Investigation of Neolithic ceramic pigments using synchrotron radiation X-ray diffraction

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Crystalline phases present in pigments scratched off the surfaces of some decorated ceramic sherds belonging to the Cucuteni Neolithic culture were successfully identified using synchrotron radiation X-ray diffraction at Daresbury Laboratory. The ceramic sherds were selected from a collection of the National Museum of Romanian History in Bucharest. The synchrotron radiation X-ray diffraction analysis revealed that the black-color pigments on the surface of a number of sherds were produced by a variety of jacobsite (Fe_2MnO_4) phases; magnetite (Fe_3O_4) was also found in one of the sherds. The red color was derived from clay slips with a high content of hematite (Fe_2O_3). Calcite ($CaCO_3$) was found in the white pigments; its presence was explained as being related to postburial deposition processes. Conclusions on technological aspects, provenance, and conservation issues are given. © *2008 International Centre for Diffraction Data.*
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Key words: SR-XRD, Neolithic ceramic pigments, archaeology, crystalline phase identification

I. INTRODUCTION

X-ray diffraction (XRD) is an established tool for the mineral phase characterization of ancient potteries and for addressing questions regarding the manufacturing techniques, origins and provenance (including trade routes and supply zones), degradation processes, weathering, authenticity, and authentication (Maggetti, 1982). Good quality XRD patterns can provide definitive answers when it comes to phase identification and quantitative analysis (Jenkins, 2000). However, the main disadvantage of an XRD phase analysis is that the data collection can be time consuming, and each diffraction pattern requires several hours to be acquired.

Recently, synchrotron radiation X-ray diffraction (SR-XRD) has been successfully used for the analysis of very small specimens in a very short experimental time. An extensive and up-to-date list of publications using SR-XRD on cultural heritage materials can be found at Soleil Synchrotron's internet site (http://www.synchrotron-soleil.fr/portal/page/portal/Recherche/ProgrammesTransversaux/MateriauxAnciens/LitteratureSynchrotron). The basic methods of data collection using a fast CCD detector and the corresponding data analysis procedures are reported elsewhere (Salvadó *et al.*, 2002; Broekmans *et al.*, 2004).

In this work, SR-XRD was applied to study the crystalline-phase composition of pigments from the surface decorations of some Cucuteni Neolithic ceramic sherds. The results on phase identification have provided useful information in the research and understanding of the archaeological ceramics.

II. ARCHAEOLOGICAL BACKGROUND

The history of the V–IVth Millennia B. C. was marked by the flourishing of some great Eneolithical civilizations in the southeastern part of Europe: Vinča, Gumelnița, and Cucuteni-Tripolye, representing moments of a remarkable cultural evolution.

Spread over a vast territory with a total area of more than 300 000 km^2 in Romania, the Republic of Moldova, and Ukraine, the Cucuteni (in Romania)-Tripolye (in Ukraine) culture is one of the last brilliant cultural expressions during the Copper Age. Cucuteni-Tripolye culture had a long evolution, being divided by specialists into three main phases: Cucuteni A, Cucuteni A-B, and Cucuteni B.

"Queen" of the prehistorical pottery, Cucutenian ceramics represent the most eloquent proof of not only the perfect mastering of pottery (production, temperature control, and clay modeling), but also of the extremely developed aesthetic sense that gave birth to genuine and unrivalled masterpieces (see Figure 1). The decorations of these wares are regarded by archaeologists as an evidence of a remarkable aesthetic sense and, at the same time, of a very complex spiritual life. The prehistoric craftsmen created characteristic decorations for each of the three evolutional stages of the culture (A, A-B, and B)—at the beginning, only with the use of incised

Figure 1. (Color online) Cucuteni ceramic objects.

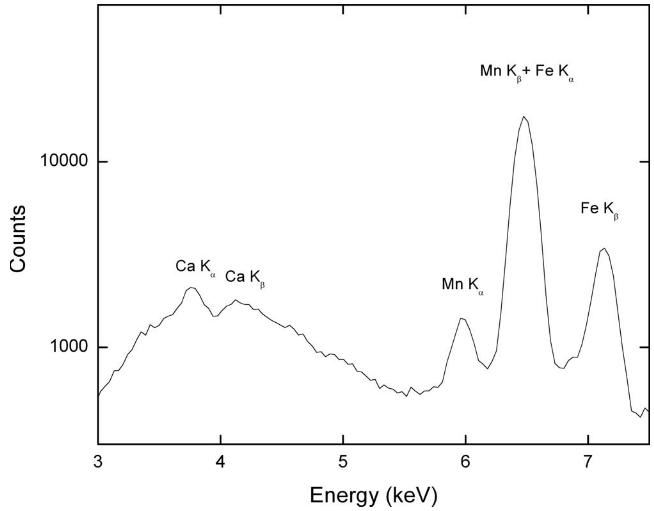

Figure 2. XRF spectrum from a black decoration in a Cucuteni sherd.

lines and flutings, and later on by the applications of colors (white, black, and red). They used the spiral as essential decorative element on the external (and sometimes internal) surface of the potteries. It was believed that the colors had magical significance: red representing life (blood), white representing good (light), and black representing evil (darkness).

Analytical results obtained on Cucuteni ceramics by using X-ray fluorescence (XRF), X-ray diffraction, and other specific mineralogical methods are reported in the literature (Ellis, 1980, 1984; Gâţă, 2000; Niculescu *et al.*, 1982; Stos-Gale and Rook, 1981; Mantu *et al.*, 2001).

III. EXPERIMENTAL

The decorated (red, white, and black) ceramic sherds used in this study were provided by the archaeologists from the National Museum of Romanian History, Bucharest. They were excavated from Poduri (Bacău County) and Izvoare (Neamţ County) sites. They were created during the Cucuteni A3 phase (around year 4300 B.C.), which was characterized by the presence of the bichrome (white on red) ware and, more often, of the trichrome ware with white, red and black decorations.

Prior to the SR-XRD experiments, extensive XRF measurements were performed at "Horia Hulubei" National Institute of Nuclear Physics and Engineering, Bucharest, on a larger number of sherds (nearly 300), to obtain information on the elemental composition of the pigments. A spectrometer consisting of a 30 mCi ^{241}Am annular γ-source, a Si(Li) detector (energy resolution 180 eV FWHM at 5.9 keV), and a conventional nuclear electronic chain were used. The XRF results revealed that the major elements in the black-color regions of the sherds were Fe and sometimes both Mn and Fe (see Figure 2), while Ca was detected in the white-color areas; relatively high amounts of Fe were also found in the red regions.

It is worth mentioning that the XRF measurements were nondestructive, allowing the analysis of the whole available sherds without the need of additional sampling. For SR-XRD measurements, it was necessary to extract a small amount of pigment powders from each sherd. Nondestructive SR-XRD analysis of a specimen in the flat-plate geometry is possible as well, but in this case long data collection times (several hours) are required to obtain good quality results (Tang *et al.*, 2001). Because it was possible to use only a minute quantity of pigment powders obtained from the sherd's decorated surface, the pigment powders were gently scratched from areas of different colors (white, red, and black) using a diamond file. Clay-based ceramic powders from the body of each sherd were also measured in order to evaluate the possible contributions to the diffraction pattern of the specimens, taking into account that the painted layer was very thin (tens of micrometers) and specimens were likely to have included clay powders from the ceramic body of the sherd.

Figure 3. (Color online) Photo of the sherds and the 36-cell specimen holder with each cell containing a different pigment scratched from each sherd.

A sample holder consisting of 36 cells (3 mm in diameter) was used. Each cell uses Scotch® tape as a backing. The powders of each pigment were pressed into a cell, and the excess powders were removed in order to have just a thin layer stuck on the backing tape. Figure 3 shows a photo of the powder specimens (left) scratched off the sherds (right). SR-XRD data were taken at Station 14.1 of the Synchrotron Radiation Source, Daresbury Laboratory (DL), Warrington, United Kingdom. An X-ray wavelength of 1.488 Å was used and the incident beam aperture was set at 0.2×0.2 mm^2. A two-dimensional diffraction pattern for each sample was recorded using a Quantum 4 ADSC CCD detector (with 2304×2304 pixels). The SR-XRD experiment on each specimen was performed in transmission mode with an acquisition time of 30 s. The total acquisition time was minimized because the holder position (i.e., from one cell to the next) was computer controlled from outside the station hutch using a preprogrammed protocol that allowed the complete set of specimens to be scanned within half an hour. Two cells in the sample holder were filled with pure silicon powders (NIST standard reference material 640b), which was used as an external standard for the calibration of the observed 2θ angles for precision phase analysis.

Data reduction of the observed diffraction patterns was performed following the procedures reported by Salvadó *et al.* (2002) and Broekmans *et al.* (2004). The diffraction data were polar transformed and azimuth integrated using the program FIT2D (Hammersley *et al.*, 1996). Mineral phase identification was carried out with the aid of the Powder Diffraction File (PDF) standard database using the search/match procedures in the X'Pert HighScore Plus and XPLOT software available at DL. To aid the phase identification pro-

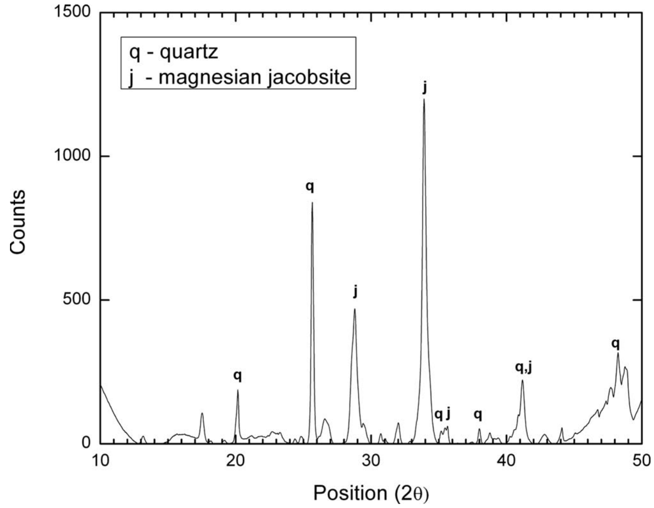

Figure 4. SR-XRD pattern for a black pigment specimen containing magnesian jacobsite and quartz.

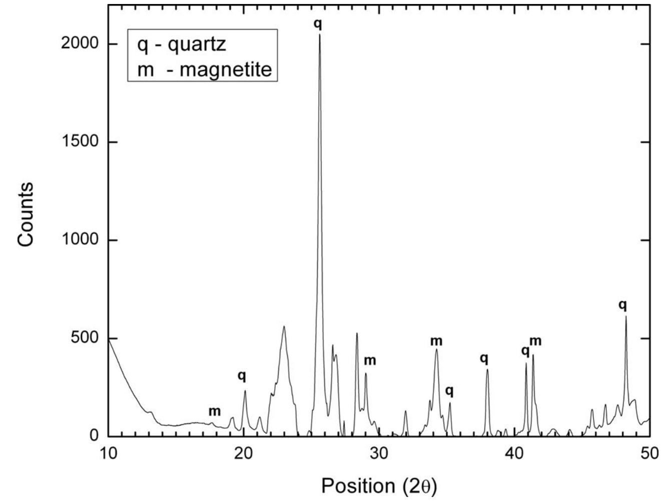

Figure 5. SR-XRD pattern for a black pigment specimen showing the presence of magnetite and quartz.

cess, background intensities from the backing tape were subtracted for the observed diffraction data using X'Pert HighScore Plus software.

IV. RESULTS AND DISCUSSION

The mineralogical crystalline phases present in fired ceramics depend upon the clay composition, kiln atmosphere, temperature reached during firing, and other factors. However, mineralogical changes to new secondary phases could take place during the burial period, and therefore postburial transformations must be considered in a precise crystalline phase analysis (Maggetti, 1982; Zoppi *et al.*, 2002).

It was already reported in a previous archaeological study (Ellis, 1984) that the surface decoration for Cucuteni-Tripolye type A pottery was obtained most likely through the applications of two or three (depending on the sherd and, more general, to the specific period of time) powdered minerals used as pigments in a clay-water suspension. They were applied on the surface of an unfired ceramic object.

By processing the diffraction data of some sherds with black decoration, for which both Mn and Fe were found by the previous XRF analysis, a variety of jacobsite (Fe_2MnO_4) from the PDF database was found to match reasonably well the positions and the relative intensities of five of their major diffraction peaks from the experimental XRD patterns. The search/match analysis of the experimental XRD patterns revealed that jacobsite was present in the black-color decoration of a number of specimens, but with a slightly modified chemical formula and lattice constants where the concentrations of Fe and Mn were reduced because of the presence of other metal atoms, such as Mg. Magnesian jacobsite (PDF 01-085-1561 and 01-085-1562) gave the best matches of the positions and relative intensities in the diffraction patterns. Figure 4 shows the experimental SR-XRD pattern for a black-pigment specimen with its diffraction peaks identified to be those of magnesian jacobsite and quartz (a phase also present in all other specimens). The presence of jacobsite in the diffraction patterns of black pigments indicates a relatively high firing temperature (about 1000 °C); similar findings were also reported by Maggetti (1982) and Ellis (1984).

In one of the sherds, the black-color pigment was found to be caused by the presence of magnetite (iron oxide Fe_3O_4) (see Figure 5). This leads to the assumption that a reducing atmosphere (rich in carbon monoxide) was used in the kiln during the firing of this pottery [also see Zoppi *et al.* (2002)]. This was a rather unusual manufacturing procedure, since all the analyses up to now (including those in this study) on A3 Cucuteni ceramics have indicated that this type of pottery was obtained through firing in oxidizing atmosphere using kilns with separated combustion and firing chambers [also see Ellis (1984) and Gâță (2000)].

The red-color pigments were the result of the presence of a relatively high amount of hematite (Fe_2O_3) (see Figure 6). Hematite was also found to be a minor phase in the bodies of the ceramic potteries. The presence of hematite suggests an oxidizing atmosphere during the firing process, in agreement with similar findings reported in the literature (Maggetti, 1982; Zoppi *et al.*, 2002).

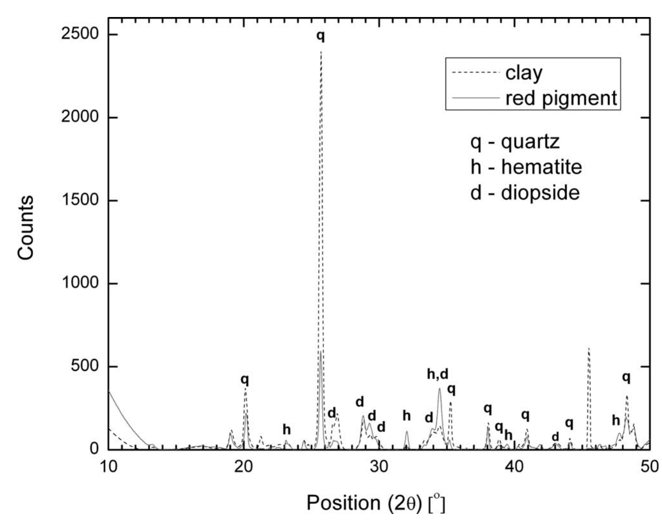

Figure 6. SR-XRD patterns of a red pigment specimen and of the ceramic body clay, showing the presence of hematite, diopside, and quartz.

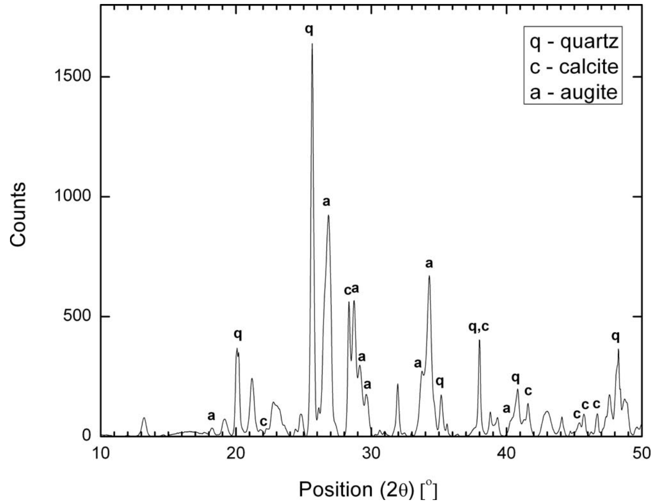

Figure 7. SR-XRD pattern of a white pigment specimen showing the simultaneous presence of calcite, augite, and quartz.

Calcite ($CaCO_3$) was found in the white-color pigment specimens. The presence of calcite in ceramic pottery might occur essentially for two different reasons: a low firing temperature or a postburial process. Calcite was reported to exist up to approximately 800 °C, a temperature at which the formation of CaO is promoted, followed by the so-called "high-temperature crystalline phase" of Ca-silicates or Ca, Al-silicates such as diopside ($CaMgSi_2O_6$) formation (Maggetti, 1982; Zoppi *et al.*, 2002). The simultaneous presence in calcareous clays of calcite and high temperature minerals clearly ruled out any hypothesis of primary calcite, strengthening the assumption of a secondary origin, because of the deposition induced by water in the burial soil. Augite, $(Ca,Na)(Mg,Fe,Al)(Al,Si)_2O_6$, was also found in the sherd with calcite (see Figure 7). This high-crystallization-temperature silicate is a solid solution of the pyroxene group minerals, which also includes hedenbergite ($CaFeSi_2O_6$) and the above-mentioned diopside. The simultaneous presence of augite and calcite in the same sherd leads to the conclusion that calcite was detected in the sherd resulting from the post-burial deposition.

Although the primary purpose of this study was to identify the crystalline phases present in the pigments, several other compounds were also searched in the clays. Quartz (SiO_2) was found to be the dominant phase in the specimens of all the clays and the pigments, and diopside ($CaMgSi_2O_6$) was identified in most of the clay specimens (see Figure 6). The presence of quartz is not surprising at all, since this phase has been found in many ancient ceramic sherds. The presence of diopside can be related to a rather high firing temperature, since this calcium silicate starts to crystallize in calcareous clays by the decomposition of calcium carbonate at a temperature of nearly 900 °C.

Our results suggest that the sources of clay were most likely local. The white- and the red-color pigments used on the potteries were locally occurring minerals, the red pigments being obtained through the alteration of iron minerals and the white pigments from calcium compounds. Firing under oxidizing conditions and at high temperatures (around 1000 °C) was used to produce most of the analyzed Cucuteni ceramic potteries.

The most interesting case is the black pigment caused by the presence of the magnesian jacobsite. If the white and red pigments were easily obtainable through the firing of clays found nearby the excavated settlements, this was not the case for the black manganese-containing clays, which have a much smaller area of spreading. The areas in which the manganese minerals are to be found—even nowadays—are the sedimentary-metamorphic ores of the Oriental Carpathians (Bistrița Mountains region) and the residual deposits in bogs and soil accumulations from the Podolian Plateau and Scythian Plateau, modern Ukraine (Ellis, 1984). This suggests that the Neolithic people specialized in gathering minerals from the surface of manganese mineral deposits and used them in producing black-decorated ceramics. The deposit that was closest to the sites where the ceramic potteries were found is Bistrița Mountains (Bălan, 1976), located just about 200 km from the excavation places.

The use of iron oxide mineral pigments would produce different colors in different firing conditions: red in an oxidizing (oxygen-rich) atmosphere and black in a reducing (carbon monoxide-rich) atmosphere. The Cucutenian craftsmen preferred to simultaneously use black ferromanganese oxides, which are stable in any firing conditions (either oxidizing or reducing), in order to produce the black decorations and iron oxides to produce the red decorations. One can conclude that the Cucutenian potters were skilled enough to simultaneously obtain red- and black-color ceramic decorations on the same pottery using different kinds of clays as raw materials even in the Vth Millennium B.C. A similar mechanism for obtaining black and red ceramic decorations was put in evidence for Cypriot ceramics (Aloupi *et al.*, 2000), but this technology was used only in the Late Bronze Age (1625 to 1050 B.C.).

Our findings suggest that the ancient Cucutenian potters realized the different characteristics of different materials (e.g., manganese bearing minerals were dissimilar to iron based minerals) and used a relatively advanced technology to obtain polychrome potteries.

V. CONCLUSION

The pigments used to decorate Cucuteni Neolithic ceramics were found to be composed mainly of iron oxides for the red hues and calcium compounds for the white color, while the black pigments contain different iron and manganese compounds, such as magnetite and jacobsite, depending on the firing conditions. These findings support the previously reported conventional XRD, XRF, and mineralogical analyses performed on Cucuteni ceramics. Our results also suggest that the decoration of the pottery surface was produced by using mineral pigments mixed with a clay-water suspension and applied as a clay slip. For obtaining the black color, ancient potters used ferromanganese oxides-based clays, probably from relatively remote regions. The identified crystalline phases have provided information on the technologies employed by ancient craftsmen, revealing their skill in obtaining polychrome potteries.

To our knowledge, this study is the first attempt of applying SR-XRD for the study of Cucuteni ceramic pigments. This powerful analytical technique has been proven to be useful in giving definite answers to phase identification of ceramic pigments. Because of the high intensities of the synchrotron radiation source, very short experimental times (1 min for each sample) and small amounts of powders were necessary to acquire good quality diffraction patterns. Therefore, by using SR-XRD and a minimal amount of powders, a very large number of ancient sherds can be analyzed. New prospects for future extensive studies on prehistoric ceramics with synchrotron radiation-based analytical techniques, such as SR-XRD, are possible; provenance, technology, and conservation issues can thus be addressed.

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