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RAMAN AND XRD STUDIES OF BLACK PIGMENT FROM CUCUTENI CERAMICS

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Abstract

The black pigment of 112 Cucuteni A and Cucuteni B pottery has been analyzed through Raman spectroscopy. The black pigment contains pyrolusite and jacobsite; quartz and anatase have only accidentally been observed. Black Carbon was also identified, but only in two samples. The spherical or oblate black corpuscles discovered at Feteşti-La Schit (Suceava county) were analyzed by means of X-ray diffractometry and Raman spectroscopy. They consist of Mn ± Fe oxihydroxides and quartz. No Mn carbonates or silicates have been identified. The mineralogical composition of the pigment applied to the pottery shards, as well as that of the raw pigment, together with the use of the same pigment over a long period of time (1100 years), suggest the exploitation of a large sedimentary mineral deposit, such as the Mn sedimentary ores from Nikopol (Ukraine).

Keywords: Cucuteni – Trypolye, ceramics, black pigment, jacobsite, pyrolusite, anatase, black Carbon, pyrochroite, hausmannite, manganite, Raman spectra.

Introduction

The aim of the present paper is the identification of black pigment on Cucuteni pottery from several archaeological sites, using Raman spectroscopy and X-ray diffractometry.

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At its peak, the Cucuteni-Tripolye culture, one of the last brilliant cultural expressions of the Copper Age, spread over an area of 350.000 km^2, throughout Romania (Cucuteni), the Republic of Moldova and the Ukraine (Tripolye). The Cucuteni culture is divided into three main phases (A, AB and B), which evolved over about 1100 years (3750 – 2700/2600 B.C.) (Mantu, 1998). The decorations of the Cucuteni pottery stand as proof of a remarkable aesthetic sense and of a very complex spiritual life. The decorative motifs used in the painting of Cucuteni ceramics were mostly spirals and, rarely, meanders, egg shapes or other geometric forms. The painted coatings are dichrome or polychrome (Dumitrescu, 1979). The main results obtained previously on the pigments of Cucuteni ceramics through the use of X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Synchrotron Radiation X-Ray Diffraction (SR-XRD) and Raman spectroscopy will be reviewed.

Stos-Gale and Rook (1981) and Niculescu et al. (1982) pointed out that the chromatophorous mineral of the dark brown pigments found on a number of Cucuteni-Tripolye shards was jacobsite. Burghelea et al. (2003) conducted a XRD study on polychrome ceramic shards belonging to the Cucuteni A2 phase. They have identified α-quartz, plagioclase feldspar, calcite, magnetite, and hausmannite in the black pigment. The presence of quartz and plagioclase feldspar both in the pigment and in the ceramics have led the authors to the conclusion that the pure pigments were finely dispersed into a clay suspension. Through XRF and SR-XRD measurements, Constantinescu et al. (2007) analyzed a series of painted (red-white-brown-black) Cucuteni shards found in Moldova (a province of Romania), at sites situated in the Bistriţa Valley (Izvoare, Calu, Căşăria, Ghelăeşti), belonging to the Cucuteni A phase. The SR-XRD analyses have shown the presence of jacobsite (Mg-jacobsite), pyroxmangite or magnetite (+quartz) in the black pigment. The XRF measurements indicated that the main chemical elements in the black pigment (dark brown or chocolate black) are Mn and Fe. Based on the Mn/Fe ratio, the authors suggested that Mn minerals from Iacobeni, a locality situated in the NW region of Moldova, were used for this pigment. Buzgar et al. (2010) analyzed a few fine ceramic shards found at Hoiseşti, Scânteia and Ruginoasa (Iaşi). The Raman analysis has shown the presence of jacobsite.

Analytical procedure

The Raman spectra were obtained at room temperature with a Horiba Jobin-Yvon RPA-HE 532 Raman Spectrograph with a multichannel air cooled (-70°C) CCD detector, using a wavenumber doubled Nd-Yag laser, 532 nm and nominal power 100 mW. The spectral resolution was 3 cm^{-1}, and the spectral range – between 200 and 3400 cm^{-1}. The Raman system includes a “Superhead” fibre optic Raman probe for non-contact measurements, with a 50X LWD visible objective Olympus, NA = 0.50 WD = 10.6 mm. Sulphur and ciclohexane bands were used for the calibration of the frequencies of the Raman spectra. The data was acquired through 2-10 second exposure, 20-50 acquisitions, at a laser magnification of 70-100%, 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 pigments were dispersed in clay suspension, which caused a powerful background noise and a weak Raman signal. Nevertheless, Raman spectra with clear bands were recorded and this allowed the accurate identification of the minerals present in the pigments.

XRD analyses were performed using a Shimadzu X-ray diffractometer LabX XRD-6000. Measurement conditions were: Cu anode, 40 kV, 30 mA, divergence slit 1.00 deg, scatter slit 1.00 deg, receiving slit 0.30 mm, scan range 2.5-120.0, continuous scan, scan speed 0.50 deg/min, sampling pitch 0.02 deg, preset time 2.40 s.

Samples

A number of 112 ceramic shards from the archaeological sites at Mihoveni, Feteşti, Preuteşti (Suceava county), Scânteia, Ruginoasa, Hoiseşti (Iaşi county), Aldeşti – Tg. Ocna, Trebeş, Rusăeşti/Poduri, Podei/Tg. Ocna and Fulgeriş (Bacău county) were analyzed, the samples under study belonging to Cucuteni phases A and B (Fig. 1). The painted coating is dichromatic (red and black) or polychrome (white, red and black). The decorative motifs are spiral, angular or unidentifiable. Whether the red motifs are painted on a white background or on the pot surface, all the polychrome shards have the limits between white and red hidden by the black pigment.

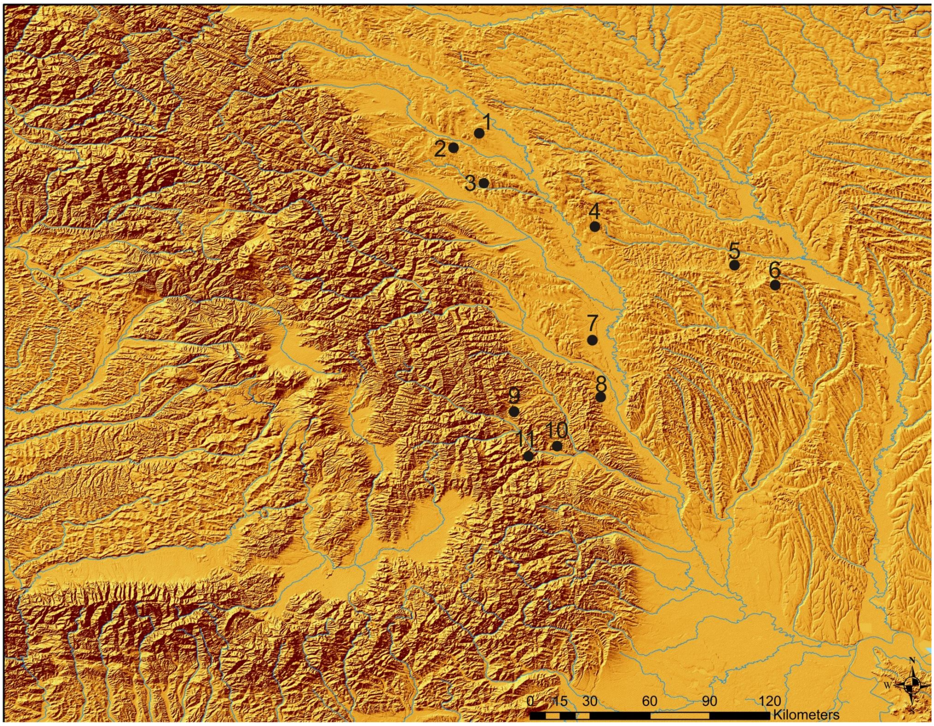

Fig. 1 The archaeological site map; Suceava county:1 - Mihoveni – „Cahla Morii" (Şcheia), 2 - Feteşti – „La Schit" (Adâncata), 3 - Preuteşti – „Haltă"; Iaşi county: 4 - Ruginoasa, 5 - Hoiseşti, 6 - Scânteia; Bacău county: 7 - Aldeşti (Cârligi, Filipeşti), 8 - Trebeş (Mărgineni) – „Cetăţuia", 9 - Rusăieşti/Poduri, 10 - Podei (Târgu Ocna), 11 - Fulgeriş (Pînceşti).

Results and discussions

The Raman spectra of the black pigment are defined by high background noise (BN) and strong fluorescence (F). However, in all the samples analyzed, a few intense spectral Raman lines are evident, which allowed us to identify the composition of the black pigment.

12 pottery shards originating from the Mihoveni site have been analyzed. The Raman spectra are shown in figure 2. In all the samples, we notice the presence of very intense Raman bands between 610-648 cm^{-1} (fig. 3). In some of the samples, two spectral bands are clearly separate, one between 610 and 625 cm^{-1}, and the other between 640 and 648cm^{-1}. On the other samples, however, a wider spectral band can be noticed, which is the result of an overlapping of the two Raman bands mentioned above. These Raman spectral lines correspond to the symmetric stretching vibration of the Mn-O bond from jacobsite (610-625 cm^{-1}) and pyrolusite (640-648 cm^{-1}). For jacobsite, the partial substitution of Mn with Mg leads to the shifting of the spectral line from 620-625 cm^{-1} (jacobsite) to 610-615 cm^{-1} (Mg-jacobsite). Also, the presence of Mn^{3+} in jacobsite makes the spectral band shift to that of hausmannite. We consider that, although jacobsite is present, intermediate members between jacobsite ($Mn^{2+}Fe^{3+}{}_2O_4$) and magnesioferrite ($MgFe^{3+}{}_2O_4$), hausmannite ($Mn^{2+}Mn^{3+}{}_2O_4$) or even magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$), are certainly also present. We believe that the determinations made by Burghelea et al. (2003) should be interpreted in this sense: the pigment determined by them is an intermediate term between jacobsite senso stricto, on one hand, and hausmannite and magnetite, on the other, with a chemical composition such as $(Mn^{2+}, Fe^{2+})(Fe^{3+}, Mn^{3+})_2O_4$. A spectral line with a lower intensity appears at about 285 cm^{-1}, which is the second Raman spectral line, by intensity, of pyrolusite. In a few samples, the most intense spectral band of quartz, from about 465 cm^{-1} (fig. 3), is also present, due to the symmetric stretching vibration of the Si-O-Si bond.

The Raman spectra of the samples from the other archaeological sites are similar to those obtained on the samples from Mihoveni. Figures 4 and 5 show the Raman spectra of the samples from Feteşti, Cucuteni phase A (15 samples) and B (15 samples), respectively. In these spectra, the same bands, characteristic for pyrolusite and jacobsite, are present, and only a few samples show the spectral line of quartz. This proves that the same black pigment was used over the entire development period of the Cucuteni culture.

The Raman spectra of the samples from the other archaeological sites are shown in figures 6 – 12. In all the samples, the same minerals are present: pyrolusite, jacobsite and, rarely, quartz. Anatase also occurs rarely (fig. 13). We believe that this mineral is either from the ceramic itself or from the ceramic clay paste used as support (raw material) for the black pigment.

The black pigment found at Feteşti (Suceava county) has a corpuscular form (fig. 14). The corpuscles are spherical or flat, the microstructure is massive to concentric, and the degree of crystallinity is reduced. Some corpuscles contain submillimetric quartz grains. The XRD analysis of the black pigment corpuscle (tab. 1) revealed the presence of quartz and Mn (±Fe?) oxihydroxides. The characteristic peaks of quartz have much higher intensities than those of Mn oxihydroxides, which confirms the low level of crystallinity of the late.

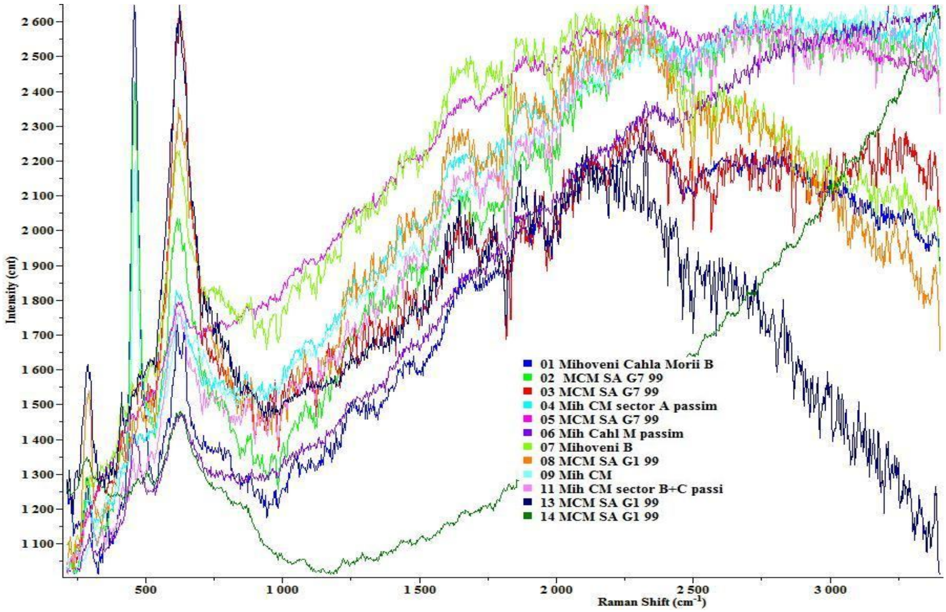

Fig. 2 Raman spectra of the black pigment from Mihoveni (Suceava county).

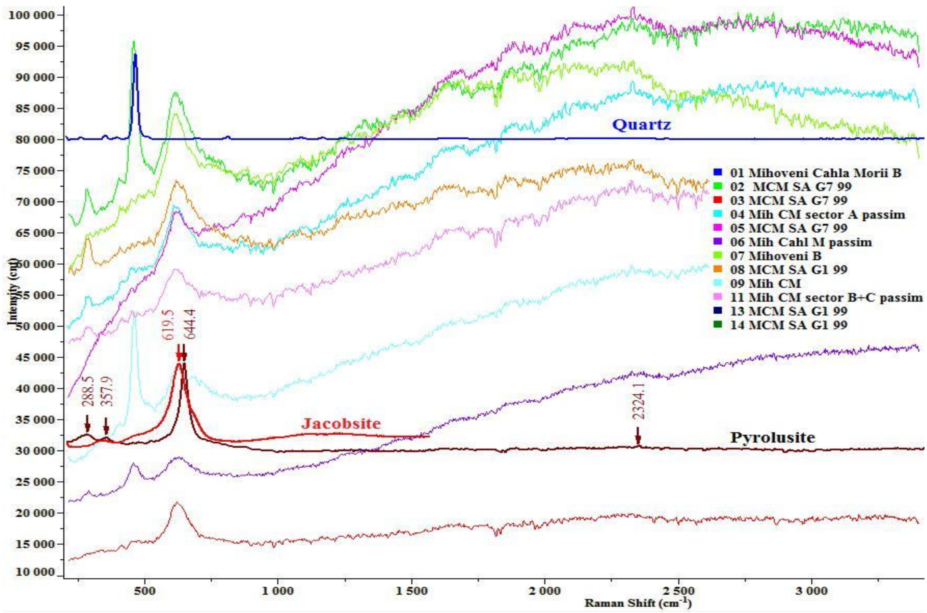

Fig. 3 Raman spectra of the black pigment from Mihoveni (the standards pyrolusite and quartz are from Buzgar et al., 2009; jacobsite is from Downs, 2006).

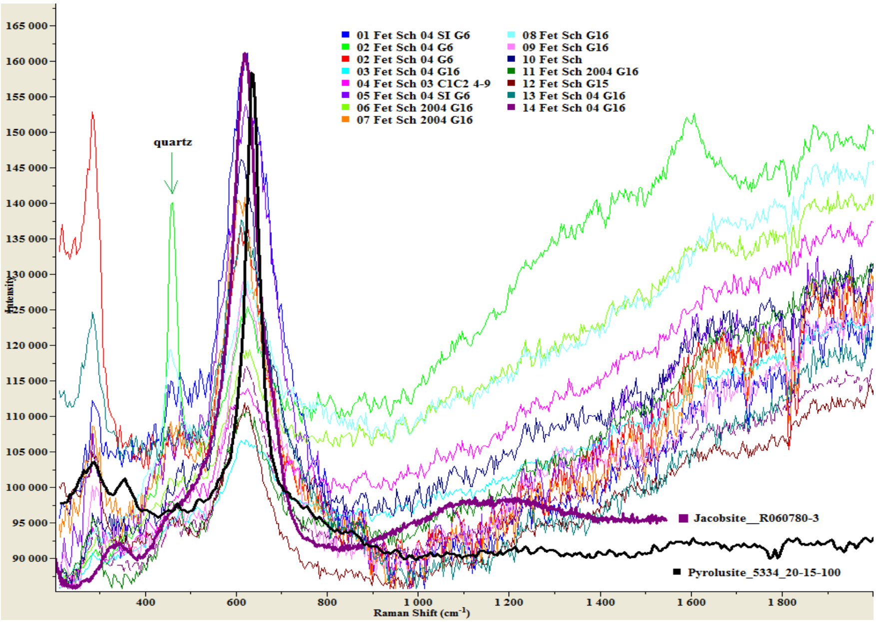

Fig. 4 Raman spectra of the black pigment from Feteşti (Cucuteni, phase A).

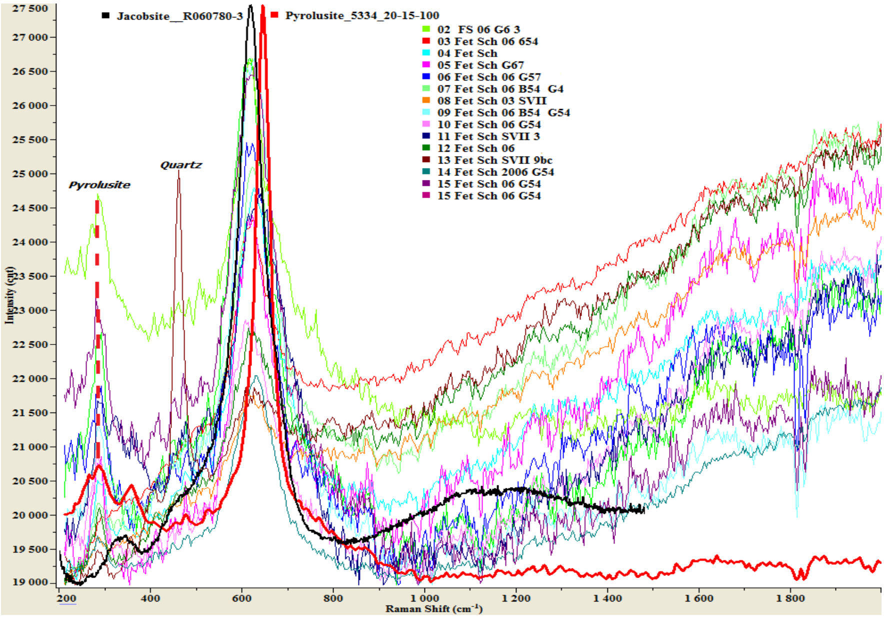

Fig. 5 Raman spectra of the black pigment from Feteşti (Cucuteni, phase B).

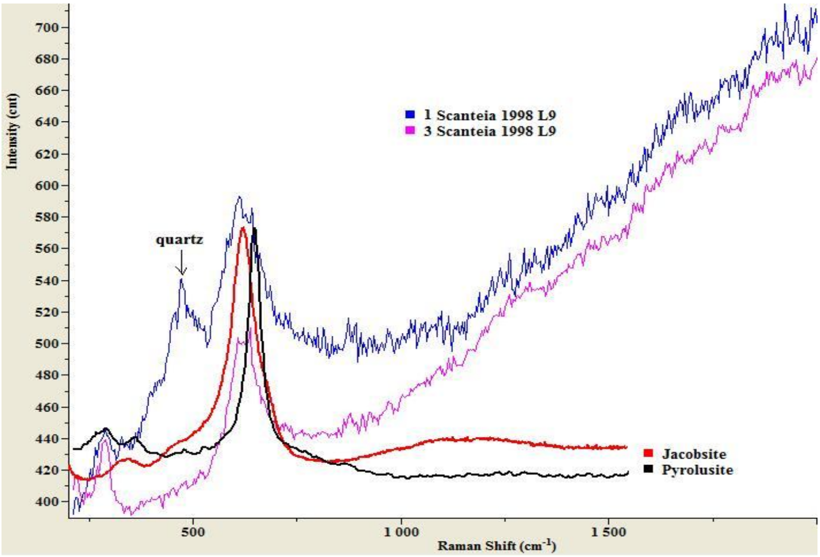

Fig. 6 Raman spectra of the black pigment from Scânteia (Iaşi county).

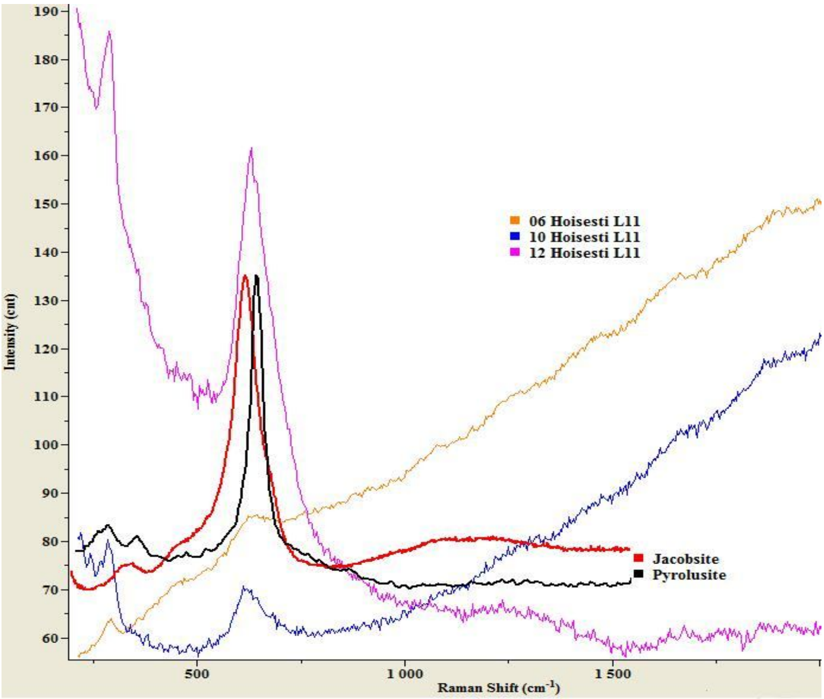

Fig. 7 Raman spectra of the black pigment from Hoişeşti (Iaşi county).

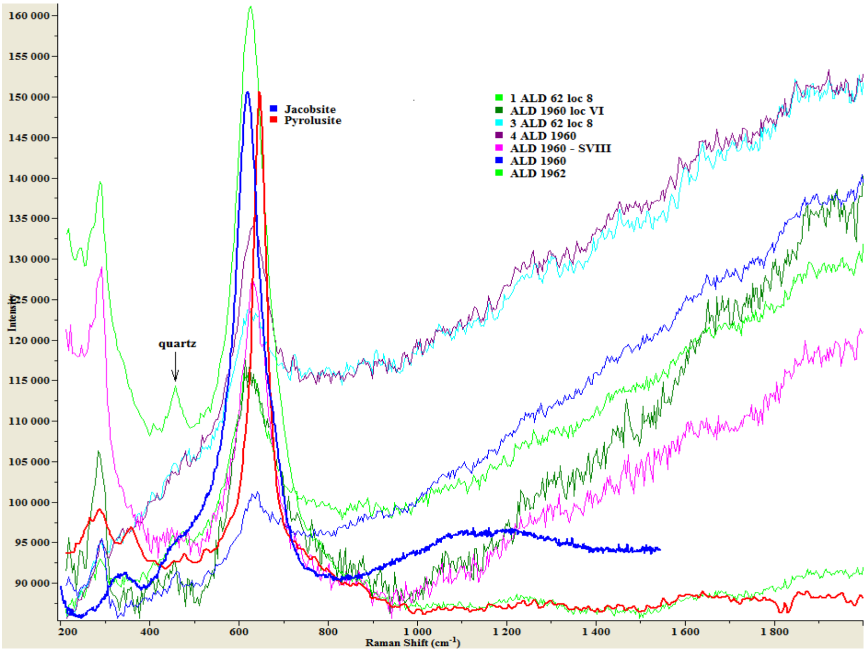

Fig. 8 Raman spectra of the black pigment from Aldeşti (Bacău county).

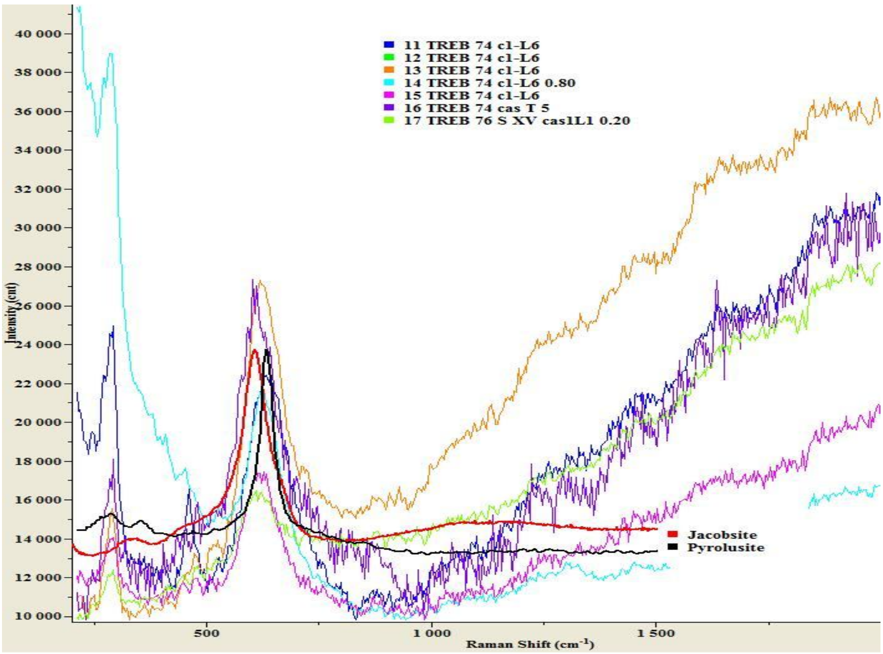

Fig. 9 Raman spectra of the black pigment from Trebeş (Bacău county).

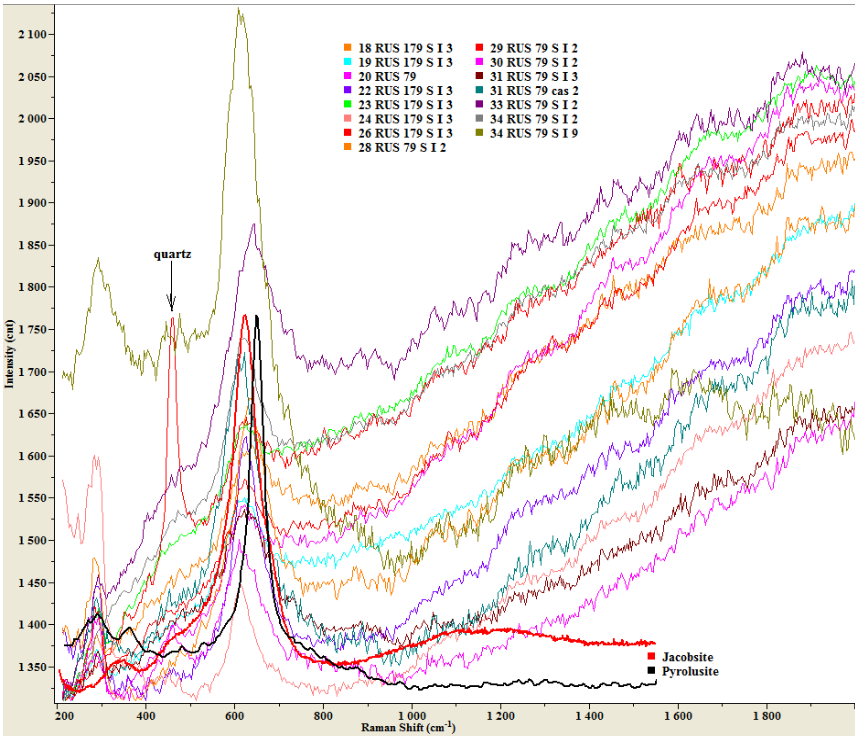

Fig. 10 Raman spectra of the black pigment from Rusăeşti (Bacău county).

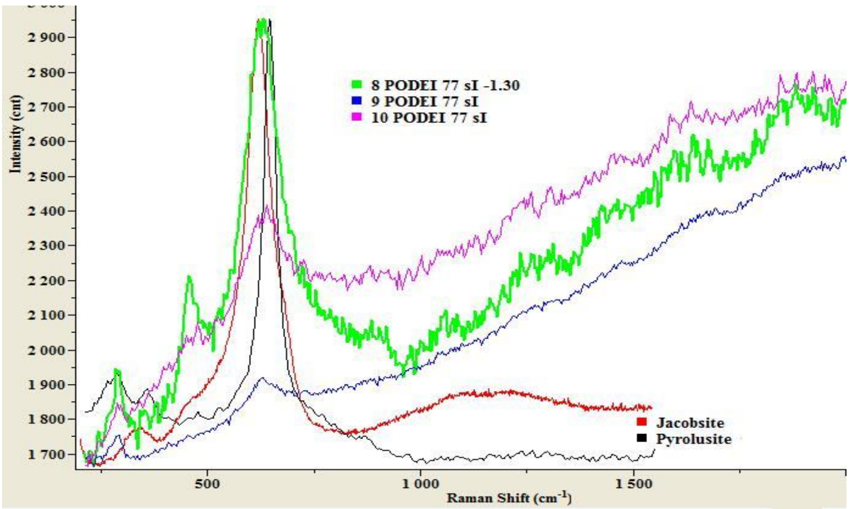

Fig. 11 Raman spectra of the black pigment from Podei (Bacău county).

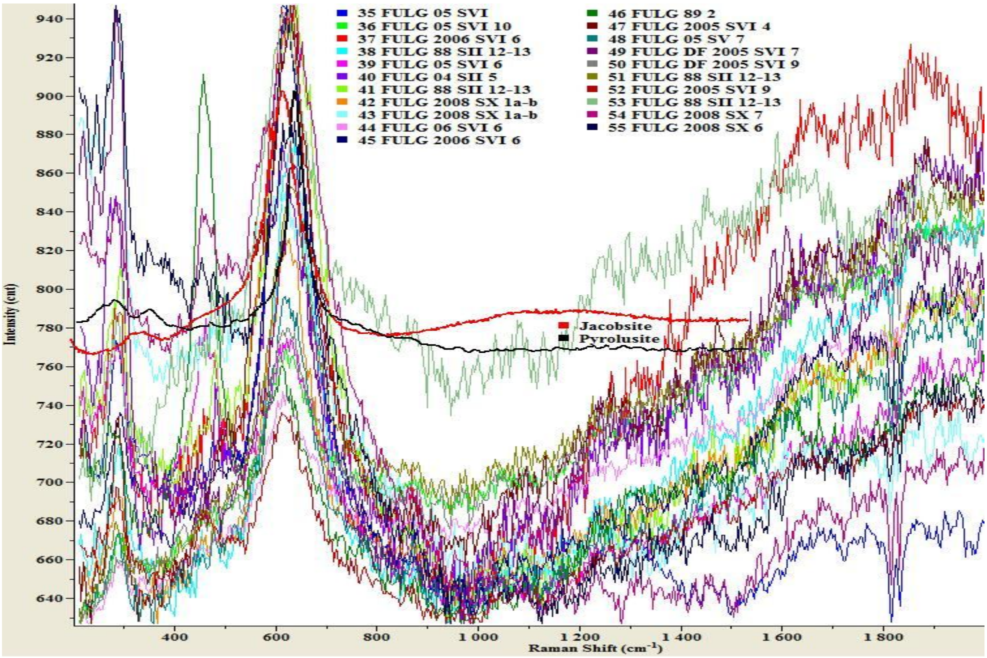

Fig. 12 Raman spectra of the black pigment from Fulgeriş (Bacău county).

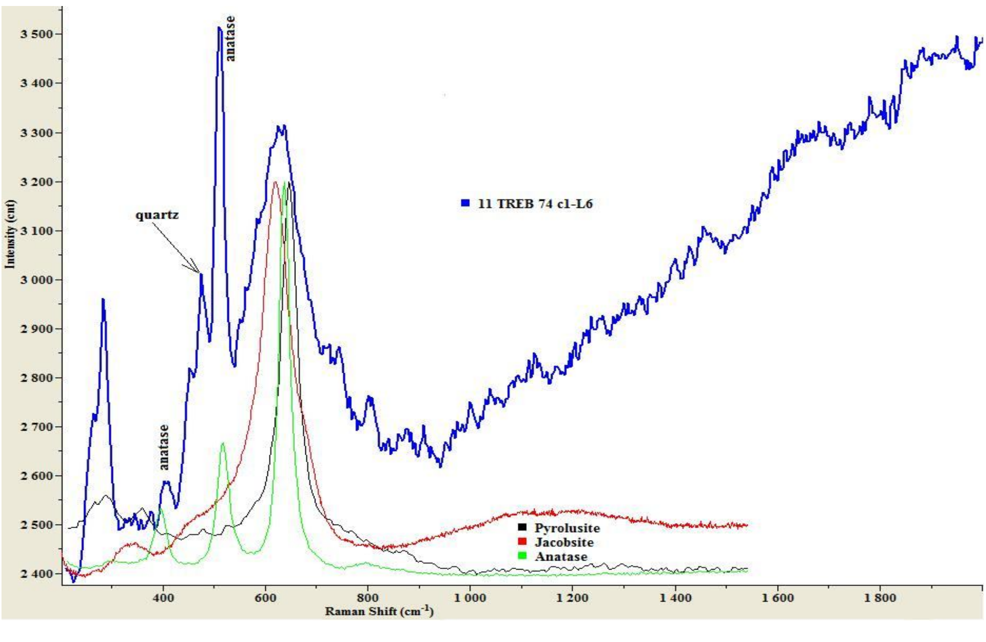

Fig. 13 Raman spectrum of the black pigment from Trebeş (Bacău county).

Fig. 14 Corpuscular black pigment discovered at Feteşti (Suceava county).

Tab. 1 XRD analysis of the corpuscular black pigment from Feteşti (Suceava county)

2 Theta	d	I abs	Irel	Mineral
12.22	7.2369153	100	0.05	
18.76	4.7261784	132	0.06	Pyrochroite
19.76	4.4891978	102	0.05	
20.82	4.2629728	355	0.17	Quartz
26.20	3.3985244	47	0.02	Manganite ?
26.62	3.3458491	2032	1.00	Quartz
27.74	3.2132522	142	0.07	Pyrolusite ?
34.46	2.6004683	52	0.03	Manganite ?
	2.56			Jacobsite
35.54	2.5238803	111	0.05	Hausmannite/Jacobsite
35.68	2.5142974	130	0.06	
35.82	2.5047907	113	0.06	
36.04	2.4900035	154	0.08	Hausmannite
36.52	2.4583701	154	0.08	Pyrochroite
37.06	2.4237797	40	0.02	Pyrolusite
37.10	2.4212583	39	0.02	
39.46	2.2817151	120	0.06	Manganite
50.12	1.8185548	371	0.18	Quartz, Pyrochroite
59.94	1.5419586	161	0.08	Hausmannite

Although jacobsite is not present (the value *d* is listed in red in table 1), we consider that, together with hausmannite, intermediary terms between hausmannite and jacobsite appear, in which a part of the Mn^{3+} (from hausmannite) is substituted by Fe^{3+} (without forming jacobsite *senso stricto*, however). This fact is indicated by several peaks very close in frequency and intensity, which are situated between the peaks of hausmannite and jacobsite (tab. 1, *d* = 2.50, 2.51, 2.52). The morphology and the microstructure of the corpuscles, as well as the differences in crystallinity between quartz and Mn (±Fe), oxihydroxides and the lack of carbonates and silicates, are characteristics of the sedimentary accumulations of Mn oxihydroxides.

The Raman study of the black corpuscles reveals the presence of pyrochroite, hausmannite, manganite, pyrolusite and jacobsite (fig. 15). Due to the symmetric stretching vibration of the Mn-O bond in the mentioned minerals, the Raman bands overlap within the recorded spectra, this overlapping being produced in the 622-660 cm^{-1} range. In the case of jacobsite, the Raman band of the standard sample is slightly shifted to the right, compared to the group of the pigment spectral lines analyzed (ranging between 622 and 660 cm^{-1}). This suggests that, within the sample, an intermediate term between jacobsite and hausmannite, such as $Mn^{2+}(Mn^{3+}, Fe^{3+})_2O_4$, is present, which confirms the results of XRD analyses.

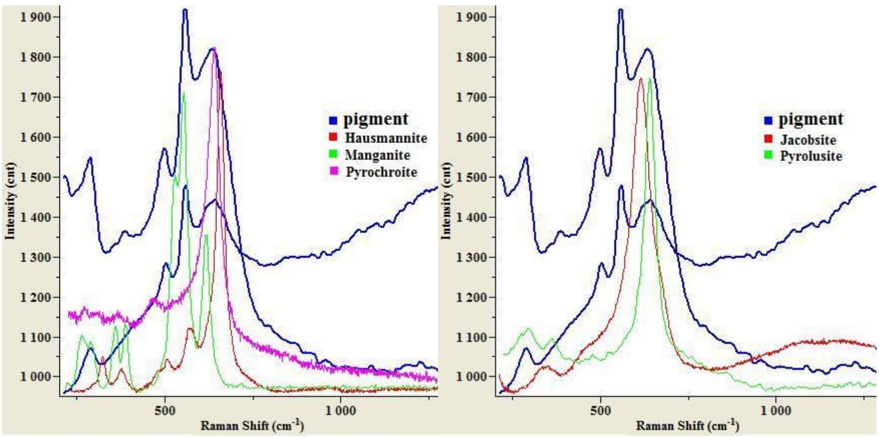

Fig. 15 Raman spectra of the corpuscular black pigment from Fetești (Suceava county). Standards: pyrolusite from Buzgar et al. (2009); jacobsite, hausmannite, manganite, pyrochroite from Downs (2006).

Conclusions

The Raman analysis of the black pigment on 112 Cucuteni-type pottery shards reveals the presence of Mn-Fe oxides, pyrolusite and jacobsite. The jacobsite has a variable chemical composition, determined by the substitution of Mn^{2+} with Fe^{2+}, and/or Mg and Fe^{3+} with Mn^{3+}. For this reason, the Raman spectral line is shifted to the left (Mg, toward magnesioferrite) or to the right (Mn^{3+}, toward hausmannite). The iron source may equally be the pure pigment or the clay suspension in which the black pigment was dispersed. The Mg source is most definitely the clay suspension. For all the samples, an overlapping of the jacobsite and pyrolusite Raman bands can be observed between 610 and 648 cm^{-1}. Only in few cases are the two spectral lines of jacobsite and pyrolusite observed separately. Apart from Mn±Fe oxides, quartz is frequently present. Only in a few cases do the Raman spectra reveal anatase and black carbon. Mn silicates are not present since, they have a better Raman response than Mn±Fe oxides, and, as a result, their presence would be marked by the appearance of the spectral lines characteristic to the stretching and bending vibrations of the Si-O-Si bond of the crystalline lattice (between 670 and 1000 cm^{-1}).

The black pigment discovered at Feteşti (Suceava county) has a corpuscular aspect and massive or concentric microstructure. XRD and Raman investigations reveal the presence of quartz and Mn±Fe oxihydroxides – pyrochroite, manganite, pyrolusite, hausmannite, as well as intermediary terms between hausmannite and jacobsite. The characteristics of the corpuscles (morphology, microstructure, mineralogical composition, degree of crystallinity) correspond to Mn sedimentary accumulations within marine basins.

The source of the black pigment employed for the painting of the Cucuteni-type pottery is the sedimentary Mn accumulation from Nikopol (Ukraine) (fig. 16).

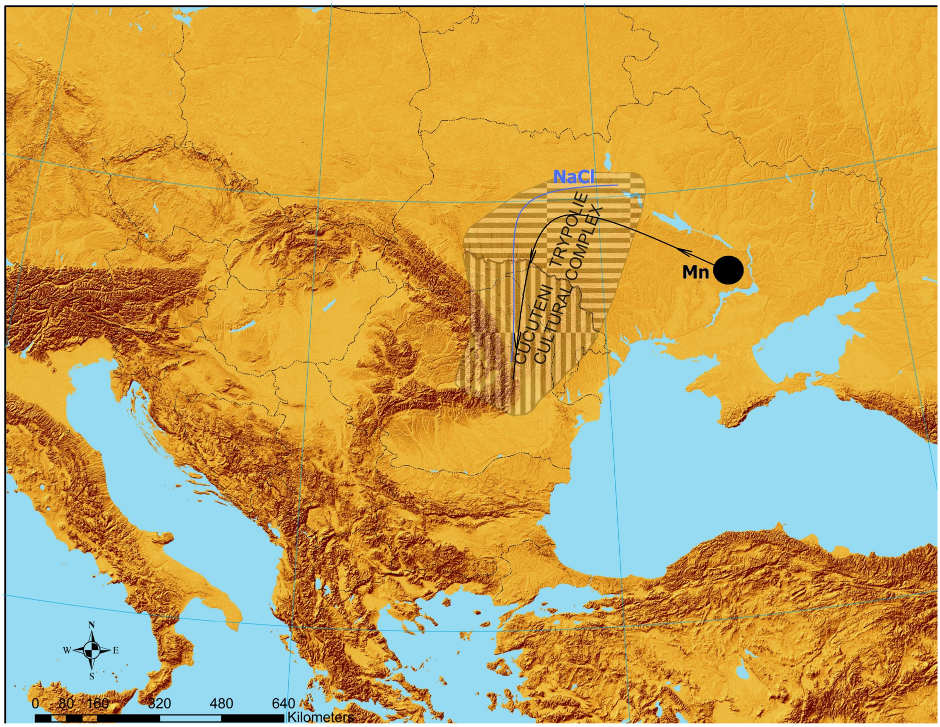

Fig. 16 The diffusion area of the Cucuteni culture and the presumed commercial routes for the black pigment from Nikopol and for the salt from the sub-Carpathian area.

In order to support our hypothesis, we took into consideration the following arguments:

1. The black pigment from all analyzed sites, be it Cucuteni A or B phase, has a uniform composition, being constituted of pyrolusite and jacobsite.

2. The use of the same pigment over a long period of time (approx. 1100 years) implies the existence of a large easily accessible raw material deposit. The oxidisation/alteration crusts of the Mn metamorphic accumulations from the Iacobeni area (Suceava county) are of reduced dimensions and, also, hard-to-reach (especially in prehistoric times).

3. The Raman analyses have not indicated the presence of Mn silicates or carbonates, or of any other mica-type silicates (the oxidisation/alteration crusts of the Mn metamorphic accumulations, such as those from Iacobeni, also contain Mn silicates and carbonates, as well as other types of silicates present within the metamorphic rock which quarters the Mn mineralisation).

4. The black corpuscular pigment discovered at Feteşti (Suceava county) has the morphology and internal structure characteristic to the corpuscles originating from the Mn sedimentary accumulation within marine basins. XRD and Raman analyses reveal the presence of quartz and Mn±Fe oxihydroxides.

As a working hypothesis, we consider that the trade route of the black pigment has also been used for the transportation of salt from the sub-Carpathian area (Cacica, Tg. Ocna) to the east.

Acknowledgments

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