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Physicochemical characterisation of pottery from the Vinča culture, Serbia, regarding the firing temperature and decoration techniques

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Abstract: A study of decorated Neolithic pottery samples from the excavation site Pločnik, Serbia, was performed using X-ray powder diffraction (XRPD), Fourier transform infrared (FTIR) and X-ray fluorescence (XRF) spectroscopy. The investigated samples belong to the era of the Vinča culture that existed in the central Balkan region from the mid VI until the first half of the V millennium BCE. The mineralogical composition of the pottery samples and comparison of the investigated pottery with thermally treated local clay indicated firing temperatures in the range from 600 to 800 °C. Two different types of white pigments were identified in white incrusted decorations: calcium carbonate and bone white (composed of crushed bones). This is the first evidence of the use of bones for decorations in pottery of the Vinča culture from the excavation site Pločnik. In addition to this, it was revealed that the potters used the iron reduction technique for obtaining black decorations.

Keywords: ancient ceramics; bone; pigments; FTIR spectroscopy; XRF spectroscopy.

INTRODUCTION

Ancient pottery is a significant source of information regarding the technological development. Physicochemical analysis of pottery from the Vinča culture excavated on the territory of Serbia complements the visual characterisation and provides information on how the Neolithic people produced and utilized their pottery (additional considerations are presented in the Supplementary material to

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this paper). The detailed mineralogical composition provides information about the firing process, such as firing temperature, firing duration and atmosphere conditions.[1] Since the mineralogical composition of pottery highly depends on the temperature,[2] not only the presence but also the absence of specific minerals and their phases can be conclusive for the firing temperature and conditions. When put in a wider context, these technological aspects provide primal and/or additional information on social developments, migrations and interactions between settlements, spread of religion, *etc*.[3]

For determination of the composition of crystalline phases in ancient pottery, X-ray powder diffraction (XRPD) has been extensively used.[4] Complementary to XRPD, Fourier transform infrared (FTIR) spectroscopy provides information about crystalline and non-crystalline minerals that are abundant in pottery, especially in pottery fired at relatively low firing temperatures.[5] An additional advantage of FTIR spectroscopy is the ability to follow specific changes in the mineral structures (*e.g.*, aluminosilicates) caused by different firing temperatures.[5–8] As a method of non-destructive elemental analysis of pottery body and the pigments, X-ray fluorescence (XRF) spectroscopy presents a powerful tool, which can provide information about the minerals and pigments discovered through the presence of key elements.[9]

Several archaeometric studies have been conducted on the pottery of the Vinča culture,[10–14] but compositional data of Vinča pottery are still scarcely available. Moreover, to the best of authors' knowledge, the characterisation of white decorations on Vinča pottery has not hitherto been performed.

The aim of this study was to determine important aspects of the technological developments of the Vinča culture, such as firing conditions used for pottery manufacture and techniques adopted to produce particular decorations using the available raw materials. Physicochemical methods such as XRPD, FTIR and XRF spectroscopy were applied to assess the composition of the ceramic body and pigments used for decoration of pottery of the Neolithic Vinča culture.

EXPERIMENTAL

Pottery samples were provided by the National Museum in Belgrade and are part of a larger collection of Serbian Neolithic pottery. In this study, ten pottery samples collected at the Pločnik excavation site in the Toplica district near Prokuplje, Serbia, were investigated. Description of investigated pottery samples is given in the Supplementary material to this paper.

Raw clay was sampled approximately 2 km north of the Pločnik excavation site from a locality that is currently in use as a source of clay material (Fig. S-1 of the Supplementary material). This clay sample was used as a potential raw material equivalent.

Pottery samples were used as powders for XRPD and FTIR analyses. The surface layer of each pottery shard was removed by scraping; then about 50 mg of each sample was scraped and powdered in an agate mortar.

X-Ray powder diffraction (XRPD) patterns were recorded at room temperature on a Philips PW-1710 diffractometer using Cu K_{α} radiation (λ = 1.54178 Å) in the 2θ range 4–65° in 0.02° steps with 2.0 s per step.

Fourier-transform infrared (FTIR) analysis was performed on the Vinča pottery samples as well as on the raw clay sample. The raw clay material was heated at 7 different temperatures for six hours (100, 600, 700, 800, 900, 1000 and 1100 °C) in air. After heating and cooling to room temperature, FTIR spectra were recorded. The FTIR spectra of all the investigated samples were recorded on a Nicolet 6700 spectrophotometer, using the KBr pellets technique in the wavenumber range from 4000 to 400 cm^{-1}. The spectra were pre-processed by extended multiplicative signal correction (EMSC) in MATLAB software (version 7.10.0.499 (R2010a), The MathWorks, Natick, MA, USA) in order to remove baseline shifts, and additive and multiplicative effects that could occur due to physical differences between the samples, *e.g.* KBr pellet thickness, scattering, *etc*.

Energy dispersive X-ray fluorescence (EDXRF) spectroscopy measurements were performed on an EDXRF spectrometer with a Canberra Si(Li) semiconductor detector and MCA analyser S35+. MicroSAMPO software was used for spectra acquisition and the measurement time was 600 s for all samples. For excitation, an annular radioisotope source ^{109}Cd (manufactured by Isotope Products) with a nominal activity of 740 MBq was used.

Qualitative EDXRF measurements were performed on the decorated side of the pottery shards and the inner body for all investigated samples. In this way, the elemental composition of the pottery body and the decorations on the surface could be assessed and compared.

RESULTS AND DISCUSSION

Estimation of firing temperature

In order to reconstruct the production techniques and better understand the knowledge and skills of the ancient potters, the firing temperature of the pottery was estimated.

X-Ray powder diffraction (XRPD) analysis. Diffraction patterns of representative pottery samples and local clay sample are shown in Fig. 1.

As it can be seen, the powder diffraction patterns of all investigated samples were dominated by quartz reflections. Besides quartz, characteristic reflections of feldspars were also detected in all samples. By comparing XRPD patterns of pottery shards with that of the raw clay sample, it can be concluded that these have highly similar mineralogical contents. The amount of material for analysis was limited due to the nature of the samples, which hindered further determination of more precise mineralogical compositions by other destructive methods. However, various archaeometric studies indicate that most likely local clay was used by Neolithic potters from the Balkan region for pottery production.[12,15,16]

The presence of illite/muscovite detected in all the investigated pottery samples indicated that the firing temperature did not exceed 900 °C, since phyllosilicates disappear at temperatures between 900–950 °C.[6,17] Even though an archaeometric study of pottery from the Selevac excavation site showed that Vinča potters routinely achieved high firing temperatures, about 1000 °C,[11] the results obtained in this work indicated lower firing temperatures for pottery from the Pločnik excavation site. The firing temperature of pottery samples classified as Vinča culture excavated on the territory of Romania at the archaeological site Limba, Alba County, was estimated at about 700 °C, and for only a few samples at 850–900 °C.[12] Two samples from Vinča culture uncovered on the territory of Serbia were investigated as a part of a wider study of Neolithic–Bronze age pottery from Central and South–East Europe and the estimated firing temperatures were below 800 °C for the majority of the pottery made from non-calcareous clay and in particular, 750 °C for a sample from the Gomolava excavation site and between 800–850 °C for a sample from the Vinča excavation site.[18] That finding is in excellent agreement with a study of comparable pottery from Karanova in Bulgaria, with an estimated firing temperature of less than about 750 °C.[19]

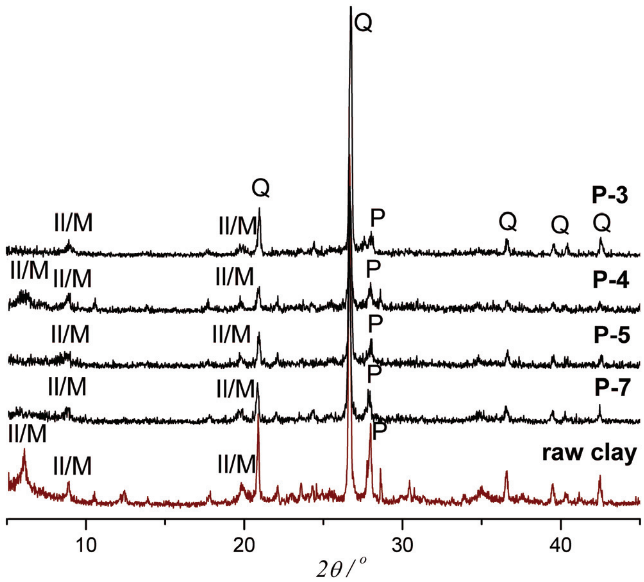

Fig. 1. XRPD patterns of representative samples from Pločnik excavation site and local raw clay, where Q designates quartz, P – plagioclase, and Il/Ms – illite/muscovite.

However, due to the poor mineralogical content of the Vinča pottery and raw clay, XRPD could only provide a rough estimate of the firing temperature. Therefore, an FTIR spectroscopic analysis of investigated samples was performed.

FTIR analysis. FTIR spectra were obtained for the ceramic body of all the investigated pottery samples and representative spectra are shown in Fig. 2. In all FTIR spectra, a doublet is present at 789 and 788 cm^{-1}, which is assigned to quartz.[20]

The wide and intensive band at about 1040 cm^{-1}, also present in all FTIR spectra, originates from Si–O stretching vibration of aluminosilicates.[20] An additional vibrational band of aluminosilicates occurs at about 470 cm^{-1}, which originated from deformational Si–O vibrations.[20] The band that occurs at about 540 cm^{-1} originated from Al–O deformational vibrations.[21] Various aluminosilicate minerals are common constituents of pottery (*e.g.*, feldspars) and they can all contribute to these bands. Therefore, signals overlap and broadening of the detected bands occurs.

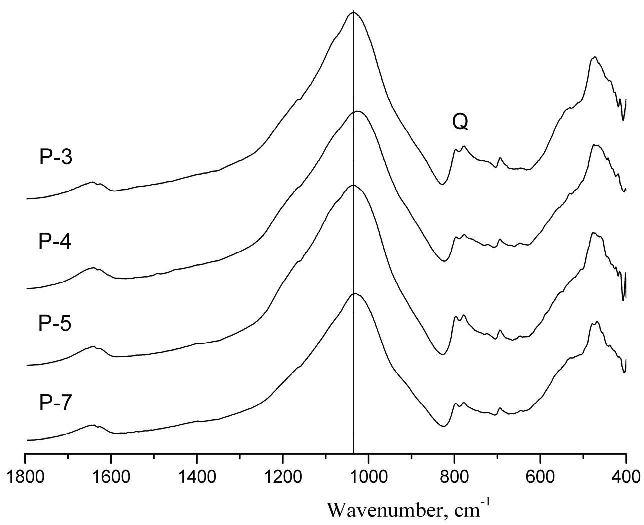

Fig. 2. FTIR spectra of representative pottery samples from Pločnik excavation site; Q designates quartz; the vertical line marks the position of the Si–O stretching band at 1040 cm^{-1}.

It was shown that the positions of specific vibrations in the crystal lattice of aluminosilicates are sensitive to changes in temperature.[5,22] According to this, determining the precise positions of specific Si–O and Al–O vibrations, can give an estimation of the temperature at which the raw clay was fired during pottery production.

With this in mind, raw clay (sampled near the Pločnik excavation site) was fired at different temperatures in air. As can be seen in Fig. 3, a shift of the band at about 1000 cm^{-1} towards higher wavenumbers was evidenced as the firing temperature was increased from 100 to 1100 °C.

The detected maxima were at 1031 cm^{-1} for 100 °C, 1040 cm^{-1} for 600 and 700 °C, 1040 and 1082 cm^{-1} (split band) for 800 °C and 1082 cm^{-1} for 900 °C. At higher temperatures, additional broadening of this band occurred and the maxima were estimated at 1081 cm^{-1} for 1000 °C and 1082 cm^{-1} for 1100 °C.

The detected positions of the Si–O stretching band for the investigated samples were as follows: 1033 cm^{-1} for P-7; 1035 cm^{-1} for P-4; 1040 cm^{-1} for P-2, P-3, P-5; 1047 cm^{-1} for P-9; 1050 cm^{-1} for P-6; 1035 and 1077 cm^{-1} (split band) for P-10; 1040 and 1080 cm^{-1} (split band) for P-3. The poor quality of

FTIR spectra for samples P-1 and P-8 did not allow precise determination of the band position, but they were estimated to be in the same spectral region of about 1040 cm^{-1}.

Hence, by comparing the positions of the Si–O stretching band in the FTIR spectra of the investigated pottery samples with the positions of the same bands obtained for thermally treated clay, it can be concluded that the firing temperature was in the range from 600 to 800 °C. This finding is in agreement with the conclusion obtained by XRPD analysis that the firing temperature did not exceed 900 °C.

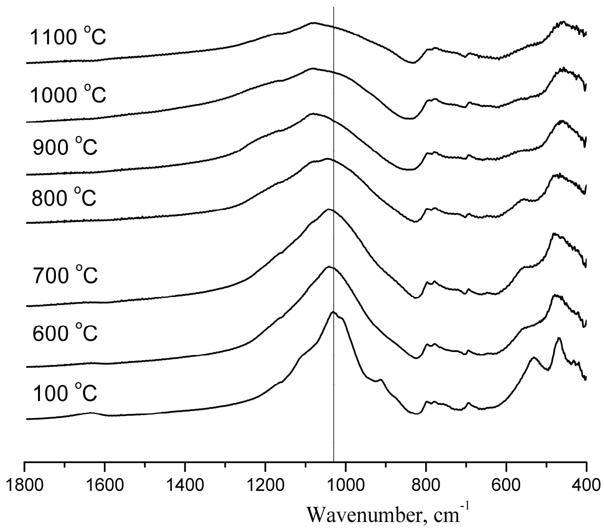

Fig. 3. FTIR spectra of raw clay from a locality near Pločnik excavation site, heated for 6 h at different temperatures; the vertical line marks the position of the Si–O stretching band at 100 °C.

Composition of pigments and decorations

In addition to the ceramic body, the coloured areas on the pottery shards were analysed by FTIR and XRF spectroscopy.

White pigments. The FTIR spectra of white pigments used for the white incrustations in the clay body of samples P-9 and P-10 are presented in Fig. 4. As is apparent from the figure, these two white pigments have significantly different spectral features.

The FTIR spectrum of the white pigment from the sample P-9 (Fig. 4a) is characterised by the presence of CO_3^{2-} bands (at 1459, 1415 and 872 cm^{-1}) and PO_4^{3-} bands (at 1091, 1047, 961, 602 and 567 cm^{-1}).[23] This finding indicates presence of hydroxyapatite [$Ca_5(PO_4)_3(OH)$] and carbonate–hydroxyapatite [$Ca_{10-x/2}[(PO_4)_{6-x}(CO_3)_x][(OH)_{2-2y}(CO_3)_y]$], which are mineral components of

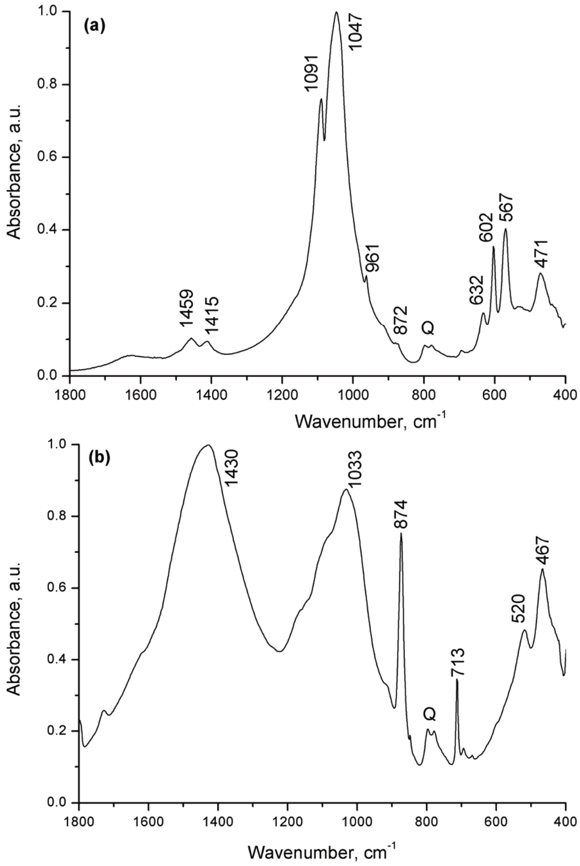

Fig. 4. Representative FTIR spectra of white pigments from samples: a) P-9 and b) P-10 with the most relevant spectral features designated (Q – quartz).

bones.[23,24] The detected PO_4^{3-} bands are sharp and well defined, which indicates that the bones were processed at a heightened temperature, most likely above 600 °C.[25] Furthermore, a presence of the characteristic band at 632 cm^{-1} in FTIR spectrum, which is highly relevant for determining the temperature of firing, was also detected in the spectrum of this sample (P-9). This band originates from the vibrational mode of hydroxyl groups within hydroxyapatite and appears upon calcination at high temperatures in air.[24] These findings are a strong indication that the bones used for producing the white decorations in sample P-9 were calcined at high temperatures between 700 and 900 °C.[23,24] Whether the bone material was fired separately or together with the clay cannot be determined with certainty. However, it is most likely that Vinča potters calcined bones before crushing them in order to produce this white pigment, because it is much easier to produce very fine powder from burned bones than from crude ones.[23,26] Therefore, it can be concluded that ancient pigment Bone White (or Antler White) obtained from calcined animal bones, teeth and/or antlers was used for the white decoration of sample P-9. Production of white inlayed decorations on pottery is recognized as a widespread practice in prehistoric Europe,[23] but there are not many studies on the composition of the material used to fill white incrustations.[23,24,26,27] This result shows that Vinča culture potters were familiar with the technique of incrusting calcined bones for obtaining the white decorations on pottery.

On the other hand, in the FTIR spectrum of the white pigment obtained from sample P-10, an intensive and broad band at 1430 cm^{-1} together with two sharp and intensive bands at 874 and 713 cm^{-1} are apparent. These bands originate from the characteristic vibrations of $CaCO_3$,[20] which is the main constituent of this particular white decorative pigment. When $CaCO_3$ is fired, the characteristic FTIR bands shift towards lower wavenumbers and the ν_4 band at 713 cm^{-1} broadens and decreases in intensity and almost completely disappears at temperatures above 600 °C.[28,29] This is clearly not the case in the FTIR spectrum shown in Fig. 4b. Therefore, it can be concluded that the Vinča potters added the $CaCO_3$ after the firing of the pottery as a consecutive production step. This is in line with visual observations of this sample, where it was postulated that additional decoration by the addition pigments was performed (see Description of samples in Supplementary material).

In the EDXRF spectra of white pigments from samples P-9 and P-10, a signal for Ca was also observed (results not shown), which is in accordance with the obtained FTIR spectroscopy results.

Detected characteristic doublet of quartz in both FTIR spectra presented in Fig. 4 and the Si–O stretching band positioned at 1033 cm^{-1} with shoulder at about 1080 cm^{-1} in FTIR spectrum of sample P-10 (Fig. 4b) related to aluminosilicates,[20] most probably originate from the underlying ceramic body collected during the scraping of the samples (the white layer of pigment was very thin and hence sampling was a difficult task) but could also be the result of impurities in the pigment mixture.

Red and black decorations. FTIR spectra of the red and black decorations were obtained for all the investigated samples and representative FTIR spectra are presented in Fig. 5, from which it can be seen that these decorations contained highly comparable spectral features: Si–O stretching vibrations of aluminosilicate minerals (at about 1000 cm^{-1}) and quartz bands at 797, 779 and 693 cm^{-1}.[20] It can therefore be concluded that both the black and red decorations do not differ appreciably in chemical composition.

The XRF spectra of red and black decorations were recorded for all the investigated pottery samples, and representative XRF spectra are presented in Fig. 6. It is apparent that a strong signal of iron is present in the spectra of both the red and black decorations. Moreover, the same trace elements were detected in the case of all red and black decorations.

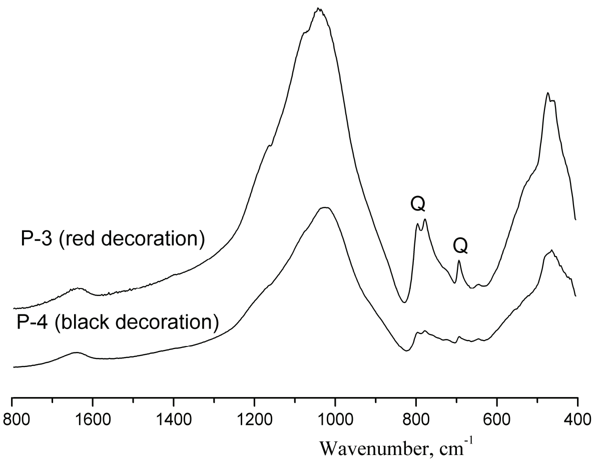

Fig. 5. Representative FTIR spectra (samples P-3 and P-4) of red and black decorations on pottery shards (Q – quartz).

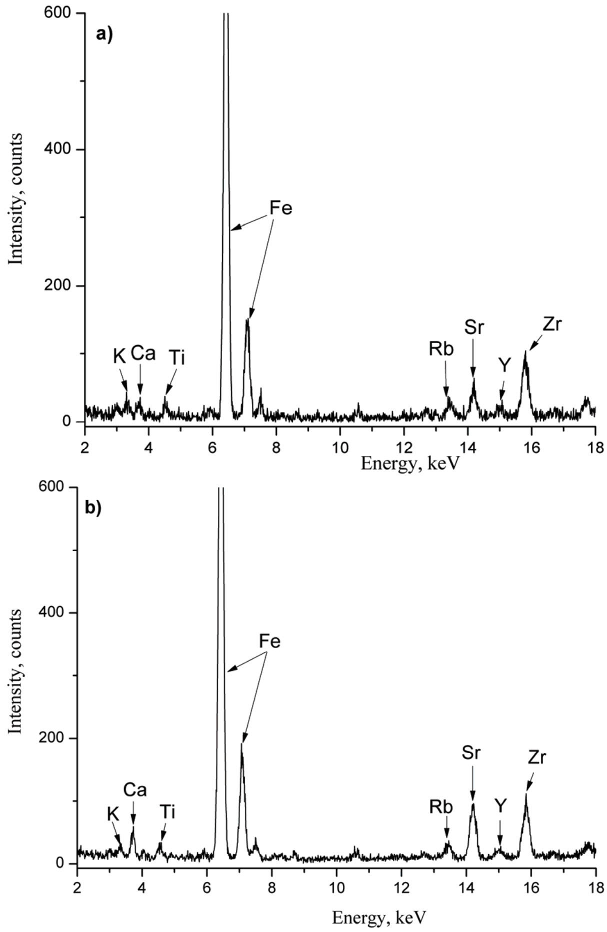

Fig. 6. Representative XRF spectra obtained directly on pottery shards: a) sample P-3, red decoration; b) sample P-4, black decoration.

This finding is relevant for the determination of the firing technique used by the Vinča potters. More precisely, it is known that in the Neolithic age on the territory of today's South–east Europe, two different techniques were used for obtaining black colour in the decorations of the pottery: *i*) manganese-reduction black and *ii*) iron-reduction black. The process in which black colours are produced during pottery firing by the reduction of ferruginous clays is widely distributed and very old, with certain indications that it is probably the oldest of all ceramic-decoration processes.[30]

In addition to this, the XRF spectra revealed that neither black decorations, nor any other part of the investigated pottery contained manganese. This finding underlines that the method for obtaining black colour on the pottery decorations was the technique of iron-reduction and not of manganese-reduction.

The detected Fe in red decoration indicates that this colour originated from hematite.

The precision of the decorations, as well as the presence of both red and black colours on several of the analysed pottery shards, shows that the technology of pottery production was on a highly advanced level in the Vinča culture.

CONCLUSION

This multi-analytical study of decorated Neolithic pottery found at excavation site Pločnik was performed in order to determine the production technology, in particular the firing temperature and characterisation of materials used for decorations. For the analysed set of pottery shards, the firing temperature was estimated to be in the range from 600 to 800 °C, based on mineralogical composition of the pottery, determined by XRPD and FTIR spectroscopy, and comparison of investigated pottery with thermally treated local clay with a similar mineralogical composition. In order to produce white decorations, the Vinča potters used different white pigments, among which calcium carbonate and the ancient pigment bone white were confirmed by the herein presented FTIR analysis. The analysed $CaCO_3$ decoration was most likely added after the firing of the pottery. Furthermore, the black decorations on the analysed pottery shards were obtained by the iron-reduction method, based on: *i*) identification of iron in the black pigments and *ii*) the lack of manganese in the analysed samples. The obtained results confirmed and further described that the ancient potters in the Vinča culture had a high level of knowledge of raw materials and craftsmanship.

SUPPLEMENTARY MATERIAL

Additional historical and archaeological information are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

ФИЗИЧКОХЕМИЈСКА КАРАКТЕРИЗАЦИЈА КЕРАМИКЕ КОЈА ПРИПАДА ВИНЧАНСКОЈ КУЛТУРИ СА ЦИЉЕМ ОДРЕЂИВАЊА ТЕМПЕРАТУРЕ ПЕЧЕЊА И ДЕКОРАТИВНЕ ТЕХНИКЕ

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Карактеризација узорака украшене неолитске керамике са археолошког налазишта Плочник је извршена применом дифракције X-зрачења на праху (XRPD), инфрацрвене спектроскопије са Фуријеовом трансформацијом (FTIR) и рендгенске флуоресцентне анализе (XRF). Испитивани узорци припадају ери винчанске културе која је постојала у региону централног Балкана од средине VI до прве половине V миленијума п.н.е. На основу минералошког састава керамике и поређења испитиваних узорака са термално третираном глином температура печења керамике процењена је на опсег од 600 до 800 °C. Идентификоване су две врсте белих пигмената у белим урезаним декорацијама: калцијум-карбонат и коштано бело (који се састоји од смрвљених костију). Ово је први доказ коришћења костију за украшавање винчанске керамике са археолошког налазишта Плочник. Такође, показано је да су древни грнчари користили технику редукције гвожђа за добијање црних украса.

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