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The Raman study of the white pigment used in Cucuteni pottery

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Abstract

Shards from Cucuteni archaeological sites of Moldavia (eastern part of Romania) were analyzed through Raman spectroscopy in order to identify the white pigment used in the decoration of Cucuteni pottery (cca. 4500–3500 B.C.). Ti-minerals, namely anatase, rutile and titanite, were identified in the white pigment of nearly all the samples. Zircon, quartz and K-feldspars were also observed in a number of samples. Kaolinite was not discovered because the Raman bands of this mineral are masked by the Raman response of the previously listed minerals. The white pigment used in the painting of Cucuteni pottery is Ti-rich kaolinitic clay which forms residual clay accumulations developed on the Tertiary volcanic rocks from the Eastern Carpathians. These residual clays may also contain zircon, quartz and feldspars.

Keywords: Raman spectroscopy, Cucuteni pottery, white pigment.

Introduction

The present paper illustrates the results of the Raman study of the white pigment from 79 shards of pottery belonging to the Cucuteni culture.

The calcholithic Cucuteni-Ariușd-Tripolie cultural complex spreads across 350.000 km^2, from the south-east of Transylvania to the Dnieper River, and it covers the time span between approximately 4.600 and 3.500 CAL. B.C. Based on the painted decoration of the pottery, the Cucuteni culture has been divided into three phases: Cucuteni A (4525/4500–4050 CAL.B.C.), A-B (4100–3800/3700 CAL.B.C.) and B (3800/3700–3500/3350 CAL.B.C.).

The ornamentation of the Cucuteni phase A pottery is characterised by polychrome painting, with the motifs – usually varied spirals and meanders – in red or white and black borderlines covering the entire surface of the pot, in a so-called *horror vacui* style. The next evolutionary phase, A-B, keeps the

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spiral and the meander as the main painted motifs, but the three colours gain equal importance and the decoration is organized in a tectonic manner with respect to the constitutive parts of the pot (rim, neck, shoulder, bottom). During the final phase of the Cucuteni culture, the decoration of the pots becomes more sophisticated. The tectonic organisation of the painted decoration is preserved but, alongside, metopes begin to be used. The meander almost disappears, while the spiralled decorative motifs are over-simplified, giving a general feeling of sobriety. Zoomorphic and anthropomorphic representations become more frequent and the three colours – red, black and white – have continuously changing values.

The white pigment used in ancient artwork has been investigated through Raman spectroscopy by several authors (Zuo et al., 1999; Wang and Andrews, 2002; Pérez and Esteve-Tébar, 2004; Middleton et al., 2005; Striova et al., 2006; Clark et al., 2007; Constantinescu et al., 2007; Bordignon et al., 2008; Hernanz et al., 2008; Raškovska et al., 2009; Bersani et al., 2010; Buzgar et al., 2010).

Hernanz et al. (2008) studied the white pigment of prehistoric rock paintings from Sierra de las Cuerdas, Spain (the middle of the 6th millennium BC – the end of the 3rd millennium BC), identifying the presence of quartz, anatase and sheet silicates. The authors concluded that the pigment is white earth (clays) from the surroundings.

Studies on painted pottery shards belonging to the Yangshao culture (Henan, China, 4200 BC) revealed the presence of anatase and quartz in the white pigment. The XRD studies carried out on these shards did not indicate the presence of kaolinite (Zuo et al., 1999). Further SEM/EDX analyses suggested that the white compound is a kaolinitic clay containing only 1.0–1.5 wt% TiO_2 (Wang and Andrews, 2002). Later, Clark et al. (2007) observed the characteristic bands for anatase, rutile and quartz in the Raman spectra, concluding that the TiO_2 forms are present as traces in an aluminosilicate matrix, and that anatase is dominating the spectra due to a better Raman signal.

In the white pigment of the prehistoric Anasazi ceramics (700–900 BC), Striova et al. (2006) identified anatase and, therefore, believe that the raw material used consisted of anatase-rich kaolinite clays.

On a Roman ceramic vessel, Middleton et al. (2005) observed the presence of rutile and anatase in the white paint, while the SEM data suggested a less than 2% titanium dioxide cotent. The white paint consisted mainly of a pure kaolinitic clay with a small anatase content. The authors suggest that the presence or absence of anatase may serve as an indicator for the source of the clay.

White pigment samples collected from Greek pottery dating from 5th – 4th century BC, discovered in Spain, have been studied through Raman spectroscopy by Pérez and Esteve-Tébar (2004). For the first time, it was found that the white pigment is composed of alumina (α-Al_2O_3 and γ-Al_2O_3). In some spectra, the bands of anatase were also revealed. The authors consider that the presence of alumina is due to the thermal decomposition of Greek bauxite at firing temperatures below 1100°C.

A Raman study of Etruscan ceramics (7th century BC) from the Cerveteri area reported, for the white samples, the presence of quartz, anatase and calcite (Bordignon et al., 2008). The results suggest the use of kaolin for the white pigment, since the Raman signature of anatase may be considered a marker of kaolin.

Raškovska et al. (2009) observed quartz, feldspar and anatase in the white parts of the glaze from the Byzantine glazed pottery (13th –14th century) from Skopsko Kale, the Republic of Macedonia.

Bersani et al. (2010) reported the presence of anatase and small amounts of quartz in the white pigment of the archaeological pottery from Parma, Italy (17th century). SEM-EDS analyses revealed a titanium concentration of 1% or lower. The authors concluded that the white coloration is due to a white clay and a small amount of TiO_2.

Painted Cucuteni shards belonging to phase A found in the Bistriţa Valley (Romania) were studied by Constantinescu et al. (2007) through XRF and SR-XRD measurements. The results showed that the white pigment is based on calcium silicate and calcium carbonate, the raw material being a light kaolinitic clay.

Buzgar et al. (2010) have studied a series of ceramic shards belonging to the Cucuteni culture – phase A (Hoiseşti, Scânteia and Ruginoasa sites), using Raman spectroscopy. For the white pigment, the spectra indicated the presence of anatase, rutile and quartz. The composition of the pigment was considered to be that of Ti-rich kaolinite clay, with a residual nature, formed through the weathering of acid igneous rocks.

The aim of the present paper is to identify the composition of the white pigment using non-contact Raman spectroscopy, as well as the location of the sources of the raw material.

Experimental

1. Samples

We have analyzed 79 samples of Cucuteni ceramic shards from the following archaeological sites: Iaşi county: Hoiseşti (8 samples), Scânteia (2); Bacău county: Aldeşti (6), Fulgeriş (13), Podei (2), Rusăieşti (10), Trebeş (6); Suceava county: Feteşti Schit (phase A–11, phase B–5), Preuteşti Halta (14), Mihoveni-Cahla Morii (2). The archaeological sites are located in the western part of the area over which the Cucuteni culture spreads (Fig. 1). Only two of the samples studied are presented (Fig. 2). More detailed images of all the samples can be found on the website of the project (rdrs.uaic.ro). Each sample was analyzed in minimum five points.

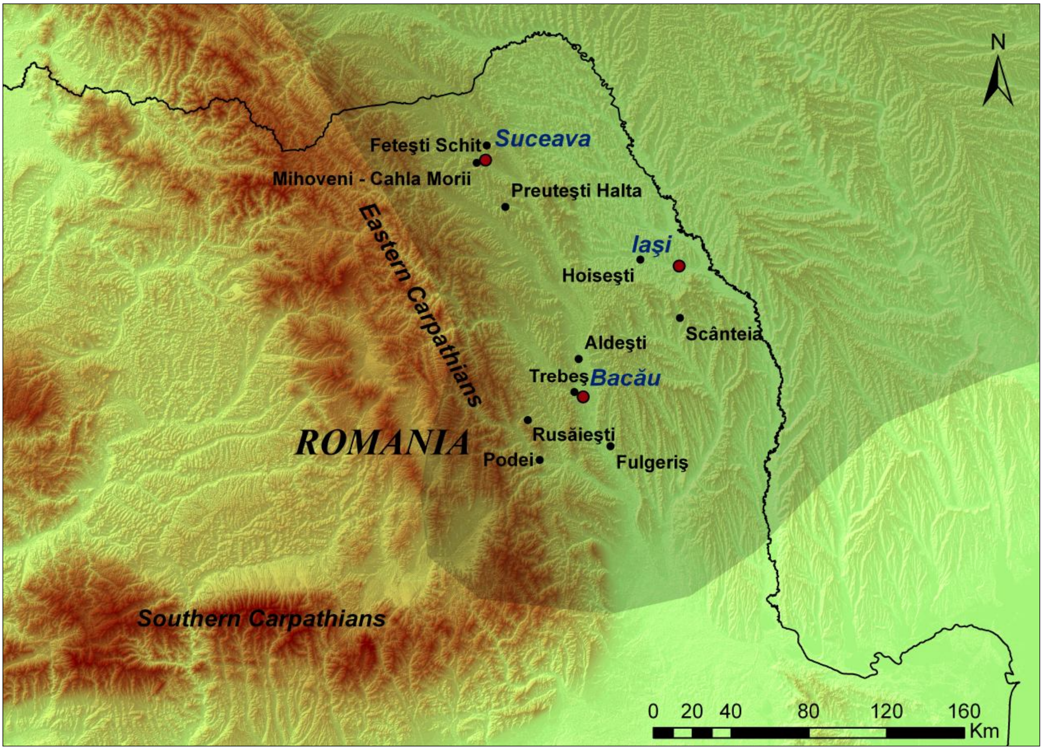

Fig. 1 Location of the archaeological sites.

Fig. 2 Two samples of Cucuteni ceramics (left – 46 FULG 89 2-2; right – 12 Preut Hlt 78 Gr 1 N7). The size of the coin is 23mm. All samples can be viewed on rdrs.uaic.ro

2. Raman spectroscopy

A Horiba Jobin-Yvon RPA-HE 532 Raman spectrograph with a multichannel air cooled (-70°C) CCD detector was used for the acquisition of the Raman spectra. The excitation source was a 532 nm Nd-Yag laser with a nominal power of 100 mW. The spectra were obtained in the spectral range between 200 and 3400 cm^{-1}, with a spectral resolution of 3 cm^{-1}. The Raman system includes a “Superhead” optic fiber Raman probe for non-contact measurements, with a 50X LWD visible objective Olympus, NA = 0.50 WD = 10.6 mm. For the calibration of the frequencies of the Raman spectra, sulphur and ciclohexane bands were used. The data was acquired through a 2–20 second exposure, 10–50 acquisitions, at a laser magnification of 50–70%, in order to improve the signal-to-noise ratio. Recording a clear Raman spectrum was a tedious task, as the spectra are superimposed on a strong fluorescence and background noise. The spectra are presented as acquired.

Results and discussion

In the samples studied, the following minerals have been identified: anatase (β–TiO_2), rutile (α–TiO_2), quartz (SiO_2), titanite ($CaTiSiO_5$), zircon ($ZrSiO_4$) and K-feldspar (KSi_3AlO_8). The presence of kaolinite ($Al_4Si_4O_{10}(OH)_8$) is certainly masked by the previously mentioned minerals, which have a better Raman signal than kaolinite (Zuo et al., 1999; Murad, 1997).

1. Anatase

Anatase was identified in the white pigment of the Cucuteni ceramics by Buzgar et al. (2010). The presence of this mineral is indicated by the characteristic bands at 392–396, 514, 633–637 and 798 cm^{-1} (Fig. 3a). The band wavenumbers are in agreement with those reported in the literature for anatase (Burgio and Clark, 2001; Buzgar et al., 2009). In some samples, anatase is present together with quartz (characteristic line at 461 cm^{-1}, Fig. 3b) or rutile (242, 438, 589 cm^{-1}, Fig. 3c). Frequently, anatase may contain a small concentration of Fe, in which case vibrations of Fe–O bonds may appear (292–298 cm^{-1}, Fig. 3b, 3d).

Anatase was observed in 38% of the samples, but the possibility of its presence in the other measurement points where it was not identified is not excluded.

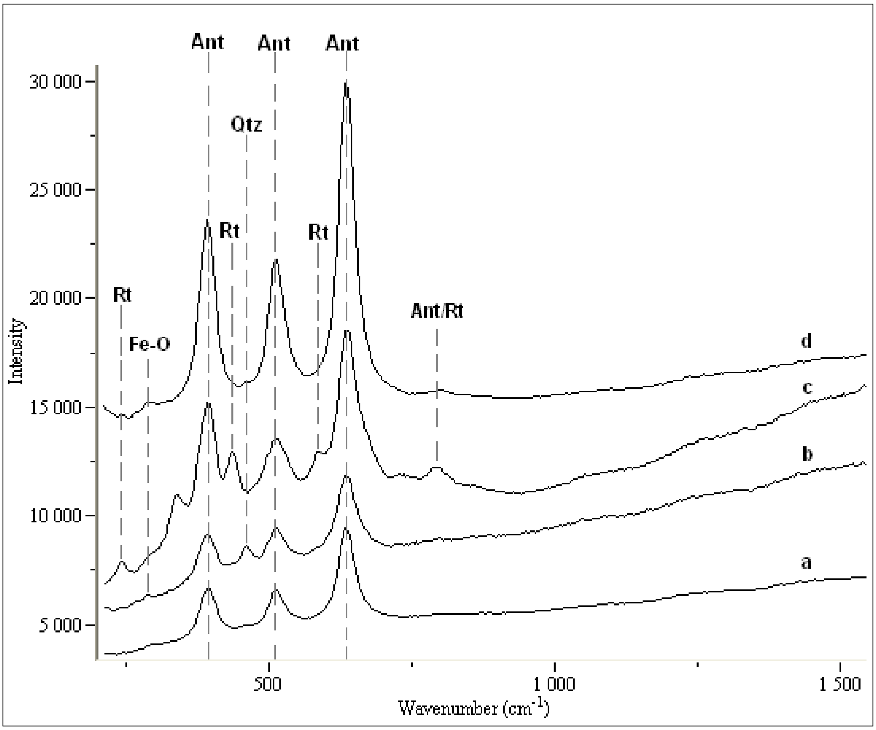

Fig. 3 Raman spectra of the white pigment samples with anatase (a–02 ALD 1960 loc VI; b–05 ALD 1960 SVIII; c–12 Preut Hlt 78 Grl N7; d – 30 RUS 79 S I 2).

2. Rutile

Rutile is basically the mineral omnipresent in the white pigment. It is the high temperature term of TiO_2. The higher frequency of appearance of this mineral in the white pigment can be explained in two ways: i) the firing of the ceramics at a temperature higher than the anatase-rutile transition point (750–950°C), which depends on various factors, including the iron concentration (Fabiana and Pasquevich, 1999); ii) the relict mineral of the protolith from which the kaolinite-rich clay was formed.

The Raman spectra of rutile present the characteristic lines at 246, 408–442 and 604–611 cm^{-1} (Fig. 4a-d). The wavenumber variation interval of the Raman band at 422 cm^{-1} is due to the differences in Fe content. As the Fe concentration increases, this Raman band shifts on the lower wavenumbers, from 422 to 408 cm^{-1}, overlaying the characteristic 411 cm^{-1} line of hematite (Fig. 4d). The presence of Fe, as in the case of anatase, is causing the appearance of the spectral lines from 283–288 cm^{-1}. Rutile is observed in the samples with a frequency of 87%.

3. Titanite

This mineral, like the titanium oxides, has a very good Raman signal, the following spectral lines being observed: 250, 319, 421, 461, 547, 604, 860, 907 and 2145 cm^{-1} (Fig. 5). The frequency of appearance is much lower than in the case of anatase and rutile, namely about 10%.

The titanium minerals (anatase, rutile and titanite) were not observed in four samples. The fact that these minerals were not found in the measurement points, however, does not mean that they are not present in the white pigment.

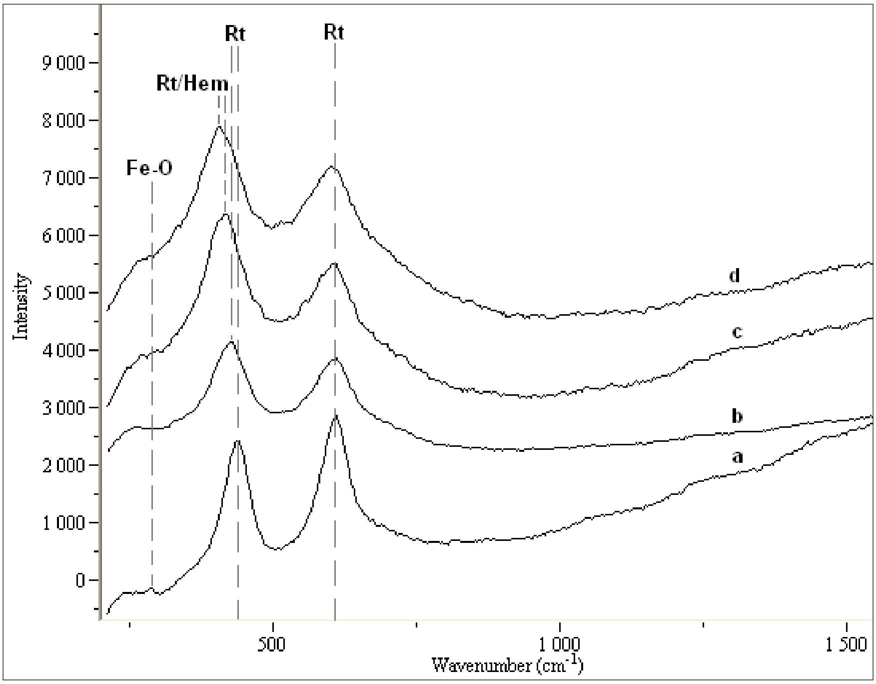

Fig. 4 Raman spectra of the white pigment samples with rutile (a–11 Fet Sch 2004 G16; b–42 FULG 2008 SX; c–46 FULG 89 2; d–50 FULG DF 2005 SVI 9).

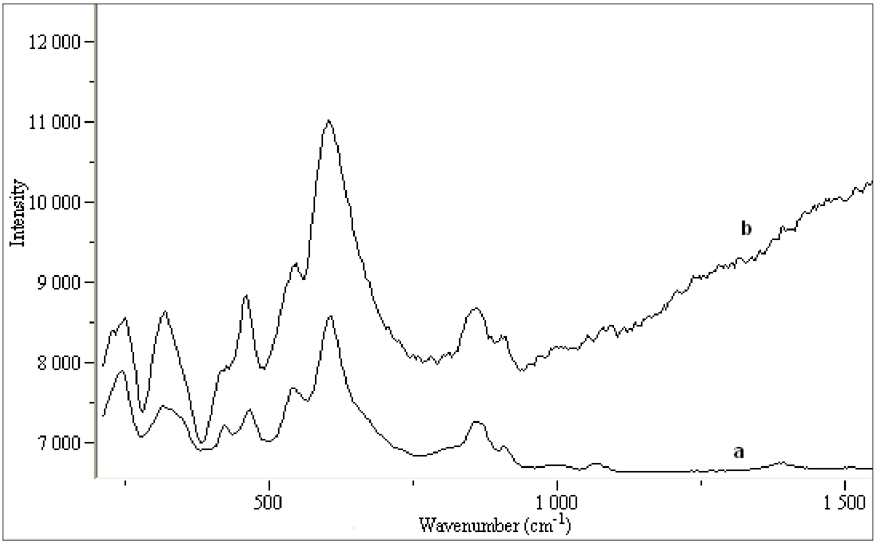

Fig. 5 Raman spectra of the titanite standard (a–Titanite_RDRS5839 – Buzgar et al., 2009) and the white pigment sample (b–08 Fet Sch 2002 G14).

4. Zircon

Zircon is an accessory mineral in igneous and metamorphic rocks, but it can also be present in clays as a relict mineral. Its presence in the white pigment is indicated by the specific spectral lines: 220, 354, 415, 438, 476, 507, 525, 637, 707, 820, 867, 971, 1006, 1187, 2256 and 2549 cm^{-1} (Fig. 6). Zircon has been observed in a small number of samples. The total absence of this mineral in the red and black pigment of the Cucuteni ceramics proves that it belongs to the white pigment. If crystals of zircon were present in the ceramic body, they would have certainly been observed in the red and black pigments.

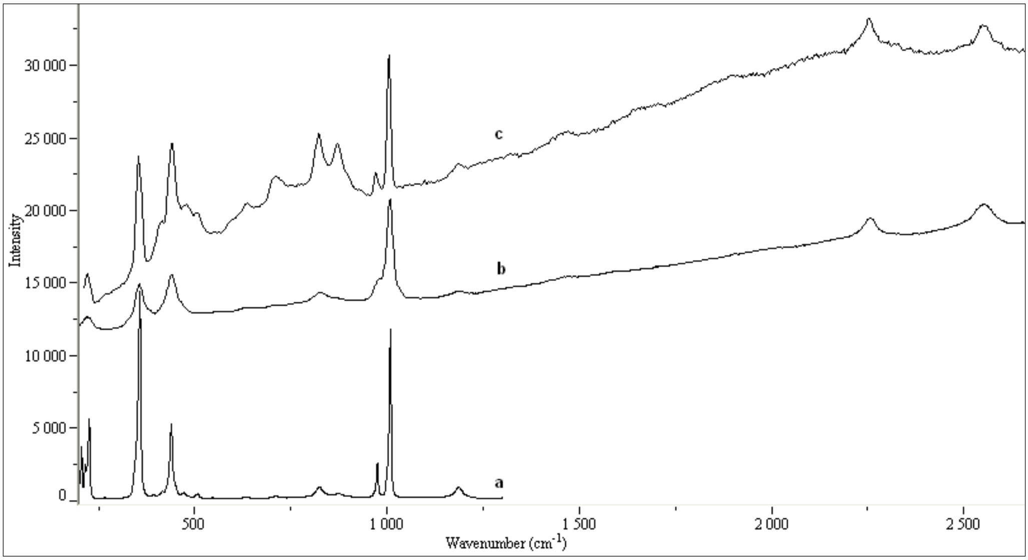

Fig. 6 Raman spectra of the zircon standard (a–R100128; b–R050286 – Downs, 2006) and the white pigment sample (c–05 Preut Hlt).

5. K-feldspar

This mineral was identified in a small number of samples (10%). The presence of K-feldspar is indicated by the triplet 457, 476, 510 cm^{-1} and the doublet 265, 285 cm^{-1} (Fig. 7b). Other bands of K-feldspar were observed at 331, 377, 408, 648, 755, 813, 995, 1115 cm^{-1}. This mineral has not been identified in the red and black pigments and, as a result, it is considered to belong, like zircon, to the white pigment, and not to the ceramic body paste.

6. Quartz

Quartz was frequently observed in the white pigment (50% of the samples). Its presence is marked by the very intense characteristic Raman band at 464 cm^{-1}, as well as the weaker ones at 261, 358, 396, 696, 798 cm^{-1} (Fig. 7d).

Constantinescu et al. (2007) indicated that Ca is the main element in the white pigment (based on XRF analyses), but calcite was observed only in one sample (based on SR-XRD analyses). Therefore, the presence of Ca can be accidental and in relation with calcite or other calcic minerals (e.g. plagioclase), and the high concentration of Si and Al can indeed indicate the presence of kaolinite (which is not a calcium silicate, as the authors suggest). In addition to this, we did not identify calcite or other carbonates in any of the approximately 400 measurement points.

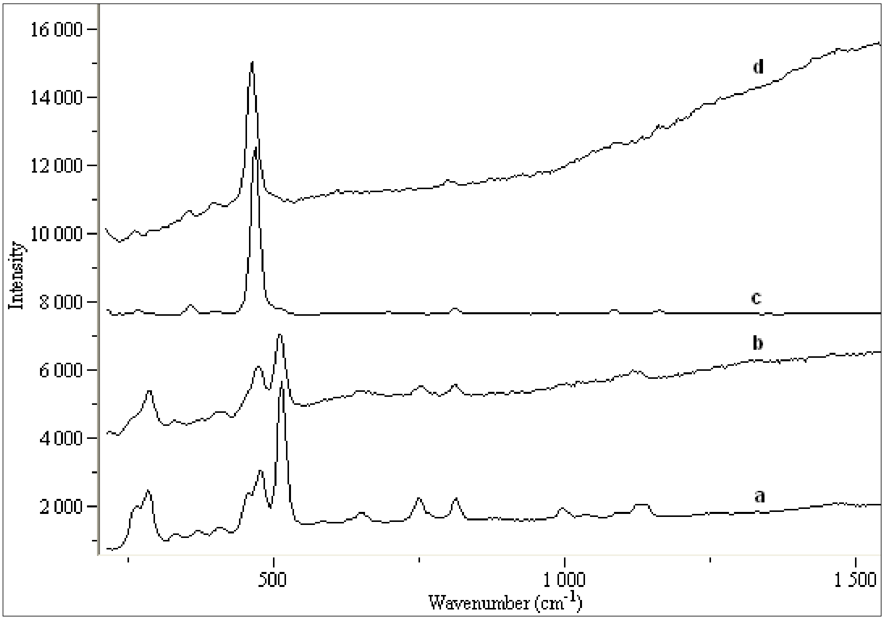

Fig. 7 Raman spectra of the K-feldspar (a–RDRS002) and quartz (c–RDRSQuartz) standards (Buzgar et al., 2009) and the white pigment (b–10 Fet Sch; d–29 RUS 79 cas 23).

Given the fact that the kaolinitic clays with TiO_2 represent the white pigment used extensively in the decoration of ceramics, a few aspects regarding the genesis of these deposits are worth mentioning. In agreement with Murray (1988), Greensmith (1989), Deer et al. (1992) and Friedman et al. (1992), kaolinite clays deposits may form through weathering or low temperature hydrothermal alteration of igneous and metamorphic rocks rich in feldspars (primary residual deposits). Kaolinite clays may also form secondary deposits, where kaolinite or its parent minerals (mainly feldspars) have been transported under suitable non-alkaline conditions and deposited in deltaic, lagoonal or other non-marine environments.

In the case of primary residual deposits, apart from kaolinite, the following relict minerals from the protolith are also present: quartz, feldspars, iron-magnesium silicates and oxides. The type and quantity of iron-magnesium silicates and oxides depend on the mineralogical composition of the protolith. Generally, based on acid igneous rocks (granite, rhyolite, dacite), kaolinitic clays which also contain quartz, feldspar, titanite, zircon, TiO_2 and small amounts of iron oxides are formed. These clays have a white color and can be used as white pigment without any preliminary treatment. The clays formed based on intermediate-basic igneous rocks (andesite, basalt, gabbro) may contain variable amounts of kaolinite, illite and montmorillonite. The ratio between kaolinite and the other two clay minerals increases with the de-gree of weathering processes. These clays also contain relict granules of iron-magnesium silicates and iron oxyhydroxides, and have a darker color – yellowish, reddish or bluish green.

A particular case is represented by the regions with post-volcanic activity (CO_2 emissions). The groundwater captures the CO_2 and the water becomes more acid. In this acid environment, feldspars and iron-magnesium silicates are completely transformed into kaolinite (with intermediate phases of illite and montmorillonite, respectively). In this residual kaolinitic clay, some quartz crystals and minerals resistant in acid environments (TiO_2, zircon) are still present. Sometimes, China clay (with a very high content of kaolinite) may form as well.

Secondary deposits contain xenocrystals of silicates, oxides, sulfides and other relict minerals accumulated simultaneously with the clay minerals.

Rarely, kaolinite may form through chemical precipitation in an acid medium from the complexation reactions of the silica gels and aluminium hydroxide. In this case, the silicates (titanite, amphiboles, pyroxenes, garnet etc.) and Fe and Ti oxides are missing. This type of deposits are very rare and are characterized by small amounts of clay.

Conclusions

Out of the 79 studied samples, the titanium minerals anatase, rutile and titanite were observed in 75 of them. The presence of rutile and titanite cannot be explained by the transformation of anatase during the firing process, at high temperature. The possibility that some ceramics were fired at temperatures higher than the one of the anatase-rutile transformation is not excluded, and, thus, a proportion of the rutile is due to anatase conversion. Certainly, titanite and most of the rutile are minerals from the unfired white pigment. In the same category are quartz, zircon and K-feldspar. If we take into account the fact that the white pigment is a kaolinitic clay and that it also contains the minerals listed above, then it is definitely a residual clay formed through the weathering of an igneous rock. Quartz and feldspar represent major minerals in the weathered igneous rock, while Ti minerals and zircon are accessory minerals. Granitoids and acid-intermediate volcanic rocks (rhyolite, dacite and andesite) fit into this category.

Based on this argument, it is believed that the source of the white pigment used in the painting of Cucuteni ceramics is represented by the residual clay accumulations developed on the Tertiary volcanic rocks from the Eastern Carpathians. In the Harghita, Gurghiu, Călimani and Bistriţei Mountains (Romania), Tertiary volcanic rocks have been subjected to intense hidrothermal transformations, forming clay with different amounts of kaolinite, of up to 100% (China clay). These deposits of residual kaolinitic clay are small in scale, but numerous. The deposits are located on an alignment parallel with the archaeological sites, 50–100 km westward (Brana et al., 1986).

The fact that more anatase than rutile has been found in the white pigment from ceramics of different ages and from different regions of the world is due to the clay used in the pigment, which is a sedimentary clay (transported and re-deposited in sedimentary basins). Such a case is found in the Dobrogea region (south of the Danube river), located approximately 200 km south of the archaeological sites studied in the present paper (Brana et al., 1986). This clay was not considered, however, for two reasons. Firstly, although it is a kaolinitic clay with anatase, is does not contain titanite and zircon. Secondly, a transport north of the Danube cannot be argued, the existence of a bridge being impossible at that time.

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