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Spectroscopic Identification of Mineral Pigments in White Decorated Prehistoric Pottery from Bulgaria

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Abstract: In the prehistoric period on the Balkan Peninsula, the technology of white decoration underwent a drastic change. At the beginning of the Neolithic white pigment was applied as paint on a polished surface. At the end of the epoch, white paste was inlaid in incised channels on the surfaces of vessels. This study is focused on the identification of mineral pigments used for white decoration of Neolithic and Chalcolithic pottery from the territory of Bulgaria. The aim of this work is to answer the question of whether the composition of the white pigment varies according to the technique of decoration (paint and inlay). A set of 41 pottery fragments from 11 archaeological sites on the territory of Bulgaria was analyzed utilizing two spectroscopic techniques: laser-induced breakdown spectroscopy (LIBS) and Fourier-transform infrared spectroscopy (FTIR). Additionally, the experimental data from the LIBS were statistically treated with the multivariate technique, principal component analysis (PCA). The results from the spectral analysis indicated that the main constituent in the white decorated sherds is calcite in various combinations with carrier materials like quartz, feldspars, and metal oxides. The statistical analysis revealed that the primal constituent in the inlaid sherds is calcite while in the painted part, the carrier material is dominant. In some particular sherds, gypsum, hydroxylapatite, kaolinite, and aragonite were also detected.

Keywords: mineral pigments; white decorated pottery; archaeometric study; Neolithic; Chalcolithic; Bulgaria; LIBS; FTIR

1. Introduction

The most widespread archaeological findings are ceramic artefacts that provide valuable information about various aspects of ancient life, from daily activities to broader societal trends [1,2]. The color decoration of pottery is one of the substantial components in the regionalization and identification of cultural characteristics in Prehistory. Pottery decorations exhibit diversity in application methods, patterns, and motifs. Since the end of VII mill. BCE, the practice of decorating ceramics with pigments, which were applied as an additional material with a color contrasting to the base, began. The pigments that were used to adorn potteries in prehistoric times on the Balkan Peninsula encompassed various shades of white, red, yellow, brown, black, and graphite. Among these colors, only the white one underwent modification in the application technique throughout the period of its utilization. The commencement of the decoration of ceramic vessels with white pigment in the Balkans refers to the end of the 7th mill. BCE [3]. White pigment was applied as paint on a polished surface at the beginning of that period. At the end of the Neolithic, the preferred application technique changed drastically, and white pigment in the form of paste was inlaid in incised channels on the surface of the vessels. The inlay technique was practiced from the Late Neolithic throughout the Chalcolithic until the beginning of the Early Iron Age, while the painting technique ceased to be practiced at the beginning of the Chalcolithic with few excepts [4].

The archaeometric analysis of pigments used during the Neolithic and Chalcolithic periods lays the foundation for the periodization and synchronization of cultural phenomena on the territory of Southeastern Europe. With the introduction of analytical techniques in archaeological science, in addition to the cultural affiliation according to the chosen periodization system, typology, and ornament style of pottery, the composition of raw materials has also been investigated. Considerable archaeometric studies on white pigments used for decorating ceramics in the Neolithic and Chalcolithic have been published in several countries in Southeastern Europe, including Greece [5–8], Romania [9–14], Hungary [15–17], Serbia [18,19], Albania [20,21], and Croatia [22,23].

The studies of the color decorations of pottery from Bulgarian territory were focused mainly on the typology and territorial distribution involved [24–28]. The analysis of the elemental and mineral content of the pigments in the decorations of Neolithic and Chalcolithic pottery in Bulgaria is at its beginning and archaeometric studies are only isolated cases and encompass a limited number of fragments [29–32].

This study aims to identify the pigments used for the white decoration of Neolithic and Chalcolithic pottery from the territory of Bulgaria and, based on the obtained results, to find out if the elemental and mineral content of white pigment varied depending on the different application techniques—paint and inlay techniques. The provided pottery fragments were analyzed using two complementary spectroscopic techniques: laser-induced breakdown spectroscopy (LIBS) and Fourier-transform infrared spectroscopy in attenuated total reflection mode (ATR-FTIR). The obtained LIBS data were further processed by the statistical technique, principal component analysis (PCA), in order to classify the fragments according to the similarities and differences in their elemental composition. This research enhanced the results of a previous study of Neolithic and Chalcolithic white pigments used for the decoration of vessels from the territory of Bulgaria analyzed by X-ray diffraction spectroscopy (XRD) [4].

The insights from this study will serve as a foundation for tracing the evolution of color decoration technology and identifying regional characteristics throughout various periods of Late Prehistory in Southeastern Europe.

2. Materials and Methods

2.1. Pottery Fragments

For this study, a total of 41 fragments of pottery from 11 archaeological sites located in Southwest, Northwest, Central, and Eastern Bulgaria were collected (Figure 1). The analyzed sherds are dated to the Neolithic and Chalcolithic periods according to Bulgarian periodization [33]. On 17 of them, decoration was applied as paint and on the other 24, it was inlaid as paste. The painted and inlaid fragments are shown in Figure 2a,b, respectively.

Figure 1. Map of Bulgaria with archaeological sites where the fragments were collected.
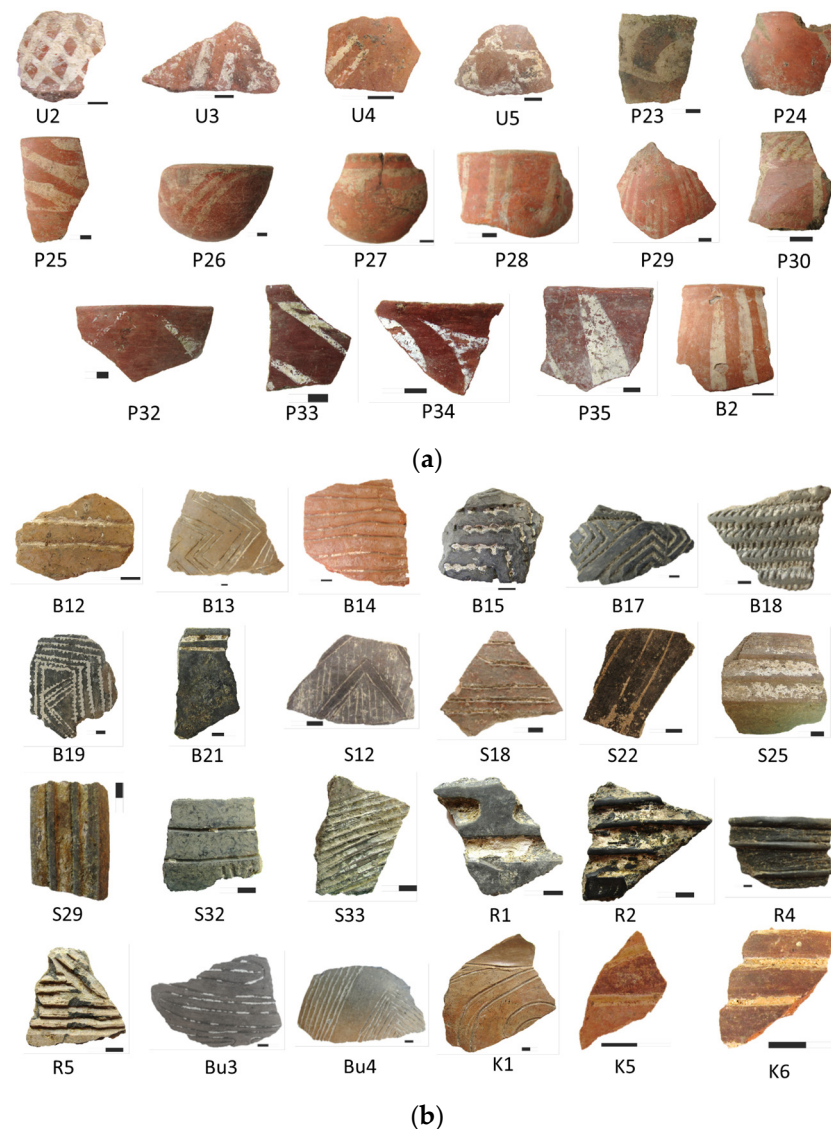
(**a**)

(**b**)

Figure 2. Photographs of the analyzed (**a**) painted and (**b**) inlaid pottery fragments with the corresponding sample IDs. The scale markers in the photos represent 1 cm.

The southwestern region is represented by 16 fragments, dated to the Early Neolithic period, from three archaeological sites: a settlement mound near Galabnik village (fragments P 23–35), settlements near Drenkovo village (fragments U 4, 5), and Ilindentsi village (fragments U 2, 3). All the fragments from the southwestern region had white decoration applied as paint on a red polished surface.

In the northwestern region, 10 fragments from two archaeological sites are presented as the following: Gradeshnitsa—Malo pole (fragments B 2, 12, 13, 14) and Brenitsa (fragments B 15, 17, 18, 19, 21). One fragment from this region (fragment B 2) is dated to the Early Neolithic, and its decoration was applied as paint on a red polished surface. The rest are dated to the Early Chalcolithic and were decorated with white paste encrusted on brown, beige, red, or grayish-black surfaces.

The central region is represented by 11 fragments from three archaeological sites: settlement mounds near Mogilovo village (fragment S 12), Starozagorski bani (fragments S 18, 22, 25, 29, 32, 33), and Buzovets village (fragments R 1, 2, 4, 5). Six of the fragments are dated to the Early Chalcolithic, one to the Middle Chalcolithic, and the other four to the Late Chalcolithic. They were encrusted with white paste on red or grayish-black surfaces.

Five fragments dated to the Early Chalcolithic from three archaeological sites were provided from the eastern region. Fragments Bu 3 and Bu 4 from Mirolyubovo and K 1 from a mound near Poroy dam are dated to the Chalcolithic. Fragments K 5 and K 6 from the Kozarevo mound are dated to the Early Chalcolithic. All of these fragments were encrusted with white paste on a black surface.

2.2. LIBS

Investigating complex materials like mineral pigments requires the application of complementary and verifying spectroscopic techniques to perform a comprehensive archaeometric study. In this research, LIBS was employed to identify the chemical elements present in the decorations. LIBS involves irradiating a sample with a focused high-power laser pulse, typically lasting a few nanoseconds. The high fluence at the focal point heats the material, causing ablation of a minuscule amount and forming a plasma plume that contains atoms and ions from the sample. Following the laser pulse, free electrons recombine with ions in the plasma, relax, and emit characteristic radiation. This radiation is directed to a spectrometer via an optical fiber. This technique can analyze materials in solid, liquid, or gaseous states [34].

LIBS analysis in this work was performed by the portative system LIBSCAN25+ (Applied Photonics Ltd., Skipton, UK). This equipment includes a Q-switched Nd:YAG laser generating a fundamental wavelength of 1064 nm, a pulse duration of 10 ns, and a nominal pulse energy of 50 mJ. It also has six spectrometers covering the 200–750 nm spectral range and optics for beam focusing and light collection. Samples were irradiated with a pulse energy of 8 mJ. The laser beam was focused perpendicularly to the sample surface using a 90 mm focal length lens. Emitted radiation from the plasma was collected using six light collection optics (three for UV–Vis and three for Vis–NIR) and transferred to the spectrometers via optical fibers. Ablation occurred in ambient air at atmospheric pressure. Signal registration was set to a delay time of 1.3 μs post-laser pulse to avoid capturing continuous background radiation from the initial plasma formation stage, with a registration gate of 1 ms. The entire spectral acquisition process was managed by LIBSoft V14 software.

Considering the inhomogeneity of the material under study and to ensure the repeatability of the results, LIBS analyses were conducted at 10 distinct points on the surface of the decoration. To ensure only the decoration was ablated without affecting the underlying substrate, a single laser pulse was applied, preceded by two cleaning laser shots. Each set of ten spectra was then averaged.

2.3. ATR-FTIR

ATR-FTIR is a widely used analytical tool for the identification of the mineral composition of archaeological ceramics. This technique detects the distinct absorption of infrared radiation by the material's functional groups, which is determined by the structure, bond vibrations, and crystal lattice. It stands out as a straightforward, rapid, and reliable approach, offering significant advantages over other mineralogical methods because it provides insights into ceramic components' crystalline and pseudo-amorphous phases. Furthermore, FTIR spectroscopy is non-invasive due to its minimal sample requirements for analysis [1].

The mineral compounds of the paints and the incrustations were identified using Fourier-transform infrared spectroscopy in attenuated total reflection mode. The analysis was performed with a Perkin Elmer Spectrum Two FTIR spectrometer, equipped with a PIKE GladiATR accessory, featuring a monolithic diamond ATR crystal (Pike Technologies, Fitchburg, WI, USA) at room temperature. For the analysis, a micro-sample from the decoration of each fragment was scraped off, ground in an agate mortar with a pestle, and then directly placed on the diamond crystal without any further preparation. Spectra were recorded in the MIR spectral region (4000 to 400 cm^{-1}) by averaging 32 interferograms at a resolution of 4 cm^{-1}. Baseline correction was performed using the equipment's software.

The spectra were plotted in OriginPro, Version 2024 (OriginLab Corporation, Northampton, MA, USA) and interpreted through comparison with the existing literature.

2.4. PCA

The LIBS results were statistically analyzed with PCA to classify the fragments according to the differences and similarities in their elemental composition.

PCA is a type of multivariate statistical technique employed to find a relationship between multiple variables and classify samples into separate groups according to their similarities and differences. In general, PCA compresses a multivariate data dimensionality into new uncorrelated variables called principal components (PCs) without significant loss of information contained in the initial data set [35,36]. The theoretical and mathematical background of PCA is explained in more detail in the literature [37].

3. Results

3.1. Elemental Composition

According to the results obtained from the LIBS analyses, Ca was the most abundant element in all of the sherds. The presence of Si, Al, Mg, K, Na, Fe, Mn, Ba, Sr, Ti, and Cr was also detected in all of the sherds. These elements had different intensities of the characteristic spectral lines in each sherd, which is an indication of their different concentrations in the pigment. The atomic and ionic spectral lines used to identify the elements are listed in Table 1. Due to the lack of suitable matrix-matched calibration standards for quantitative determination, the LIBS analyses were limited to elemental identification and semi-quantitative analysis.

Table 1. Spectral lines used for the detection of the elements in the LIBS analysis. The Roman numerals I and II refer to spectral lines emitted from neutral atoms and singly ionized atoms, respectively.

Element	Wavelengths (nm)
Ca I	457.85, 458.14, 458.59, 487.82, 527.03 *, 671.77
Ca II	315.89, 317.93, 393.36, 396.85
Si I	250.69 *, 251.61, 252.41, 252.85, 288.16
Al I	308.22 *, 309.27, 394.40, 396.15
Mg I	285.21, 382.93, 383.23, 516.73 *
Mg II	279.55, 280.27
Fe I	271.90, 275.01, 293.69 *, 302.06, 344.10, 356.54, 357.01, 358.12, 374.55
Ti I	498.17, 499.10
Ti I	323.45, 328.77, 334.19, 334.90, 336.12, 337.75 *, 338.38
Sr I	460.73
Sr II	407.77, 421.55 *
Ba I	553.55
Ba II	455.40, 493.41 *
Na I	449.42 *, 589.00, 589.59
K I	404.41 *, 693.88
Mn I	403.08, 403.31, 403.45
Mn II	259.37 *
Cr I	357.87, 359.35, 425.43, 427.48 *

* Characteristic spectral lines employed to conduct the statistical analysis with PCA.

To classify sherds with same elemental composition based on variations in their spectral line intensities, the LIBS results were statistically analyzed with PCA. The input data for the performance of PCA were the intensities of the selected spectral lines of the detected elements. The intensity of the chosen spectral line was normalized by dividing the integrated peak area by the total light intensity emitted from the plasma for each of the recorded spectra. This normalization was performed to minimize the dependency of the instrument response to fluctuations in laser fluence and matrix effects [38].

PCA showed that the first two principal components accounted for 62.06% of the cumulative variance (PC 1 explained 48.02% of the variation and PC 2 14.04%). The PCA

loading plot and score plot are shown in Figure 3a,b, respectively. The loading plot shows how the variables influenced the PCs and displays the correlation between the variables, and the score plot indicates the projection of the data onto the PCs.
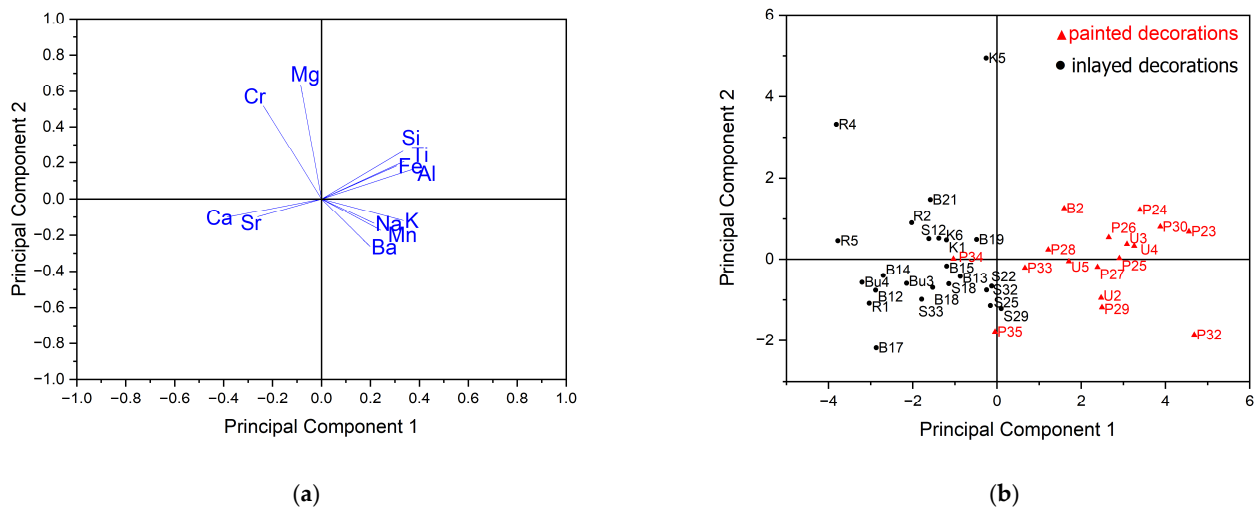

(**a**)

(**b**)

Figure 3. Results from PCA based on normalized spectral line intensities obtained from LIBS spectra: (**a**) Loading plot of the first two principal components; (**b**) Score plot of the first two principal components.

The loading plot indicates that PC 1 was mainly influenced by calcium, aluminum, and potassium and, to a lesser degree, by silicon, iron, titanium, and sodium, while on PC 2, magnesium and chromium had a dominating contribution (Figure 3a). The loadings for calcium and strontium exhibited very strong proportionality, meaning that strontium also increased in fragments with increased calcium content. It can be explained by the fact that strontium is normally involved in natural clayey formation. In particular, it is common for Sr^{+2} to be incorporated in calcite (Cal) and the other polymorphs of calcium carbonate crystal during their growth because of the ability of carbonates to interact with various divalent metals [39]. Strontium can easily substitute calcium in carbonates, sulfates, feldspars (Fsp), mica (Mca), clays, etc., due to the similarities in their ionic radius and charge [40,41]. Due to the simultaneous elevated content of calcium and strontium in the inlaid sherds, it can be deduced that, most likely, the white pigment was based on some of the polymorphs of calcium carbonate.

From the loading plot, it can also be seen that silicon, aluminum, iron, and titanium had a very strong positive correlation. This proportionality is not surprising since iron and titanium are common constituents of soils and sedimentary rocks [42,43], and it is quite natural for iron and titanium oxides to be found as inclusions in aluminosilicates. For instance, kaolinite (Kln), one of the prevalent clay minerals resulting from the chemical weathering of aluminosilicates, naturally contains varying amounts of iron oxides, which gives it various hues [44]. Also, it is quite possible for more stable and harder minerals such as quartz (SiO_2) (Qz) and the TiO_2 polymorphs rutile (Rt) and anatase (Ant) to remain as residual phases in clays during their precipitation [45,46].

The loadings for sodium, potassium, barium, and manganese were also positively correlated. The correlation between these elements can be explained most likely with the presence of alkali Fsp. Barium Fps are classified as a subgroup of alkali Fsp, which are formed when barium substitutes potassium in a mineral structure. The occurrence of barium Fsp is mostly associated with manganese deposits [44].

The PCA score plot demonstrates the apparent separation between the painted sherds and inlaid sherds, mainly along the direction of PC 1 (Figure 3b). Most of the painted sherds are clustered in the positive part of PC 1, and the inlaid sherds in the negative part. It can be seen that the inlaid sherds are characterized by an increased content of calcium

and strontium compared to the painted sherds. Hence, it can be deduced that the prime constituent in the inlaid decorations is Cal.

On the other hand, the increased content of aluminum, silicon, iron, titanium, potassium, sodium, barium, and manganese was attributed to most of the painted sherds. Consequently, aluminosilicates and clay minerals like Qz and Fsp could predominate in painted decorations. Only two of the painted sherds were clustered with the inlaid ones (P34 and P35). This means that fragments P34 and P35 have a mineral content of the white pigment that is very similar to that of the white paste used for inlay.

Some outlier sherds were also observed. Fragments R 4 and K 5 are clearly separate from the rest. They are positioned at the most positive part of PC 2, which, according to the loadings, is associated with elevated magnesium and chromium content. In the LIBS spectra, these two fragments exhibited the most intense magnesium and chromium characteristic spectral lines compared to the rest of the fragments. The occurrence of elevated chromium concentrations in soils, clays, and sediments is associated with the weathering of ultramafic rocks, which are relatively poor in silicon and rich in magnesium [47].

3.2. Mineral Composition

The ATR-FTIR spectroscopic analysis revealed the characteristic vibrations of various minerals associated with the white color of the pottery decorations. Some representative spectra of selected samples are shown in Figure 4. The most prominent mineral that was present in almost all the investigated samples was Cal. It was identified through the characteristic vibrations of the carbonate group (CO_3^{2-}) (Figure 4a, denoted with black labels): a strong, broad band centered around 1420–1410 cm^{-1} identified as the asymmetric stretching (v_3), an intense narrow band at 874–872 cm^{-1} assigned to the out-of-plane bending (v_2), a narrow band at 713–712 cm^{-1} due to the in-plane bending (v_4) mode, and the weak bands at 2514 and 1794 cm^{-1} resulting from the ($2v_2 + v_4$) (not shown in the Figure) and ($v_1 + v_4$) combination modes, respectively [48]. In some of the spectra, mainly of samples dated to the Neolithic, the asymmetric stretching (v_3) band exhibited a slight shift at 1440–1450 cm^{-1} and broadening, which is an indicator of reformed Cal resulting from the firing of pottery [49]. This corresponds with the assumption that the early Neolithic pottery was decorated before firing [3].

The spectra of two of the samples revealed the distinctive features of aragonite (Arg). Sample K6 contained only Arg, while sample K1 had a mixture of Arg and Cal. Arg, like Cal, is a naturally occurring form of $CaCO_3$. Arg's spectral features were similar to Cal's, with slight shifts in most of the bands and the appearance of some new bands, shown in Figure 4a with red labels. These features include a doublet at 713 and 699 cm^{-1} (v_4, C–O in-plane bending); a narrow band at 855 cm^{-1} (v_2, out-of-plane bending); a weak peak at 1082 cm^{-1} (v_1, symmetrical stretching); the strong broad peak centered around 1472 cm^{-1} (v_3, asymmetrical stretching); and a weak peak at 1787 cm^{-1} (combination of v_1 and v_4) [50].

In nature, both Arg and Cal can be precipitated from the shells of different marine species, either separately or coexisting in different shell structures [50]. This is evidenced by the spectrum of K1, where both polymorphs of calcium carbonate are present. LIBS also confirmed the presence of Arg by detecting the relatively strong presence of strontium (Sr) in K1 and K6, as some studies have found a correlation between the concentration of Sr and the precipitation of Arg [51]. It was observed that the relative intensity of the Sr spectral lines was the highest in K6.

Gypsum (Gp) was identified in four of the samples (P26, P33, B19, Bu3) through the fundamental sulfate (SO_4^{2-}) and water vibrations: (v_3) asymmetric stretching (sulfate) at 1113 cm^{-1}; a strong (v_4) bending doublet (sulfate) at 668 and 598 cm^{-1}; (v_2) bending (sulfate) at 469 cm^{-1}; (v_3) and (v_1) O–H stretching (water) at 3535 and 3404 cm^{-1}, respectively, and (v_2) H–O–H bending (water) at 1682 and 1621 cm^{-1} [52]. A representative spectrum is shown in Figure 4b, with the assigned characteristic peaks labeled in red.
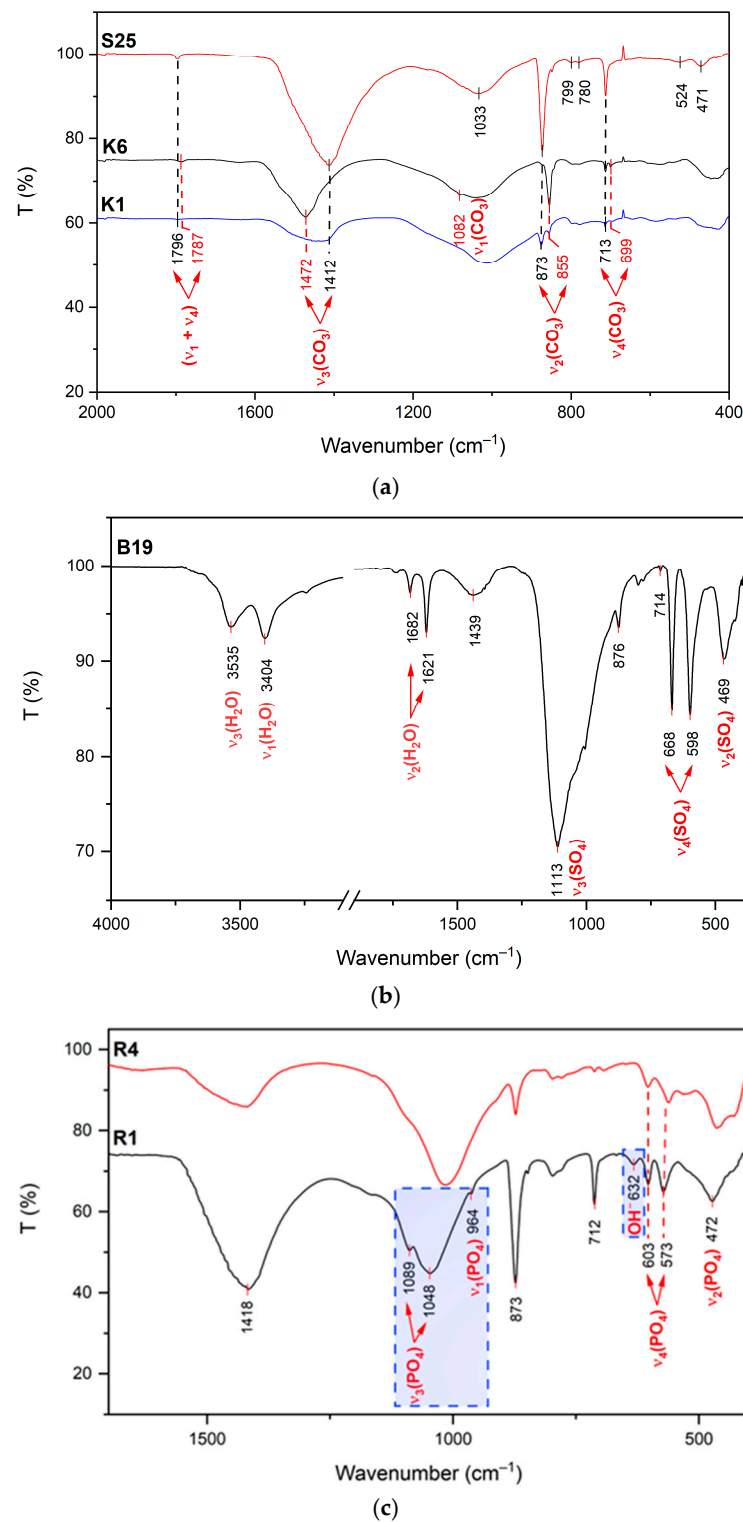
Figure 4. Representative FTIR spectra of selected samples: (**a**) IR spectra of samples S25, K6, and K1 show the assigned characteristic peaks of Cal, Arg, and a mixture of both within the 2000−400 cm^{-1} spectral range. The peaks denoted in black refer to Cal, and the peaks in red refer to Arg; (**b**) The IR spectrum of sample B19 shows the assigned characteristic peaks of Gp within the 4000−400 cm^{-1} spectral range; (**c**) IR spectra of samples R1 and R4, revealing the presence of Hap (the red labels) within the 1700−400 cm^{-1} spectral range. The characteristic peaks of the phosphate (PO_4^{3-}) and hydroxyl (OH^-) groups, highlighted in the blue rectangles of the R1 spectrum, are missing from the R4 spectrum, which infers a significant presence of magnesium.

Three samples dated to the Early Chalcolithic (B17, R1, and R4) showed the presence of hydroxylapatite (Hap). Two spectra are presented in Figure 4c, with the peaks associated with the mineral labeled in red. Only sample R1 exhibited all of the distinctive phosphate and hydroxyl bands of Hap: asymmetric stretching (v_3) of phosphate at 1089 and 1048 cm^{-1}; symmetric stretching (v_1) of phosphate at 964 cm^{-1}; bending (v_4) of phosphate at 603 and 573 cm^{-1}; bending (v_2) of phosphate at 472 cm^{-1}; and the vibrational mode of OH$^-$ at 632 cm^{-1} [53]. The characteristic peaks of the phosphate (PO_4^{3-}) and hydroxyl (OH$^-$) functional groups, highlighted in the figure's blue rectangles of the R1 spectrum, are absent in the R4 spectrum. This could be attributed to the increased concentration of magnesium (Mg) in the Hap lattice, resulting in the broadening and loss of resolution of the phosphate-derived bands and a decrease in the intensity of the OH$^-$-derived band, as observed in other studies [54]. LIBS confirmed this by detecting an increased relative intensity of Mg in R4 compared to the other samples.

In all samples, various clay minerals were detected through their primary Si–O stretching (1200–700 cm^{-1}) and bending (600–400 cm^{-1}) modes [55]. Qz was identified by its doublet at 799 and 780 cm^{-1} [56]. Additionally, noticeable characteristics in the spectral range of 600–400 cm^{-1} indicate the likely presence of Fsp and iron oxides [56–58].

Comprehensive information on the analyzed sherds and the mineral content of the white decoration is synthesized in Table 2.

Table 2. Synthesis of the pottery information with the corresponding mineral content of the decorations (Hem—hematite; Mag—magnetite; min—minor; tr—traces; EN—Early Neolithic; EC—Early Chalcolithic; MC—Middle Chalcolithic; LC—Late Chalcolithic).

Sample ID	Type of Decoration	Epoch	Culture	Archaeological Site	Mineral Content of the White Pigment
U2	paint	EN	Kremenik—Anzabegovo	Ilindentsi	Qz, Hem, Fsp, Cal
U3	paint	EN	Kremenik—Anzabegovo	Ilindentsi	Qz, Hem, Fsp, Cal
U4	paint	EN	Anzabegovo—Vrushnik	Drenkovo	Qz, Hem, Fsp, Cal (tr)
U5	paint	EN	Anzabegovo—Vrushnik	Drenkovo	Qz, Mag, Fsp, Cal (tr)
P23	paint	EN	Galabnik I	Galabnik	Qz, Hem, Fsp
P24	paint	EN	Galabnik I	Galabnik	Qz, Hem, Fsp, Cal (tr)
P25	paint	EN	Galabnik I	Galabnik	Qz, Hem, Fsp, Cal (tr)
P26	paint	EN	Galabnik I	Galabnik	Gp, Qz, Fsp
P27	paint	EN	Galabnik I	Galabnik	Qz, Hem, Fsp, Cal (min)
P28	paint	EN	Galabnik I	Galabnik	Qz, Hem, Fsp, Cal (tr)
P29	paint	EN	Galabnik I	Galabnik	Qz, Hem, Fsp, Cal (tr)
P30	paint	EN	Galabnik I	Galabnik	Qz, Hem, Fsp, Cal (tr)
P32	paint	EN	Galabnik I	Galabnik	Cal, Qz, Fsp
P33	paint	EN	Galabnik I	Galabnik	Cal, Gp (tr), Qz, Hem, Fsp
P34	paint	EN	Galabnik I	Galabnik	Cal, Qz, Fsp
P35	paint	EN	Galabnik I	Galabnik	Cal, Qz, Hem, Fsp
B2	paint	EN	Gradeshnitsa	Gradeshnitsa—Malo pole	Qz, Hem, Fsp, Cal (min)
B12	inlay	EC	Gradeshnitsa	Gradeshnitsa—Malo pole	Cal, Qz, Fsp
B13	inlay	EC	Gradeshnitsa	Gradeshnitsa—Malo pole	Cal, Qz, Fsp
B14	inlay	EC	Gradeshnitsa	Gradeshnitsa—Malo pole	Cal, Fsp
B15	inlay	EC	Vadastra IV	Brenitsa	Cal, Fsp
B17	inlay	EC	Vadastra IV	Brenitsa	Cal, Hap, Fsp
B18	inlay	EC	Vadastra IV	Brenitsa	Cal, Fsp
B19	inlay	EC	Vadastra IV	Brenitsa	Gp, Cal (min), Fsp
B21	inlay	EC	Vadastra IV	Brenitsa	Cal, Fsp
S12	inlay	EC	Karanovo V	Mogilovo	Qz, Cal, Hem, Kln, Fsp
S18	inlay	LC	Karanovo VI	StZ Bani	Qz, Cal, Hem, Fsp
S22	inlay	LC	Karanovo VI	StZ Bani	Qz, Cal, Hem, Kln (tr), Fsp
S25	inlay	LC	Karanovo VI	StZ Bani	Cal, Qz, Hem, Fsp
S29	inlay	LC	Karanovo VI	StZ Bani	Cal, Qz, Hem, Fsp
S32	inlay	EC	Maritza I	StZ Bani	Cal, Hem, Qz, Fsp
S33	inlay	EC	Maritza I	StZ Bani	Cal, Hem, Qz, Fsp

Table 2. *Cont.*

Sample ID	Type of Decoration	Epoch	Culture	Archaeological Site	Mineral Content of the White Pigment
R1	inlay	EC	Boyan III-Vidra and Polyanitsa II, III	Buzovets	Hap, Fsp
R2	inlay	EC	Boyan III-Vidra and Polyanitsa II, III	Buzovets	Cal, Fsp
R4	inlay	EC	Boyan III-Vidra and Polyanitsa II, III	Buzovets	Hap, Fsp
R5	inlay	MC	Boyan IV-Spantsov and Polyanitsa IV	Buzovets	Cal, Fsp
Bu3	inlay	C		Mirolyubovo	Gp, Cal, Hem, Qz, Fsp
Bu4	inlay	C		Mirolyubovo	Cal, Hem, Qz, Fsp
K1	inlay	C		Poroy	Cal, Mag, Arg, Fsp
K5	inlay	LC		Kozarevo mound	Qz, carbonate (tr), Hem, Mag, Fsp, Cal
K6	inlay	LC		Kozarevo mound	Arg, Qz, Fsp

4. Discussion

During the Neolithic period, the method of white decoration evolved progressively. Initially, the material used resembled a paint-like substance with varying densities and shades of white, but gradually, close to the end of the epoch and at the beginning of the Chalcolithic, preference was given to inlay paste with a specific density, strength, and uniform white color, suitable for incrustation.

This archaeometric study shows significant diversity in the raw materials used to prepare white pigment in the decoration of ceramic vessels during the Neolithic and Chalcolithic on the territory of Bulgaria. The main colorant mineral present in almost all sherds was Cal. According to the available information from the archaeometric investigations of mineral pigments, the use of Cal as a prime white colorant was ubiquitous in all territories of the Balkan Peninsula regardless of the technology of application, epoch, cultural affiliation, or geographical area [9,10,13,15,18,20,29,30]. In all of the analyzed fragments, aluminosilicates and clay minerals like alkali Fsp and Qz, as well as metal oxides, were found as carrier substances. These minerals may have been either intentionally added to achieve certain qualities of the pigment or impurities of the raw material itself [59,60].

The statistical analysis with PCA based on the results from LIBS indicated that the material used in the two types of decorations, paint and inlay, was distinguished mainly by the content of carrier additives. In the painted decorations, Cal was highly mixed with clay minerals, whereas Cal was the dominant constituent in the inlaid. In most of the painted sherds, ATR-FTIR detected Qz, Fsp, and iron-bearing minerals like Hem and Mag as a predominant ingredient, which was also confirmed by LIBS and PCA. The only exceptions were four of the sherds with major Cal content (P 32, 33, 34, and 35). The inlaid decorations exhibited the presence of various minerals in addition to the predominant mineral Cal.

The LIBS and PCA results demonstrated that titanium was increased in painted sherds compared to inlaid ones. This means that the white pigment in the painted sherds contained titanium-bearing minerals. Among the main mineral sources of titanium were the TiO_2 polymorphs, Rt and Ant, and ilmenite ($FeTiO_3$). Ilmenite can form continuous solid solutions with Hem [61], which was detected by ATR-FTIR in all of the painted sherds. This explains the simultaneous increase in titanium and iron in the painted decoration, as denoted by the results of the LIBS and PCA. Deposits of titanium-bearing minerals in Bulgaria are primarily located in the southern and western regions, specifically in Sakar, Strandzha, Rila, Vitosha, Western Rhodope, and in the Western Balkan Mountains [62]. On the territory of the Balkans, titanium-bearing minerals in the white paint were found only in Chalcolithic pottery from eastern Romania, which reported the presence of Ti-rich kaolin clay [63]. However, TiO_2 is presented in clays only as an impurity. Therefore, its presence

can be considered as a local characteristic of the mineral deposits rather than intentionally added as a colorant.

In Bulgaria, Gp has been identified in the composition of white pigments both alone and in combination with Cal. It was detected in two painted sherds (P26 and P33 from Galabnik, in the southwestern region) and in two inlaid pieces (B19 from Brenitsa, in the northwestern region, and Bu3 from Mirolyubovo, in the eastern region). Some of the Gp deposits in Bulgaria are located in these three regions. In the southwest, the deposit is located in the Blagoevgrad area; in the northwest, the deposits are along the Iskar River valley; and in the east, the deposits are near the city of Burgas [62]. While Gp was primarily used during the Early Chalcolithic, it was also found in two objects from the Early Neolithic (P26 and P33). The fragments from Galabnik are, to date, the earliest materials containing Gp in their decoration found on the Balkan Peninsula. Beyond Bulgaria, the use of Gp in white pigments has been documented only at the archaeological site of Topoliţa in Eastern Romania [9], Thessaly in Greece [64], and Hungary [65].

The inlaid fragments exhibited a greater variety of mineral constituents compared to the painted ones. In addition to the Cal, Kln, Arg, Hap, and Gp were found in particular fragments. In two of the sherds from the central region (S12 from Mogilovo and S22 from Starozagorski Bani, Stara Zagora district), Kln was detected. In our previous study, white-encrusted Late Neolithic pigment from the same region were examined, and the presence of Kln was detected in two of the sherds [32]. Kln deposits are found in many places in Bulgaria especially in northeastern region (Shumen and Rousse districts) also in the northwestern region (Vidin district), in the western region (Pernik and Sofia districts), in the southern region (Haskovo district), in the central region (Panagyurishte district), in the southeastern region (Yambol district), etc. [62]. Since Kln in the white paste was observed only in fragments from the Stara Zagora region of Bulgaria, its presence in the decorations can be identified as a distinctive characteristic of that area. Other regions of the Balkan Peninsula where Kln in white-encrusted paste has been reported are only in Dimini, Greece [6], and Baradla cave (Aggtelek), Hungary [16]. In order to confirm these observations, studies of a larger amount of pigments from the entire territory of Southeastern Europe should be carried out.

The presence of Hap in the white encrustations appeared in the Bulgarian territories during the Late Neolithic [32]. Pottery fragments with Hap are spread in northern Bulgaria, along the Danube River. They were observed in three of the sherds from two regions (B17 from Brenitsa, northwest region; and R1 and R4 from Buzovets, northern part of the central region). It is well known that Hap is a biogenic mineral that builds up to 70% of the mammals and human bones. Therefore, it can be stated that the white paste in these sherds most probably was made of ground bones. Hap is found in white-encrusted paste mainly in Croatia, Serbia, Hungary, and Romania along the lower Danube valley [10,14,18,23]. Based on the available information about Hap's presence in white pigment's composition, the trade and cultural connections between the populations inhabiting the lower Danube region can be indicated.

Arg is found in two of the sherds (K1 and K6). Arg develops in karst cavities within limestone rocks due to the influence of surface waters, or in cracks of volcanic rocks due to the effects of hydrothermal solutions [66]. Arg deposits in Bulgaria are found only in the northwestern region (the Iskar River Gorge of the Balkan Mountains) and in the southern region (Haskovo district) [62]. It is also known that Arg makes up the shells of many marine organisms and is a major constituent of pearls [66]. Because these fragments were found in the seaside region of Bulgaria (where shells are an available resource), it can be assumed that the material used for pottery decoration was most likely of biogenic origin. To date, no other published information exists on the use of Arg in white decoration from Bulgaria's territory. Although Arg was detected in only two samples, this indicates an innovation in the technique of white pigment preparation. Analyzing a larger quantity of samples from these archaeological sites and their surrounding areas is needed to confirm the indigenous character of the innovative technology of Arg decoration.

Although calcite was widely used as a white pigment throughout the Balkan Peninsula, different additives were used in various regions, allowing for the identification of distinct distribution areas. During the Neolithic period, the white pigment had a relatively uniform mineral content, primarily composed of Cal and kaolin clay with admixtures of Gp, found in specific territories of Hungary, Romania, Bulgaria, and Greece. In northwestern Romania and northern Hungary, Kln was predominantly used as white pigment.

During the Chalcolithic period, Kln was found in southeastern Thessaly, Greece, central Bulgaria, and eastern Romania. Additionally, the use of ground bones, identified as Hap, began during the Chalcolithic. These were mainly found in samples from southern Hungary and along the lower reaches of the Danube River.

5. Conclusions

This paper reported the results from an archaeometric study of the white pigments used for two types of decorations of pottery, inlaid and painted, from the territory of Bulgaria. A total of 41 Neolithic and Chalcolithic pottery from 11 archaeological sites were analyzed by two complementary spectroscopic techniques. The elements in the sherds were detected utilizing laser-induced breakdown spectroscopy (LIBS), and the obtained data were statistically treated by the multivariate chemometric technique, principal component analysis (PCA). The minerals in the decorations were determined via Fourier-transform infrared spectroscopy in attenuated total reflection mode (ATR-FTIR).

The results from the study revealed that the main mineral in most white pigments was Cal, which was combined with carrier materials like Qz, Fsp, and metal oxides. Although Cal exists in almost all of the decorations, some differences between painted and inlaid sherds were found. The two types of decorations were mainly divided according to their presence of a carrier substance, which prevailed in the painted ones while Cal was dominant in the inlaid ones. Also, the composition of painted decorations was relatively identical, whereas among the inlaid ones, diverse mineral content occurred. The addition of Gp, Hap, or Arg was found in particular inlaid fragments from different regions of Bulgaria. Incorporating mineral ingredients like Gp, Hap, and Arg reflects emerging tendencies in decoration techniques and potters' knowledge of minerals and their properties.

This study will help archaeologists to expand their understanding of ancient societies, their technological progress, and their cultural and trade interactions.

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