is very important not only for archaeologists but also for professionals working in the field of conservation chemistry [12, 13].

Until quite recently, the archeologists in Lithuania have been using basically the visual observation method to characterize the pottery and amber of the Bronze Age. In general, such visual observation is necessary, but it is only the first step of the investigation. Thus, there is a need of a more detailed chemical and physical analysis of pottery and amber. Therefore, in the present study our attention has been focused on the characterization of different pottery and amber samples

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found in Lithuania using powder X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The pottery and amber samples for this investigation were collected at two archaeological complexes (*Turlojiškės* and *Benaičiai*) located in different regions of Lithuania.

EXPERIMENTAL

The Bronze Age pottery and amber samples found in the Lithuanian villages *Benaičiai* (Western Lithuania) and *Turlojiškės* (Southern Lithuania) were chosen for the characterization. The *Benaičiai* archaeological complex is situated in *Kretinga* district, *Darbėnai* municipality, *Benaičiai* village, eastwards from the *Šventoji* river, on its left bank, between Šventoji and a nameless rivulet. The *Turlojiškės* archaeological complex is situated in a large peaty area of over a hundred hectares in *Kalvarijos* district and municipality, in *Turlojiškės* village as well as in the neighbouring villages along the right bank of the *Kirsna* river. The exact locations of the above mentioned archaeological complexes are presented in Fig. 1.

The pottery samples were characterized by powder X-ray diffraction analysis (XRD) performed with a D8 Bruker AXS powder diffractometer using $CuK\alpha_1$ radiation. The amber samples were characterized by powder X-ray diffraction analysis (XRD) performed with a PANalytical X'Pert PRO powder diffractometer equipped with a conventional X-ray tube also using $CuK\alpha_1$ radiation. The morphology and microstructure of the pottery and amber samples were examined by scanning electron microscopy (SEM) on a JOEL 820 scanning electron microscope. In order to avoid charging, the samples were lightly coated with Au/Pd.

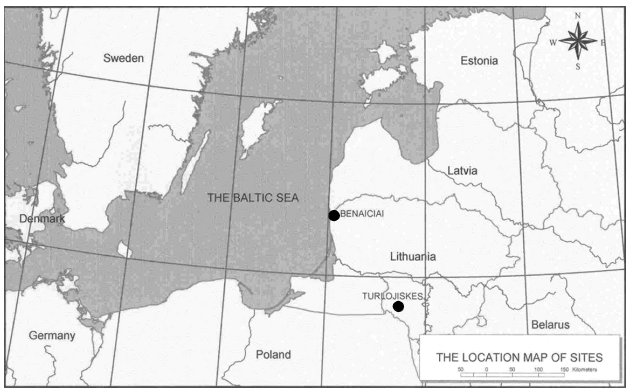

Fig. 1. Locations of archaeological complexes of *Benaičiai* and *Turlojiškės*

RESULTS AND DISCUSSION

The phase purity of the archaeological pottery samples were investigated by powder XRD analysis. As was expected, the X-ray diffraction patterns of the ancient pottery specimens (see Fig. 2) exhibited a multiphasic character of the investigated polycrystalline samples. The results obtained from the XRD analysis data are summarized in Table 1. As it is seen, quite different phase composition was determined for two historical ancient pottery samples obtained from different archaeological complexes. The *Benaičiai* pottery is characterized by the presence of quartz as the main phase, ant muscovite, titanite and sodium anorthite as secondary phases. The presence of large amount of the quartz phase in the *Turlojiškės* pottery was determined as well. However, the main crystalline component of this ceramic sample is evidently calcite. Secondary phases, such as muscovite, calcium hydrogen sulphate and nontronite were also identified. Therefore, only two common phases, quartz and muscovite, were found to be in both ancient pottery samples obtained from different places of Lithuania. These results suggest that the manufacture of the two historical ancient pottery samples was different. The presence of calcium carbonate in the *Turlojiškės* pottery clearly confirms this assumption. Apparently the firing temperature of the pottery from *Turlojiškės* is lower as compared with the calcination temperature of the ceramic sample from *Benaičiai*.

Archaeological amber samples were also examined by powder XRD analysis. Buchberger et al. [14] has used capillary electrophoresis and determined that the Baltic amber inclusion droplets contain water, in which a variety of inorganic cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, Br^-, NO_3^-, SO_4^{2-}) may be dissolved. Accordingly, the crystallization of inorganic salts during the formation of amber could possibly take place as well. The XRD patterns of two archaeological amber samples are shown in Fig. 3. As it was expected, the X-ray diffraction

Table 1. **Phase analysis data for the *Benaičiai* and *Turlojiškės* pottery samples**

Pottery sample	Phases obtained from XRD analysis	Comments
Benaičiai	SiO_2 (quartz)	Main
	$(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$ (muscovite)	Secondary
	$CaTiO(SiO_4)$ (titanite)	Secondary
	$(Ca,Na)(Si,Al)_4O_8$ (sodium anorthite)	Secondary
Turlojiškės	$CaCO_3$ (calcite)	Main
	SiO_2 (quartz)	Secondary
	$(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$ (muscovite)	Secondary
	$CaH_2(SO_4)_2$ (calcium hydrogen sulphate)	Secondary
	$Ca_{0.1}Fe_2(Si,Al)_4O_{10}(OH)_2 \cdot 4H_2O$ (nontronite)	Secondary

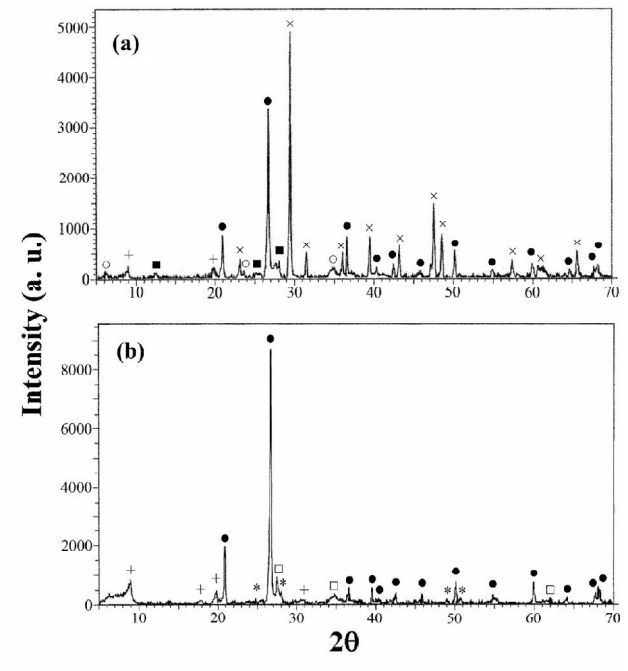

Fig. 2. X-ray diffraction patterns of historical ancient pottery from: (a) *Benaičiai* and (b) *Turlojiškės*. The crystalline phases are marked: SiO_2 (●), $(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$ (+), $CaCO_3$ (×), $CaTiO(SiO_4)$ (□), $(Ca,Na)(Si,Al)_4O_8$ (*), $CaH_2(SO_4)_2$ (■), $Ca_{0.1}Fe_2(Si,Al)_4O_{10}(OH)_2 \cdot 4H_2O$ (○)

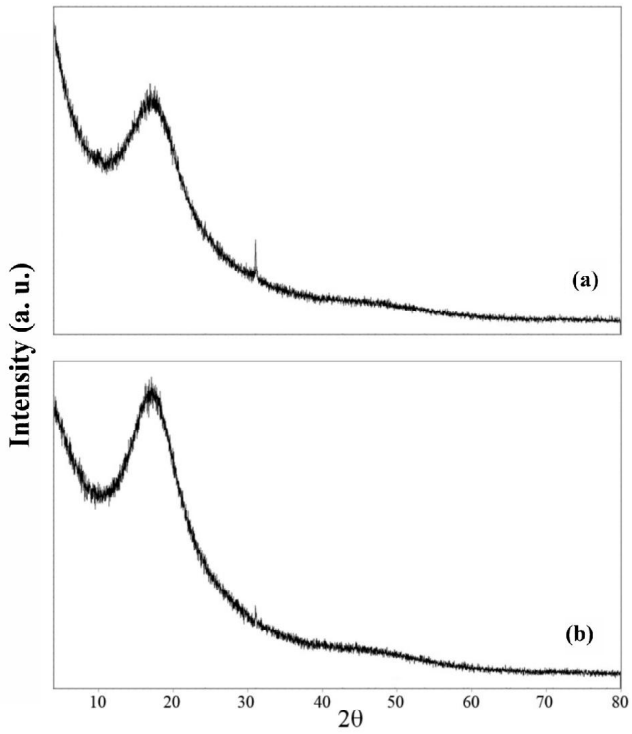

Fig. 3. XRD patterns of archaeological amber samples from the villages of *Benaičiai* (a) and *Turlojiškės* (b)

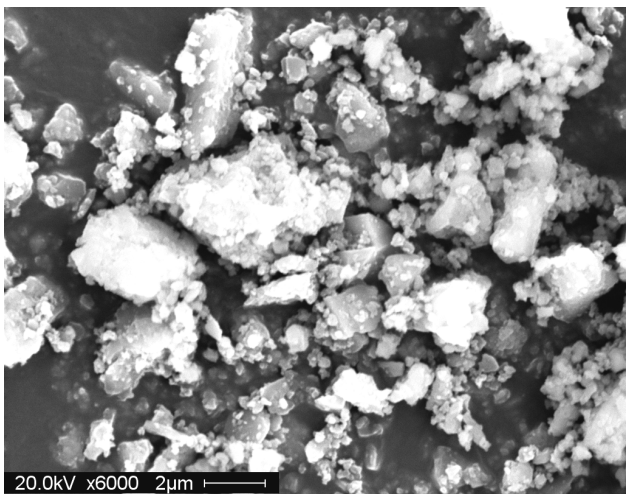

Fig. 4. SEM micrograph of archaeological pottery sample from the village of *Benaičiai*. Magnification ×6000

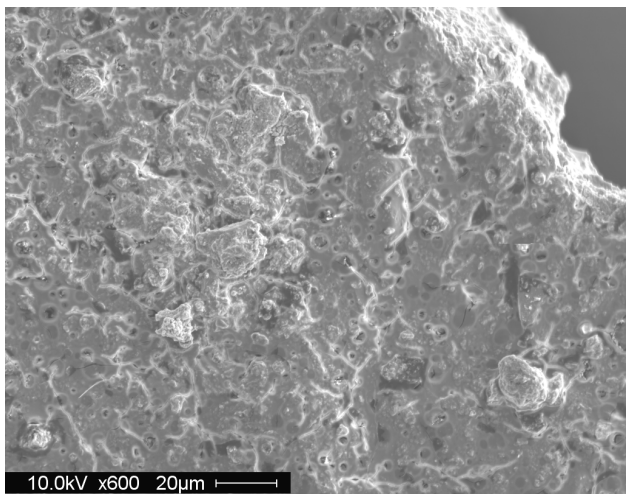

Fig. 5. SEM micrograph of archaeological pottery sample from the village of *Turlojiškės*. Magnification ×600

patterns of the amber specimens exhibited amorphous character. Both XRD patterns indicated an unidentified an amorphous humps between 2θ = 10–25°, reaching the maximum height at around 18°. No peaks due to an insignificant crystallization of metal salts could be identified in both XRD patterns. On the other hand, the XRD patterns of the archaeological amber samples contain rather sharp and intensive peak at around 2θ ≈ 32.0°. Surprisingly, this diffraction peak is the most intensive diffraction line for the quartz (SiO_2) phase [PDF 46–1045]. These results suggest for the first time to our knowledge that during the formation of amber, a small amount of silica was trapped inside it. Apparently, the sample excavated in the *Turlojiškės* archaeological complex contains a higher amount of SiO_2 phase.

Scanning electron microscopy (SEM) was employed for the investigation of specific surface morphological features of the ancient pottery and amber. The SEM micrographs can give a direct view on densification, which is a very informative feature of the technology used for the fabrication of pottery [15]. The micrograph obtained in secondary electron mode for the pottery sample from the *Benaičiai* village is shown in Fig. 4. As it is seen, the surface of the pottery from *Benaičiai*

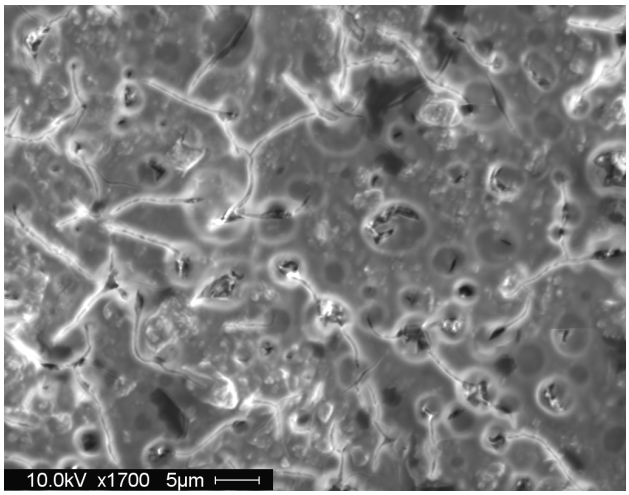

Fig. 6. SEM micrograph of archaeological amber sample from the village of *Turlojiškės*. Magnification ×1700

contains volumetric plate-like grains with a different crystallite size ranging from 200 nm to 3 μm. Therefore, the micrograph from the *Benaičiai* pottery sample re-veals a broad distribution of agglomerates of fine particles with a porous structure. One can recognize from the morphology observed that this specimen was fired in a multi-step technology at relatively high temperatures [15, 16]. Fig. 5 shows the surface features of the historical pottery from the archaeological complex of *Turlojiškės*. The SEM image of this sample from *Turlojiškės* shows a flat surface containing spherically shaped pores (2–5 μm). The voids and cracks of various arbitrary shapes are also seen. This allowed us to interpret that the pottery from *Turlojiškės* was fired at relatively low temperatures. Moreover, such microstructure is characteristic of the ceramics sintered in one time [16].

The textural properties of the amber samples were also investigated by SEM. It is interesting to note that the microstructure of both archaeological amber samples irrespective of their origin was found to be almost identical. A scanning electron micrograph of the representative historical amber sample is shown in Fig. 6. Evidently, the surface of amber is exceptionally smooth, however, it contains many prolonged cracks. Spherical and ellipsoidal droplets of inclusions of 1–3 μm size can be also clearly seen.

CONCLUSIONS

Archaeological pottery and amber samples found in the Lithuanian villages *Benaičiai* (West Lithuania) and *Turlojiškės* (Southern Lithuania) were characterized by XRD and SEM methods. The XRD analysis clearly showed that the investigated pottery samples were polycrystalline materials and composed of different phases. The XRD results revealed that in the amber samples a small amount of quartz was trapped inside. To our knowledge, such observation has not been previously reported. Moreover, we have demonstrated that scanning electron microscopy is an indispensable means for the characterization of ancient pottery and amber.

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LIETUVOS ARCHEOLOGINIŲ RADINIŲ APIBŪDINIMAS XRD IR SEM METODAIS

Santrauka

Šiame darbe archeologiniai keramikos bei gintaro pavyzdžiai, iškasti Benaičių (Vakarų Lietuva) ir Turlojiškių (Pietų Lietuva) archeologinėse radimvietėse, buvo tirti rentgeno spindulių difrakcine (XRD) analize ir skleidžiamąja elektronine mikroskopija (SEM). XRD tyrimai parodė, kad archeologinės keramikos pavyzdžiai yra sudaryti iš daugelio kristalinių fazių. Be to, keraminės šukės, rastos skirtingose radimvietėse, pasižymi ganėtinai skirtinga fazine sudėtimi. Pirmą kartą, mūsų duomenimis, pastebėta, kad archeologiniai gintaro pavyzdžiai savo sudėtyje turi nedidelius kiekius kristalinės kvarco fazės. Padaryta išvada, kad skleidžiamoji elektroninė mikroskopija yra itin vertingas archeologinių radinių tyrimo bei apibūdinimo metodas.