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Spectroscopic Study of White Pigments in the Decoration of Neolithic Pottery in the Region of the Thracian Valley, Bulgaria

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Abstract: Throughout history, ceramics have been the most abundant artifacts in archaeological discoveries. Within the Neolithic period in present-day Bulgaria, skilled artisans applied additional materials to decorate their pottery, evolving in composition and application techniques such as painting or incrustation. This study is focused on the investigation of white pigments used in decorating Early and Late Neolithic pottery from Madzherito, Kaloyanovets, and Hadzhidimitrovo—archaeological sites located in the Thracian Valley, Central South Bulgaria, affiliated with the cultural groups of Karanovo I and IV. Thirteen ceramic sherds were investigated through archaeometric techniques, including Fourier-transformed infrared spectroscopy in attenuated total reflection mode (ATR-FTIR) and laser-induced breakdown spectroscopy (LIBS). LIBS data underwent further analysis using principal component analysis (PCA). The results revealed that calcite, enriched with diverse fillers like quartz, clays, feldspars, and metal oxides, was the primary raw material for white decoration throughout the entire period. Talc emerged as an addition to calcite in the paint of two Early Neolithic sherds. The presence of hydroxyapatite and kaolinite in Late Neolithic pottery was also observed. The inclusion of supplementary ingredients in the primary formula for crafting white decorations signifies either the emergence of novel trends in manufacturing techniques or serves as evidence of vessels imported from adjacent territories.

Keywords: archaeological pottery; Neolithic; Karanovo culture; Thracian Valley; white pigments; archaeometry; mineralogical composition; FTIR; LIBS; PCA

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1. Introduction

In archaeological excavations, ceramic artefacts are usually the most commonly discovered items across all epochs. Their study forms the foundation for interpreting the archaeological and anthropological aspects of the site, addressing fundamental scientific questions about their origin, production methods, use, age, and preservation condition. Also, pottery is considered one of the most informative finds on archaeological sites given that sometimes it is the sole indicator of human presence. It serves as a time capsule that provides valuable knowledge about numerous aspects of our ancestors' lifestyle, such as their religio-mythological system, cultural attribution, technological advances, trade relationships, economic activities, social and cultural practices, etc. [1,2].

Following different fashion trends and socio-cultural exchange, the decoration of archaeological pottery exhibits diversity in execution, application methods, motifs, and ornaments. Throughout prehistory, additional materials have been used to apply different colors, creating contrasts with the base. The color palette is limited to white, yellow, red, various shades of brown, and black.

White pigmented decorations are a distinctive characteristic of pottery within the material culture of early agricultural communities in the Balkans, starting from the second phase of the early Neolithic (6000–5700 BC) [3,4]. White-painted ceramics are identified as a key criterion for belonging to the Balkano-Anatolian cultural block. This encompasses the initial stages of the Starčevo culture, Koprivec II, Karanovo I, Protosesklo, Nea Nikomedia, the first phase of the West Bulgarian painted pottery culture, Kriš I in Banat, Podgori I in Albania, and Horizons V-III in Hadzhilar [3]. In Bulgaria, based on the ornamental style and painting technique, four cultural regions with their specific characteristics can be distinguished: Gradešnica-Kârča in Northwestern Bulgaria, Kremikovtsi in central Western Bulgaria, Kremennik-Anzabegovo in Southwest Bulgaria, and Karanovo I in Thrace [5].

Over time, the technology of decoration evolved across the entire Balkan Peninsula, encompassing advancements in raw materials, application techniques, and stylistic arrangements [6]. A notable example of this evolution is observed in the development of decorated ceramics in the Thracian Valley during the Neolithic, specifically associated with the Karanovo I-IV culture. In the early Neolithic, a distinctive feature of the ceramic assemblage was a red-slipped surface adorned with white paint, serving as a diagnostic characteristic for the Karanovo I culture in Northern Thrace [7]. The application of ornaments occurred before firing, following extensive surface polishing. After thermal treatment, the white-colored paint contrasted against the red or brown base [3]. In the subsequent period, in the Karanovo II culture, evolving in the northern part of the Thracian Valley, this type of decoration disappeared [8]. The ornamentation of vessels underwent a complete transformation, utilizing alternative techniques that excluded pigments. This stylistic shift persisted and evolved during the subsequent periods of the Karanovo culture in Thrace. Only in the late Neolithic—Karanovo IV culture, in the eastern parts of the Thracian Valley, was pigment reintroduced as part of the ornamental repertoire, but with a radically different decoration technique. The pigment was applied as a white, non-uniform paste made of differently sized grains, inlaid on the outer or inner surface of the vessels, most likely after firing, indicating a completely new technology. This white incrusted decoration persisted up to the end of the Chalcolithic (~4100/4050 BC) [6].

White pigments used in prehistory are based mostly on naturally occurring mineral deposits [9]. Technological advancements have led to the recognition of the raw materials, composition, and structure of the white pigment, the preparation technique, and the stylistic arrangement as cultural and chronological indicators in archaeological science. Systematic archaeometric research plays a crucial role in contextualizing the studied material within archaeology, laying the foundations to address fundamental archaeological questions regarding the specifics of the epoch, potential technological exchange, trade routes, etc. Across the Balkan Peninsula, significant archaeometric studies on pigments used for decorating ceramics in the Neolithic have concentrated mainly on Greece [10–13] and Romania [14–16]. In the remaining Balkan countries, studies are rather sporadic, focusing on a limited number of ceramic fragments. Nonetheless, a discernible dependency in the use of various raw materials can be traced across different epochs [17–20]. In Bulgaria, the archaeometric analysis of pigments used for decorating Neolithic pottery is still in its early stages and exhibits a sporadic nature [6,21–24].

This article presents research focused on the white pigments utilized in decorating Neolithic pottery discovered in Central South Bulgaria, specifically within the region of Thrace. The study examines the white decorations of 13 ceramic fragments, collected from three distinct archaeological sites. These artefacts span the Early to Late Neolithic periods, associated with the Karanovo I and Karanovo IV cultures. To conduct a comprehensive analysis, mineralogical investigations are carried out using two complementary archaeometric techniques: Fourier-transformed infrared spectroscopy in attenuated total reflection mode (ATR-FTIR) and laser-induced breakdown spectroscopy (LIBS). The data obtained from LIBS are further processed using the multivariate chemometric technique of principal component analysis (PCA). The primary objective of this research work is to trace the evolution of coloristic decoration throughout the entire Neolithic period in this specific region attributed to trade and cultural interactions with neighboring areas to the north and west. By comparing the findings with those from other adjacent cultures, this study aims to enhance our understanding of trade and cultural exchanges, placing Karanovo I and IV within the broader archaeological context of Neolithic cultures in the Balkano-Anatolian cultural block.

2. Materials and Methods

2.1. Description of the Samples

For our investigation, thirteen fragments discovered during excavations at the archaeological sites of Madzherito, Kaloyanovets settlement mound, and Hadzhidimitrovo in the Thracian Valley were selected. These fragments are dated to the early to late Neolithic period and are associated with Karanovo I and Karanovo IV cultures. The exact geographical locations of the archaeological sites in the Thracian Valley are illustrated in Figure 1. A comprehensive description of the ceramic sherds, including their designation, photographic images, type of decoration, historical and cultural affiliation, and the archaeological site where they were excavated, is presented in Table 1.

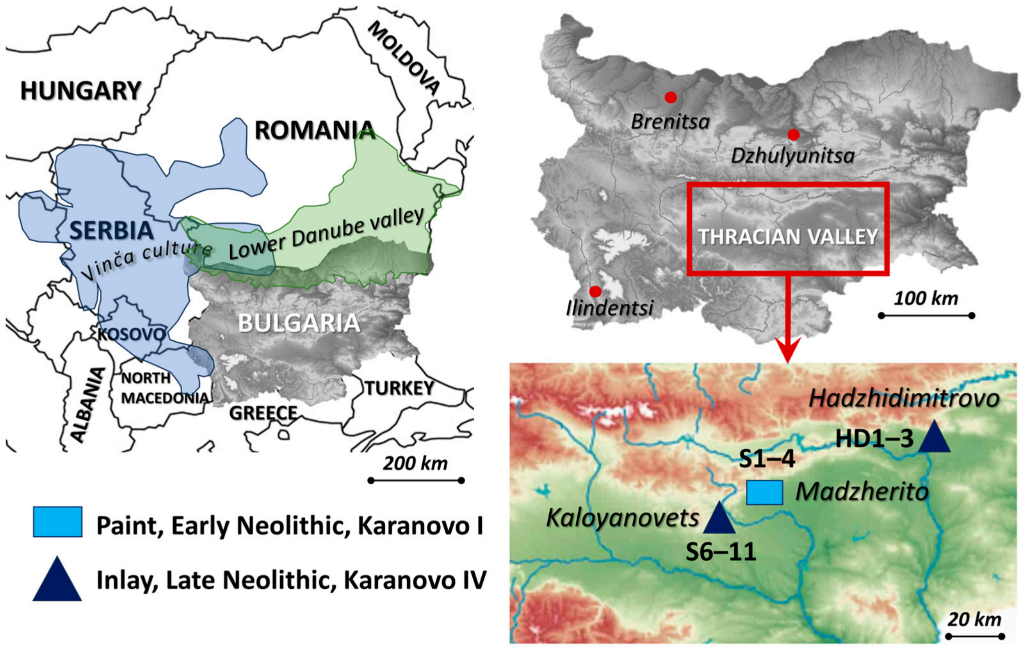


Figure 1. Geographical distribution, contextualized within a broader archaeological framework, of the archaeological sites in the Thracian Valley (marked by the red rectangle) depicting sample collection locations, types of decoration, historical epochs, and cultural affiliations.

Table 1. A comprehensive description of the examined ceramic sherds with white decoration. The black rectangle beneath each photograph represents a scale of 1 cm.

Sample ID	Image of the Ceramic Sherd	Type of Decoration	Epoch	Culture	Archaeological Site
S1		Paint	Early Neolithic	Karanovo I, Azmak version	Madzherito
S2		Paint	Early Neolithic	Karanovo I, Azmak version	Madzherito
S3		Paint	Early Neolithic	Karanovo I, Azmak version	Madzherito

Table 1. *Cont.*

Sample ID	Image of the Ceramic Sherd	Type of Decoration	Epoch	Culture	Archaeological Site
S4		Paint	Early Neolithic	Karanovo I, Azmak version	Madzherito
S6		Inlay	Late Neolithic	Kaloyanovets-Karanovo IV	settlement mound Kaloyanovets
S7		Inlay	Late Neolithic	Kaloyanovets-Karanovo IV	settlement mound Kaloyanovets
S8		Inlay	Late Neolithic	Kaloyanovets-Karanovo IV	settlement mound Kaloyanovets
S9		Inlay	Late Neolithic	Kaloyanovets-Karanovo IV	settlement mound Kaloyanovets
S10		Inlay	Late Neolithic	Kaloyanovets-Karanovo IV	settlement mound Kaloyanovets
S11		Inlay	Late Neolithic	Kaloyanovets-Karanovo IV	settlement mound Kaloyanovets
HD1		Inlay	Late Neolithic	Karanovo IV	Hadzhidimitrovo
HD2		Inlay	Late Neolithic	Karanovo IV	Hadzhidimitrovo
HD3		Inlay	Late Neolithic	Karanovo IV	Hadzhidimitrovo

The Early Neolithic period is represented by four ceramic sherds with white-painted decoration on a red burnished surface (S1–4). These artefacts were excavated in 2016 from an archaeological site situated near the village of Madzherito, south of the city of Stara Zagora, in the area known as Mogilkata. The structures from the early Neolithic are attributed to the Azmak variant of the Karanovo I culture (5990–5840 cal BC) [25].

The settlement mound near Kaloyanovets, located south of the city of Stara Zagora, reveals the evolution of the Late Neolithic culture Kaloyanovets—Karanovo IV in Southern Bulgaria. Six ceramic fragments (S6–11) were chosen for analysis from those excavated at this site. The distinguishing feature is the presence of incised lines on a brown, beige, or greyish-black surface with white-incrusted ornamentation, providing evidence for a seamless evolutionary transition from the Late Neolithic to the Early Chalcolithic [26].

Three ceramic sherds from the pottery assemblage excavated from the Late Neolithic site in the area of Hadzhidimitrovo, Yambol region, were chosen for analysis. The distinctive features include a grey-black burnished surface adorned with intricate incised lines encrusted with white material (sherds HD1 and HD2), as well as a light red surface with the same style of decoration (sherd HD3). This assemblage is also associated with the Karanovo IV culture [27].

2.2. Analytical Methods

The mineralogical characterization of the white decorations on the chosen pottery fragments was conducted through a complementary approach, which involved two well-established spectroscopic techniques in the archaeometric field [2,28,29], along with multivariate chemometric analysis. Although LIBS investigations have been conducted on inorganic pigments, including white ones, in diverse materials such as murals, painted potteries, porcelain, and other historical objects [30–33], we acknowledge the limited availability of published studies specifically focused on the application of LIBS in studying white decoration on archaeological ceramics.

2.2.1. Fourier Transformed Infrared Spectroscopy in Attenuated Total Reflection Mode

The molecular composition of the white decorations was determined qualitatively using ATR-FTIR. The analysis was performed with a Perkin Elmer Spectrum Two FTIR spectrometer equipped with a PIKE GladiATR accessory (monolithic diamond ATR crystal, Pike Technologies, Fitchburg, WI, USA). To acquire well-resolved spectra from each white decoration, a micro-sample was taken and ground in a clean agate mortar with a pestle. The analyses were conducted at room temperature without any additional preparation. The spectra were obtained in the MIR spectral region, spanning from 4000 to 400 cm^{-1}, through the averaging of 32 scans with a resolution of 4 cm^{-1}. A baseline correction was performed by the equipment software. The spectra were presented in transmittance (% T) and interpreted by comparison with the literature.

2.2.2. Laser-Induced Breakdown Spectroscopy

LIBS was utilized for elemental identification. The analysis was conducted using the portable LIBSCAN25+ system from Applied Photonics Ltd. (Skipton, UK). The equipment comprised a Q-switched Nd:YAG laser operating at a fundamental wavelength of 1064 nm, with a pulse duration of 10 ns and a nominal output pulse energy of 50 mJ. Additionally, the system included six spectrometers covering the spectral range of 200–750 nm, along with beam-focusing and light-collecting optics. The samples under investigation were exposed to a pulse energy of 8 mJ. The laser beam was focused perpendicular to the object's surface using a lens with a focal length of 90 mm. The radiation emitted from the plasma was collected by six lenses, three designed for UV-VIS and the remaining three for VIS-NIR. Subsequently, the collected radiation was transferred to the spectrometers via optical fibers. Ablation took place in ambient air at atmospheric pressure. The LIBS system was equipped with LIBSoft V14 software, responsible for controlling data acquisition and displaying spectra. During the initial stage of plasma generation, continuous background radiation was emitted. To avoid the capture of this radiation, signal registration was carried out at a delay time of 1.3 μs after the laser pulse, and the registration gate was set to 1 ms.

The analyses were performed on both the decoration and the ceramic slips of the sherds. Given the non-uniformity of the material under investigation and to guarantee result consistency, analyses were conducted at 10 distinct points on the surface of the sherd. Before each analysis, two cleaning pulses were applied. Subsequently, the results obtained from each set of ten spectra were averaged to enhance accuracy and repeatability.

The absence of suitable matrix-matched calibration standards presents a challenge in quantifying the identified elements. Consequently, the analysis was confined to element identification and a semi-quantitative approach. This involved determining the intensities of spectral lines for detected elements in decorations in comparison to the same spectral lines in the ceramic slips.

To mitigate the influence of the instrument response variations due to the matrix effects and pulse-to-pulse fluctuations in the laser fluence, the integrated peak areas of selected spectral lines were normalized to the total emission intensity from the plasma [34].

2.2.3. Principal Component Analysis

The similarity in elemental content poses a challenge in distinguishing sherds with different mineral pigments in their decorations. To address this issue and facilitate a clearer visualization of chemical variations in the sherd's decorations, PCA based on the LIBS data was employed, using the differences in the normalized intensities of selected spectral lines from the main elements detected. The spectral lines were carefully chosen to ensure they were not affected by overlapping with other spectral lines.

3. Results

3.1. Molecular Composition

The ATR-FTIR spectroscopic investigations reveal persistent features in the molecular composition of the white decorations. In the Supplementary Materials, ATR-FTIR spectra for all samples are presented and organized by relevant archaeological sites (refer to Figures S1–S3). The presence of $CaCO_3$ is identified in all samples through the primary vibrations of the carbonate group: a strong, broad band centered around 1420–1418 cm^{-1} attributed to the asymmetric stretching (υ_3), an intense narrow band at 874–873 cm^{-1} resulting from the out-of-plane bending (υ_2), and a narrow band at 713–712 cm^{-1} ascribed to the in-plane bending (υ_4) (highlighted by blue rectangles in Figures S1–S3 in the Supplementary Materials) [35].

Clay minerals are identified by the distinctive Si-O stretching and bending modes within the spectral range of 1200–700 cm^{-1} and 600–400 cm^{-1}, respectively [36]. Quartz is also consistently detected in all samples due to its distinctive doublet at 799 and 779 cm^{-1} [37]. Additionally, the likely presence of feldspars and iron oxides is indicated by discernible features in the 600–400 cm^{-1} spectral region [1,37,38]. However, the precise identification is obscured due to the overlap of various bands.

The distinctive vibrations of talc separate samples S1 and S3 from the rest in the dataset. In Figure 2a, the infrared spectrum of sample S1, spanning the range from 4000 to 400 cm^{-1}, reveals notable peaks attributed to calcite and talc. The highlighted spectral region within the red rectangle exhibits a sharp band at 3677 cm^{-1}, signifying the stretching mode of Mg_3OH, and a very weak band at 3661 cm^{-1}, indicative of the $Mg_2Fe^{2+}OH$ stretching vibration, suggesting a minor iron presence in this mineral. These bands are characteristic of talc. Additional distinguishing features of talc manifest in the 1200–400 cm^{-1} range, with well-defined absorption bands associated with Si–O and OH group vibrations. The most prominent band, taking on a distinct shape at 1018 cm^{-1}, is assigned to the in-plane Si–O stretching mode. The absorption band at 671 cm^{-1} corresponds to the bending vibration of the OH groups (Mg_3OH), while a slightly lower position at 665 cm^{-1} reveals an absorption band linked to the iron content in talc. The band around 531 cm^{-1}, appearing as a shoulder, is connected to the perpendicular Mg-O vibration mode, and the bands at 466 and 451 cm^{-1} arise from the translation vibrations of the OH groups and the Si–O–Si bending vibrations, respectively [36].

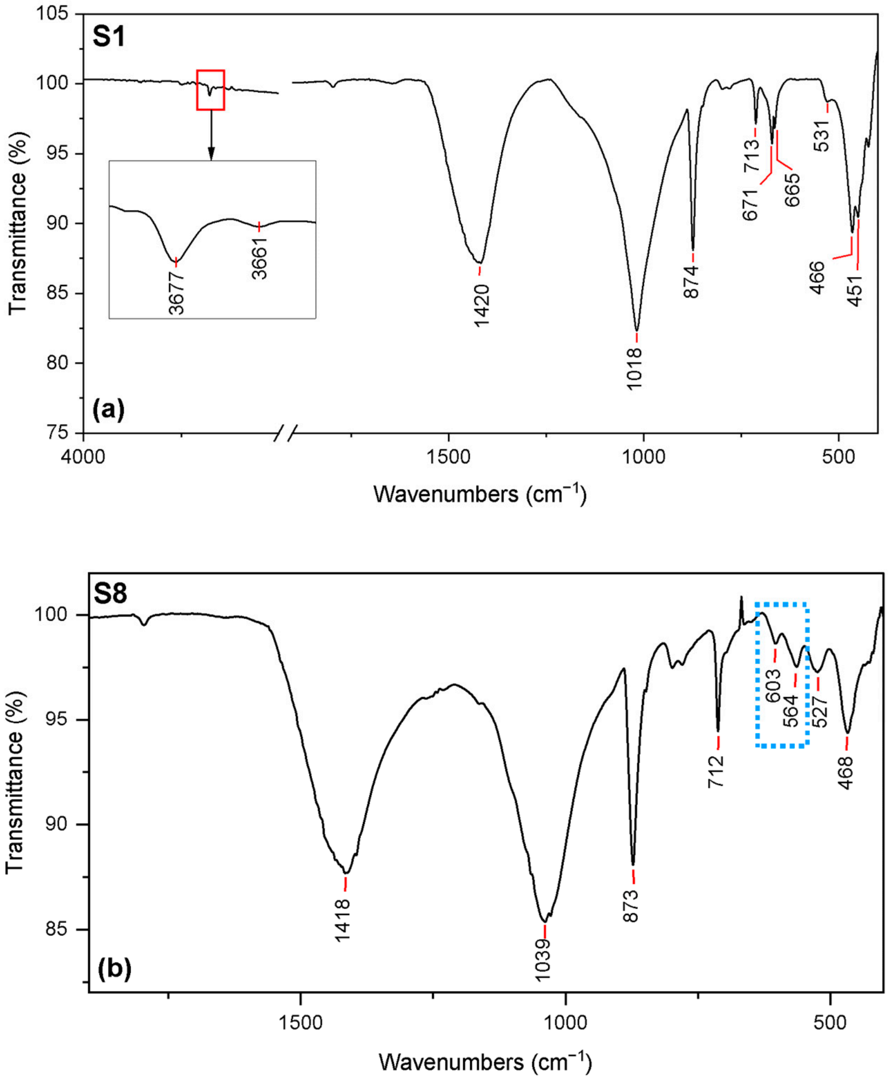


Figure 2. (**a**) IR spectrum of sample S1 showing characteristic peaks of calcite and talc within the 4000−400 cm^{-1} spectral range. The highlighted peaks in the rectangle at 3677 and 3661 cm^{-1} specifically denote the presence of talc. (**b**) IR spectrum of sample S8 plotted within the 2000−400 cm^{-1} spectral range revealing the presence of calcite, iron oxides, and two distinctive bands associated with the vibrations of the PO_4 group, as indicated by the dashed blue rectangle.

Three samples collected from the Late Neolithic settlement mound of Kaloyanovets (S6, S8, and S11) show distinct characteristics associated with phosphate-bearing minerals. In Figure 2b, the infrared spectrum of sample S8, spanning the 2000–400 cm^{-1} spectral range, is displayed. Notably, the vibration bands of calcite (1418, 873, and 712 cm^{-1}) and iron oxides (527 and 468 cm^{-1}) are evident. Within the region marked by the dashed blue rectangle, two distinguishable peaks at 603 and 564 cm^{-1} are observed, attributed to the bending vibration (υ_4) of the PO_4 functional group [39]. However, other distinctive bands are not visible, likely due to significant overlap with adjacent bands.

3.2. Elemental Composition

In all of the studied sherds, the primary elements identified are Si, Al, Ca, Fe, and Mg, with Ca notably being the most abundant element in the decorations. This suggests the utilization of calcium-rich minerals as the white pigment in the decorations, such as calcite, as identified by ATR-FTIR. Additionally, minor elements such as Ti, Sr, Ba, Na, K, Mn, Cr, and Li are consistently detected in all the sherds. Spectral lines corresponding to all the identified elements are observed in both the decorations and the slips of the ceramics, but with varying relative intensities. The wavelengths of the atomic and ionic spectral lines responsible for detecting these elements are detailed in Table S1 in the Supplementary Materials.

Figure 3 displays the PCA score plot of the analyzed decorations in the space defined by the first two principal components (PCs), which collectively account for 77.99% of the total variance. Specifically, PC1 contributes 57.64% and PC2 contributes 20.35% to the overall variance. The loading plot indicates that PC1 is primarily influenced by Al, Si, Ca, and Fe, whereas PC2 is influenced by Mg and Cr.

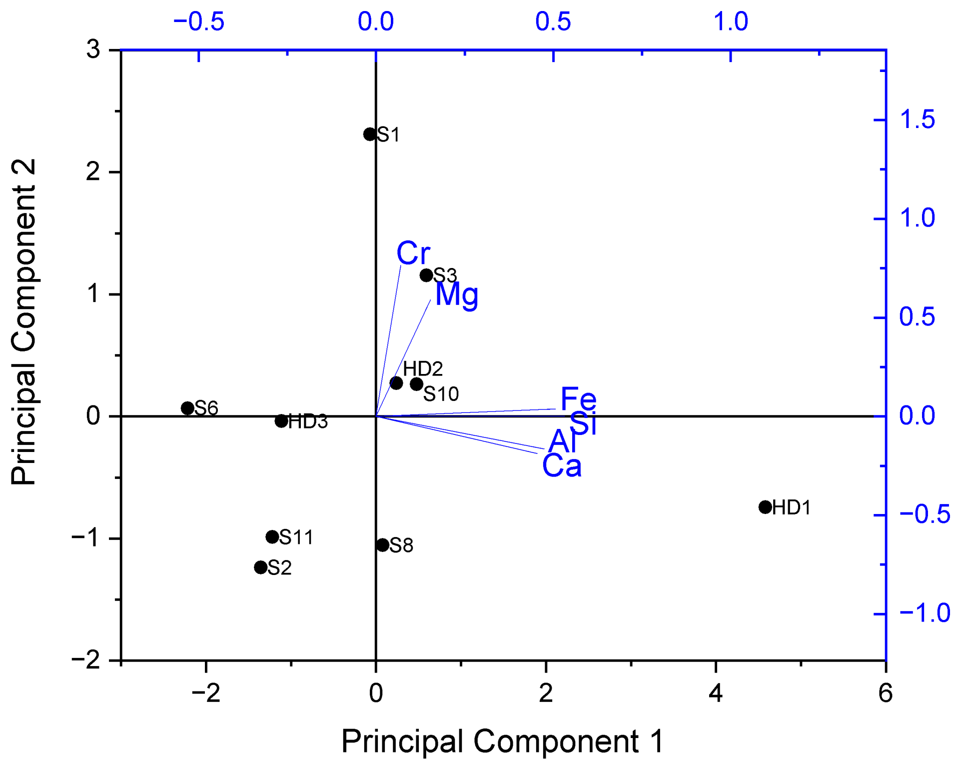
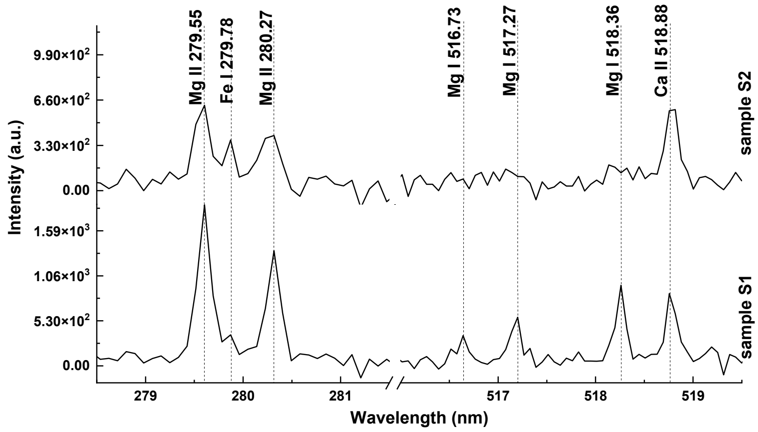


Figure 3. Score plot and loading plot of the first two PCs obtained by means of PCA of the decorations analyzed by LIBS.

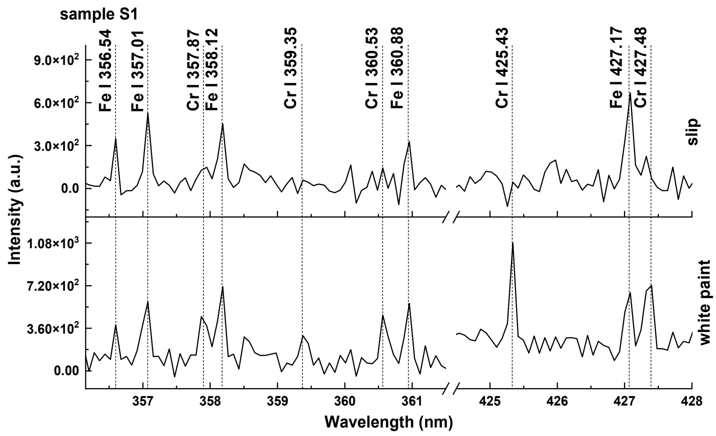
While the PCA graph does not reveal a clear clustering of the sherds, it does highlight the presence of outlier sherds, suggesting potential differences in mineral content. Notably, Sample HD1 stands out as it is distinctly separated from the other sherds. It is characterized by the highest positive score on PC1, which, considering the loadings, is associated with a higher content of Ca, Al, Si, and Fe.

On the other hand, sherds S1 and S3 exhibit the highest positive values on PC2, indicative of a higher content of Mg and Cr in these specific sherds. The spectral features showing the elevated content of magnesium in the white decoration are depicted in Figure 4a. It compares two sections of the LIBS spectra obtained from one of these sherds (S1) and a sherd without a magnesium increase (S2). It is evident that the magnesium spectral lines in the white decoration of sherd S1 exhibit higher intensity than the corresponding spectral lines in the decoration of sherd S2. The heightened magnesium content in the decorations of S1 and S3, in comparison to the slips, implies the utilization of magnesium-rich minerals as the white pigment.

The increased concentration of chromium in the decorations of the same sherds, as opposed to their slips, is evident in Figure 4b. This figure illustrates two sections of LIBS spectra detected from the decoration and the slip of sherd S1.



(**a**)



(**b**)

Figure 4. (**a**) Two sections of the LIBS spectra from 279 nm to 282 nm and from 516 nm to 519 nm detected from the white decorations of sherds S1 and S2. The labeled spectral lines include those of magnesium (279.55 II nm, 280.27 II nm, 516.73 I nm, 517.27 I nm, and 518.36 I nm), iron (279.78 I nm), and calcium (518.88 II nm). (**b**) A comparison of the LIBS spectra obtained from the white paint and the slip of sherd S1, highlighting two spectral ranges (356–361 nm and 425–428 nm) with labeled spectral lines of Cr and Fe.

4. Discussion

The spectroscopic approach employed in this study distinctly unveils a conservative trend in the composition of the white pigment utilized for adorning Neolithic pottery in the Thrace Valley, specifically within the Karanovo I and IV cultures. This research builds upon a previous study that examined the white decorations of ceramic fragments from Madzherito (S1–4) and Kaloyanovets (S6–11) using X-ray diffraction spectroscopy (XRD) [6]. The findings are validated and enhanced with additional insights gained from FTIR and LIBS techniques.

Throughout the Neolithic period, the technique of white decoration underwent a gradual evolution, transitioning from a white consistency close to paint with diverse density and color nuances to a paste with distinct density, strength, and white color used for inlay. It is known that the most common prehistoric white pigments are calcite, gypsum, kaolinite, talc, apatite, and huntite [40,41]. Irrespective of the territory, era, or decorative style, calcite remained extensively utilized. Serving as a primary raw material, the knowledge of its use remains unaffected by trade and cultural traditions. The utilization of calcite-based white decoration has been observed all over the Balkan Neolithic [16,18,19,21,24,42].

The main pigment material is typically enhanced by various fillers and carriers, including quartz, clays, feldspars, and metal oxides, as identified through ATR-FTIR. These minerals are likely derived from the raw material itself [43] or intentionally added for specific purposes [44]. LIBS corroborates these findings by detecting major elements such as Si, Al, Fe, and Mg, and minor elements including Ti, Sr, Ba, Cr, Na, K, Mn, and Li. [43,44].

Based on the results from PCA, which highlights sample HD1 for having the highest concentrations of aluminum, silicon, and iron, in addition to calcium in the decoration, it can be inferred that there might be the presence of aluminosilicates, most likely kaolinite, in the decoration of this sherd. However, the ATR-FTIR analysis does not reveal any visible spectral features that could corroborate this assumption.

The presence of specific additives to the white material for decoration indicates local specificities and allows for the regionalization and distinction of ceramic technological groups. The highest amount of Mg in the decorations of S1 and S3 detected by means of LIBS and the PCA is aligned with the identification of talc in these sherds via ATR-FTIR, as it is a magnesium-bearing mineral ($Mg_3Si_4O_{10}(OH)_2$). On the other hand, chromium is recognized as a minor element by LIBS but with the highest relative amount in S1 and S3. It is possible that Cr naturally occurs in talc, since during the mineral's formation, small quantities of Cr, Ti, or Al can substitute the Si in the end-member formula of the talc [45,46]. Based on studies published so far, in addition to in Madzherito, talc has been identified in the white-painted pottery from two more archaeological sites: near Ilindentsi in South-West Bulgaria [23] and Dzhulyunitsa in North Bulgaria (both sites are shown in Figure 1) [21]. All sites are dated to the same period but belong to three different cultural groups. More analyses are needed to determine the relationship of the ceramics and to ascertain whether they have spread through trade routes. The studies on the pottery assemblage of Dzhulyunitsa containing talc in the decoration conclude that these vessels have been imported from elsewhere. The rationale behind this assertion, as indicated by the authors [21], is that the mineralogy of the few white paints found on these vessels does not align with materials typically sourced within the local Lower Danubian corridor, while talc detected in Ilindentsi was sourced from local talc-bearing marble deposits [23]. In the site near the village of Madzherito, both techniques for preparing white paint based on calcite are known with or without the addition of talc, suggesting that some geological deposits of raw material for this mineral could be located in the area. However, at this stage of research, this assumption remains speculative and is not conclusively justified. To the authors' knowledge, there are no archaeological studies in this direction specifically concerning the local geological deposits in this particular region. Moreover, so far, the presence of talc is observed only in the Early Neolithic, which restricts its use to this period only. The spread of this technology with the addition of talc to the white pigment probably moved from southwest to northeast.

The potential presence of phosphates is only detected through ATR-FTIR, as LIBS could not verify this result due to the detection limit of the equipment used. This finding could be associated with the use of hydroxyapatite as a material for the white pigment. The recipe for the white paste includes crushed bones. The use of this material only began during the Chalcolithic period, identified as apatite or hydroxyapatite through archaeometric analyses. This materials has been identified in samples mainly in the southern parts of Hungary and along the lower Danube valley (these regions are shown in Figure 1). There is only one report in the literature on the use of this mineral for decoration in the early Chalcolithic settlement in Brenitsa (the site is indicated in Figure 1), Vratsa region, in North-West Bulgaria [47]. This is considered atypical for the territory of Bulgaria and is an indicator of imported vessels from neighboring territories.

However, during the Late Neolithic on the Balkan Peninsula, there is evidence for the use of hydroxyapatite in the white paste for inlay pottery and later ceramic cult objects only in Serbia, related to the Vinca culture (the territory of which is depicted in Figure 1) [18,48]. The detection of this mineral in the incrusted pottery from Kaloyanovets is a singular case and likely indicates the importation of ceramic vessels.

5. Conclusions

This paper presents a study on the white pigments employed in decorating Early and Late Neolithic pottery from the archaeological sites of Madzherito, Kaloyanovets, and Hadzhidimitrovo, situated in the Thracian Valley, Central South Bulgaria. These sites are associated with the cultural groups of Karanovo I and IV. The mineralogical composition of 13 ceramic sherds is investigated using complementary archaeometric techniques: Fourier-transformed infrared spectroscopy in attenuated total reflection mode (ATR-FTIR) and laser-induced breakdown spectroscopy (LIBS). The data obtained from LIBS are further processed using the multivariate chemometric technique of principal component analysis (PCA).

The findings reveal that the primary raw material used for white decoration throughout the entire period is calcite, enriched with various fillers and carriers, including quartz, clays, feldspars, and metal oxides. Talc is identified as an addition to calcite in the paint of two Early Neolithic sherds. The presence of hydroxyapatite and kaolinite in Late Neolithic pottery is also inferred.

In this microregion, where a single recipe for preparing white paint was preserved for an extended period, possibly utilizing a single deposit, the presence of another type of mineral composition suggests its introduction from external sources, possibly through trade routes. The addition or utilization of other ingredients such as talc and apatite reveals new trends in manufacturing techniques, a potter's knowledge of minerals and their properties, and a desire for innovation. This was likely driven by trade and cultural connections with neighboring regions to the north and west.

However, the limited studies across the entire territory of Bulgaria suggest the need for broader geographical exploration including archaeometric analyses of the pigments found on a greater variety of ceramic and cult objects.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min14020152/s1, Figure S1: IR spectra of samples S1–4 within the 2000–400 cm^{-1} spectral range. The characteristic absorption bands of calcite are denoted in the blue rectangles and a dashed line showing the central positions of the peaks; Figure S2: IR spectra of samples S6–11 within the 2000–400 cm^{-1} spectral range. The characteristic absorption bands of calcite are denoted in the blue rectangles; Figure S3: IR spectra of samples HD1–3 within the 2000–400 cm^{-1} spectral range. The characteristic absorption bands of calcite are denoted in the blue rectangles; Table S1: Wavelengths of spectral lines used for element detection in the LIBS analysis. The Roman numerals I and II denote spectral lines emitted from neutral atoms and singly ionized atoms, respectively.

Author Contributions: Conceptualization, V.A., V.T., V.M. and A.P.; Data curation, V.A. and V.T.; Formal analysis, V.A. and V.T.; Funding acquisition, V.T.; Investigation, V.A. and V.T.; Methodology, V.A., V.T. and V.M.; Project administration, V.T. and V.M.; Resources, A.P.; Supervision, V.M.; Validation, V.A. and V.T.; Visualization, V.A. and V.T.; Writing—original draft, V.A. and V.T.; Writing—review and editing, V.A., V.T., V.M. and A.P. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

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