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SPECTROSCOPIC STUDY OF COLOUR TRACES IN MARBLE SCULPTURES AND ARCHITECTURAL PARTS OF MONUMENTS OF ARCHAIC PERIOD IN DELPHI, GREECE

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ABSTRACT

Non-destructive analysis by means of portable X-ray flourescence (pXRF) and Raman spectroscopy of color traces on sculptures and architectural parts from the Delphi Museum, Phokis, Greece, are presented. These sculptures and architectural parts are dated to the Archaic period (7th – 6th c. B.C.). The main question to be answered is the mineral/pigment used for each part and therefore to reconstruct the color palette of the artists. For this research, sixteen archaeological exhibits of the Delphi museum were analyzed with two different spectroscopies, and the white, red, black, yellow and blue pigments were identified.

KEYWORDS: Raman spectroscopy, XRF, pigment analyses, Delphi Museum, marbles.

1. INTRODUCTION

Painting has always been a form of expression since early human dawn. From the first Palaeolithic cave drawings until today, spectacular painted images represent past cultures and the history of mankind in general, including religious objects (Aubert et al., 2014; et al., 2008; Bratitsi et al., 2019).

It is well known from ancient sources the existence of colours on the surface of sculptures and architectural parts. The term "γραπτά ανδρεία" ("grapta andreia - written/ painted statues") leaves no doubt about the color of the sculptures (Brekoulaki, 2008). This consolidated view of the whiteness of the sculptures dominated the period of neoclassicism (1750 -1900), as evidenced by J.J. Winckelmann (1717 - 1768), who considered white marble to be more beautiful (Brecoulaki, 2008; Brinkmann, 2007).

From the early 19th century, however, art lovers, architects and scientists, without prejudice to the superiority of white in the artworks and after archaeological discoveries of excavations in Greece and southern Italy of sculptures with rich color residues, have started to reconsider the multi-color in ancient Greece (Østergaard, 2009; Tiverios and Tsiafakis, 2002).

The blue – red pair of colours advocated for the coloration of the sculptures is apparently due to the fact of the better preservation of these pigments through time (Brinkmann 2007). In 1780 the work of Stuart, Revett, Pars and Chandler in three Athenian buildings of the 5th century BC - the Propylaea, Thisio and the small church of Ilissos – reveals clearly the use of colours for decoration purposes. As Brekoulaki (2008) reports, extensive references to the practice of colouring ancient sculptures are also made by C. R. Cockerell after the discovery of the archaic temple of Aphaia in Aegina with very impressive findings of ancient color variety.

The ancient Acropolis pediment compositions, from the relief of Persian wars that came to light and which preserve rich traces of colours, confirm the practice of ancient colourful decoration (Boardaman, 1982).

In the extended catalogue of Acropolis sculptures edited by H. Schuchhardt, E. Langlotz and W. H. Schrader in the 1920s and 1930s all visible traces of pigments were mentioned (Brinkmann 2007). Moreover, V. von Graeve and G. Wolters investigate the Great Alexander's sarcophagus from Sidon, which retains extensive color traces (Brecoulaki 2008; Brinkmann 2007).

Since then and by combining literary sources and studying works of the archaic and Hellenistic era, relevant research works were presented (Stieber, 2010).

Concerned the archaic sculptures, which are also the subject of this work, it is worth to note that during the decade 1970s - 1980s an extensive mention of colours in sculptures took place (Boardman 1982). Furthermore, it is notable the detailed and analytical description of colours in the statue of the daughter of Frasikleia, by N. Kaltsas in the Catalogue of Sculptures of the National Archaeological Museum of Athens (Despinis and Kaltsas 2014).

V. Brinkmann has since 1981 studied in detail the sculptures of the Temple of Aphaia in Aegina and the Greek tombstones in Munich sculpture Museum and focused on the application of new methods in photographic technique to the discovery and documentation of ancient colours with emphasis on their potential diagonal lighting (Vlasopoulou 2012; Brinkmann 2007). As for Delphi archaic monuments with coloured remains notable is the extensive report to the multi-coloured frieze of the Siphnian treasury (Brinkmann 1994; Alfeld et al., 2017).

In the present work a case study is presented to evaluate color traces of specific archaeological sculptures from the Archaeological Museum of Delphi in the archaic period. For this purpose, pXRF and Raman beams pointed to a focal area of the object serves the aim of discovering the kind of natural oxide properly prepared and used for painting, in a versatile, fast and inexpensive manner.

2. MATERIAL AND TECHNIQUES

The site of the analyses was the Archaeological Museum of Delphi, Phocis, Greece. The sculptures and architectural parts that have been studded in this work are shown in Table 1 all dated to Archaic Period (mid 8th – mid 5th c. B.C.). Figures 1 and 2 present characteristic non-destructive setting for in situ XRF measurements.

The analytical techniques used were XRF and Raman spectroscopies, in order to identify the pigments used. Both techniques were performed using two portable non–destructive instruments (Vandenabeele et al., 2004; Bersani and Madariaga, 2012).

XRF Spectroscopy

For the qualitative determination of chemical elements that compose the colorants used, we used the handheld XRF analyser Skyray EDX pocket III equipped with a 40kV mini W-Target X-Ray Tube and a Single Collimator of 6mm diameter. This instrument provides rapid and simultaneous analysis of elements in the range from Sulfur, (S) (16) to Uranium (U) (92). For data acquisition from XRF handheld instrument a build-in software was used for the data point set of each measurement get saved as Unicode ASCII file format being compatible for further analysis with specialized software (see, results and discussion section). Here the research question is a qualitative evaluation (and not quantitative), and the calibration for specific set of samples (e.g. soil, metal et.c) was not used except the build-in shutter calibration.

Raman spectroscopy

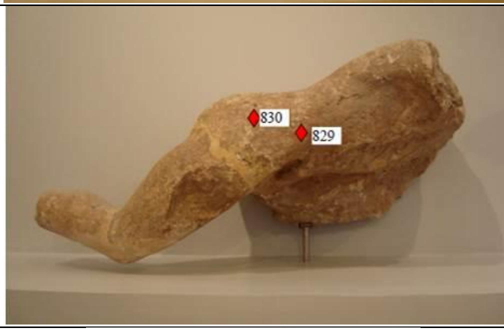
As for the Raman analysis we used the DeltaNu RockHound handheld Raman Spectrometer for the determination of the chemical compounds. It has a near infrared 785 nm diode laser in order to minimize fluorescence of the organic medium. The resolution is 8 cm^{-1}. The spectra were acquired in the wavenumber range of 200 cm^{-1} up to 2000 cm^{-1}. Prior to measurements, calibration tests were conducted in ideal pigment samples made for this purpose (Katsaros, 2009; Katsaros Liritzis and Laskaris 2009), to ensure the correct Raman shift measurement and operation. Also, on the employment of Raman technique a build-in software was use for the export of spectrum datasets on Unicode ASCII file format for further processing with specialized software (see, results and discussion section).

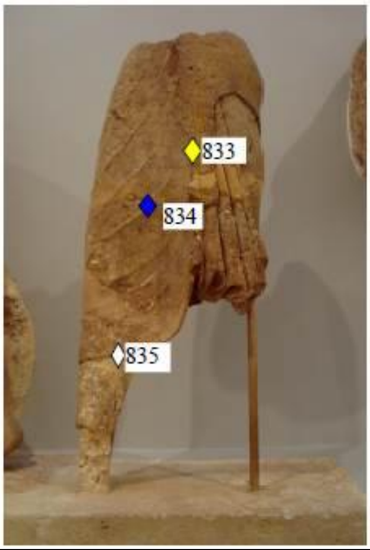
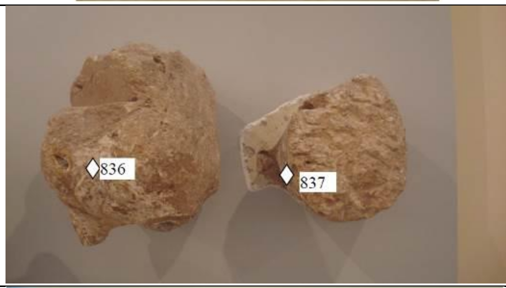
Figure 1. XRF measurement on an Embossed forked metopes of the Sikyonian treasure (hall III) (Artefact's numbering in Museum's catalogue: 1323, 1210 & 1381) see Table 1.

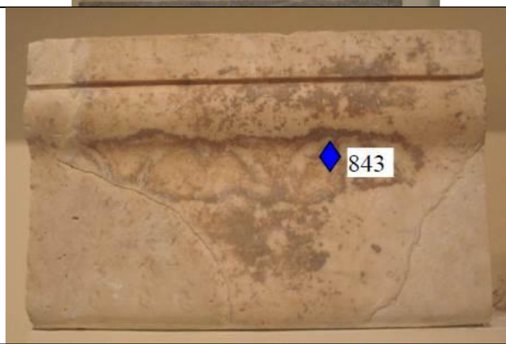
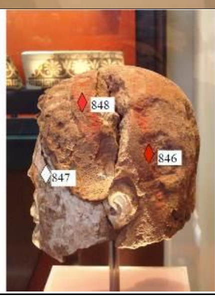
Figure 2. XRF measurement on a Marble cape from the archaic temple of Apollo (Artefact's numbering in Museum's catalogue: 4815), see Table 1.

Table 1. Artefacts studied in this work with their Museum catalog numbering and the numbering of measuring points

<table>
<tr><th>Archaeological artifact (sculpture or architectural part)</th><th>Photo (with sampling points)</th><th>Artefact's numbering in Museum's catalogue</th></tr>
<tr><td rowspan="2">Embossed forked metopes of the Sikyonian Treasure (-560B.C.)</td><td>
</td><td>1323 & 1210 & 1381</td></tr>
<tr><td>
</td><td>1322</td></tr>
<tr><td rowspan="2">Porous western pediment of the archaic temple of Apollo with a gigantomachia (battle between Olympian gods with giants the sons of Gaia). Above: giant fallen in his knee rather the Egelados, ~510 B.C.(hall IV). It shows traces of red, which in some places are very bright and cover relatively large areas.

Lower: Goddess Athena. The garment is decorated with white meanders (edges and crease in the middle).</td><td>
</td><td>5258</td></tr>
<tr><td>
</td><td>2547 & 4903</td></tr>
</table>

<table>
<tr><td>Part of a man's body. With macroscopic and microscopic observation spots in white, blue and yellow were identified.</td><td></td><td>1795</td></tr>
<tr><td>Parts of horses from the chariot, which were in the center of the pediment.</td><td></td><td>5259 & 5261</td></tr>
<tr><td rowspan="2">Eastern pediment of the archaeological temple of Apollo made of Parian marble (hall IV). Above: Lion stinging deer. Colors appear on the lions' curled mane, their flat surface being painted yellow, and their niches reddish. A red pigment was also detected in the deer's body.
Lower: Lion ripping a bull. Macroscopic and microscopic observations have found traces of red pigment in the bull's body, possibly dyeing the blood from the wounds inflicted on the lion with its nails and teeth.</td><td></td><td>2546</td></tr>
<tr><td></td><td>2555</td></tr>
</table>

Marble cape from the archaic temple of Apollo, which it represents Winged Victory on the Furry Road (Hall IV) Above: Marble akrotirion of Apollo archaic temple. Traces of blue appear on various parts of the clothing of the form. The meander that adorns the garment also retains traces of blue.		4815
Above: Part of marble rain gutter on the east side of its archaic temple Apollo (hall IV). It is made of Paros marble. It has traces of blue on the written meander that is on the abacus, as well as on the flowers, which decorate the rest of the surface. Lower: Part of marble Gutter of the archaic temple of Apollo consisting of three welded sections on the east side of the archaic temple of Apollo. Macroscopic and microscopic examination of the surface revealed traces of black pigment.		8196
		8195
Head of a female statue of the Athena Pronaia Doric Temple, 500-520 B.C. (room IX). According to Amandry (1981), this is a sculpture depicting Athena herself. Maintains vivid traces of multicolor. The face of the form is almost completely covered with white pigment, while the hair has a bright red color.	 	23826

3. RESULTS AND DISCUSSION

Table 1 also presents the sampling points for each archaeological part where both XRF and Raman analysis employed.

Figure 3 to 9 show a representative Raman spectrum for each colour along with reference spectrums (Clark and Franks 1975; Bell, Clark and Gibbs 1997; Caggiani, Cosentino and Mangone 2016).

All measured Raman spectra were quite noisy due to the existence of organic compounds from the burial environment and also a partial contamination from adjacent colors, therefore a pre-processing procedure such as baseline correction, Savitzky - Golay smoothing and normalization was followed prior to the main process of spectra for the pigment identification (Ferraro Nakamoto and Brown 2003).

Analysis of Raman spectra in summary for all sampling/color points, reveal vibrations of: lead carbonate ($2PbCO_3.Pb(OH)_2$), goethite mineral ($Fe_2O_3.H_2O$), iron Oxide (Fe_2O_3), mercury sulfide (HgS), Copper carbonate ($2CuCO_3.Cu(OH)_2$), calcium copper silicate ($CaCuSi_4O_{10}$) and carbon (Bell, Clark and Gibbs 1997).

The analysis of all archaeological parts with pXRF spectroscopy revealed elements, such as, Calcium (Ca) and Lead (Pb) for white pigments, Iron (Fe) for yellow, Iron (Fe) and Mercury (Hg) for red, Copper (Cu) for blue and Carbon (C) for black (see, Kakoulli 2010; Katsaros 2009, 2012; Katsaros et al., 2009; Siddall, 2018).

Table 2 presents the sampling points, the major elements found from XRF qualitative analysis and the pigment identified by Raman spectroscopy. It is revealed that occasionally the macroscopic reminiscent traces of color suits the real expected color of the respective image. For example, blood is red ochre or vermillion, face is white of lead, hairs as red ochre, rain gutter either black of carbon, or blue azurite/lazurite, tunic as blue azurite / Egyptian blue, and lion's mane as yellow.

The Raman spectra though in most cases are spiky and difficult to identify major oxide, which however has been confirmed by pXRF based on the major element of the respective oxide. This spiky -noisy- data sets is an often encountered practice of obtained spectra, which produces a fuzzy result, and even applying any sophisticated machine learning algorithm, still it is not easy to compare with ideal standard sample spectra. Nevertheless, the dual use of Raman and pXRF provides an interesting complementarity (Mustafa Mohamend et al., 2017).

Both XRF and Raman analysis and process of all measurements was made with scientific software Spectragryph (F. Menges "Spectragryph - optical spectroscopy software", Version 1.2.6, 2017).

In marble surfaces, pigments have been identified of certain oxides, yet, the interpretation of X-ray fluorescence images of archeological artifacts, in general, is complicated by the presence of surface relief and roughness. Arrangements of detectors has overcome this problem (Brecoulaki 2014; Gasanova et al., 2017; Alfed et al., 2017; Smilgies et al., 2012; Kopczynski et al., 2017).

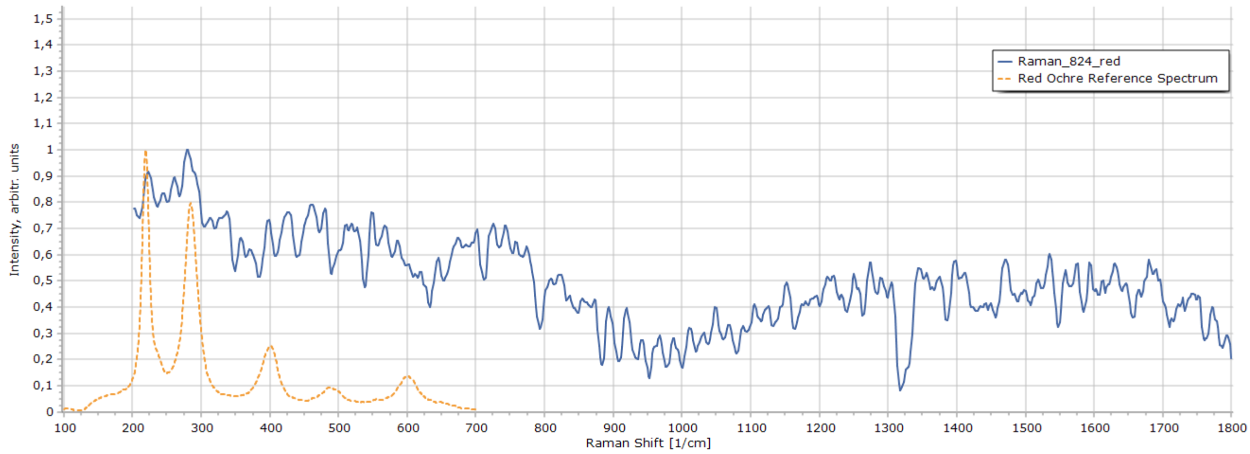


Figure 3. Raman spectra of No 824 measurement along with reference spectra

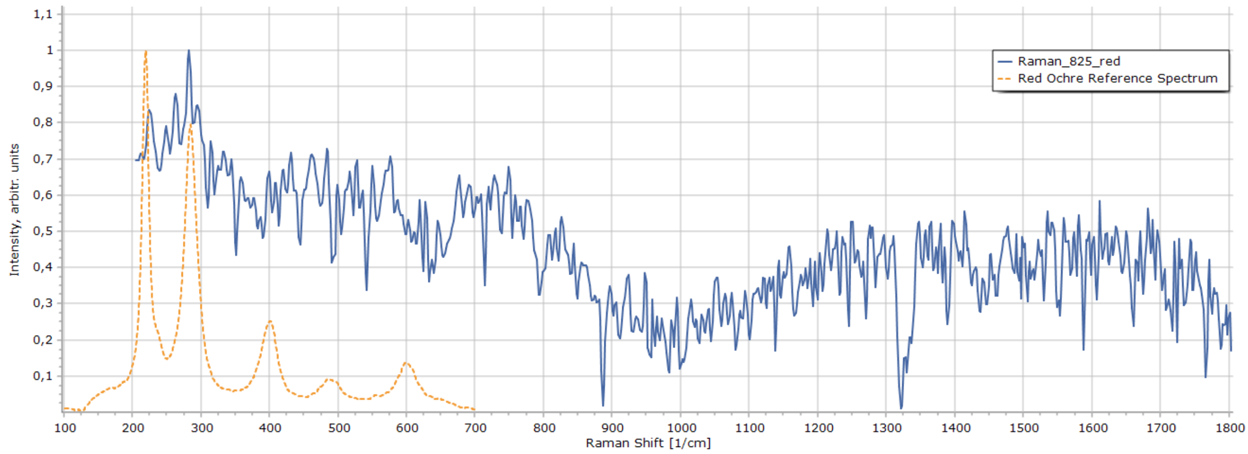


Figure 4. Raman spectra of No 825 measurement along with reference spectra

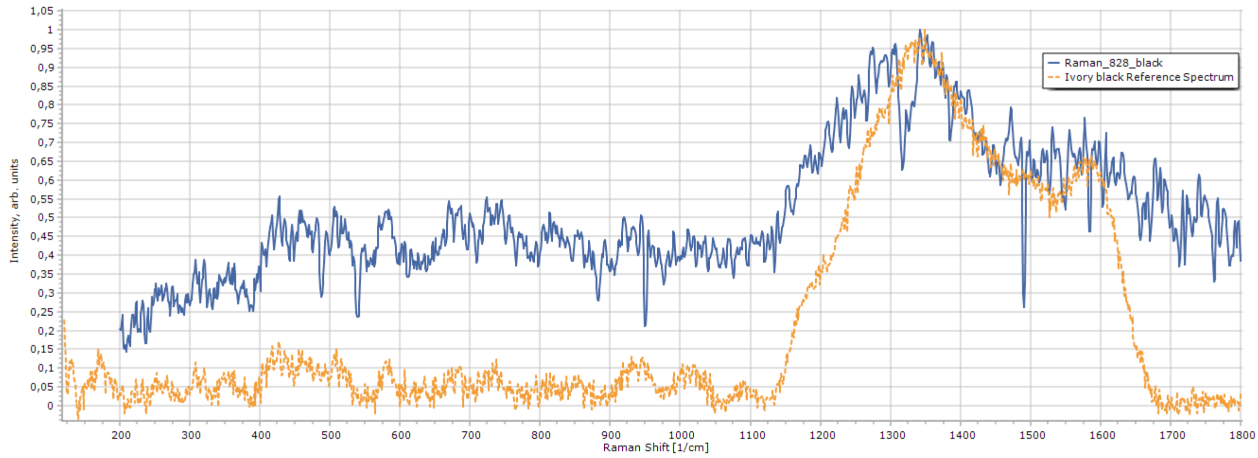


Figure 5. Raman spectra of No 828 measurement along with reference spectra

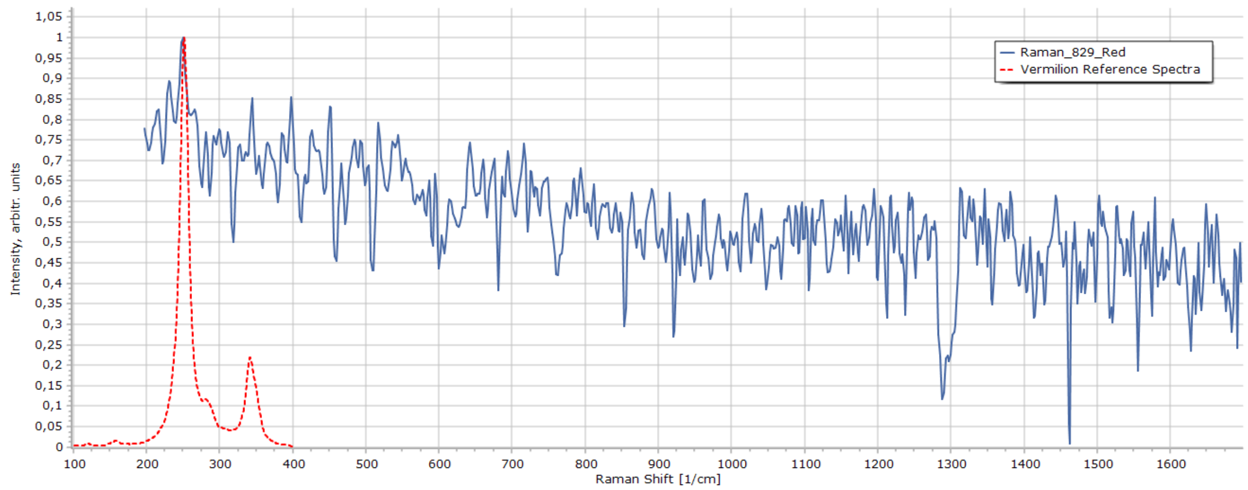


Figure 6. Raman spectra of No 829 measurement along with reference spectra

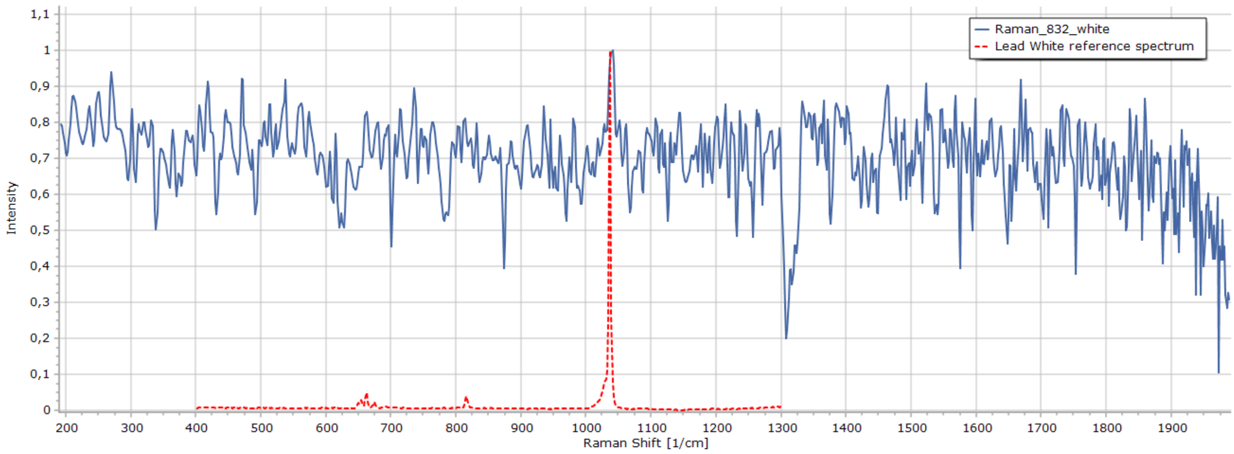


Figure 7. Raman spectra of No 832 measurement along with reference spectra

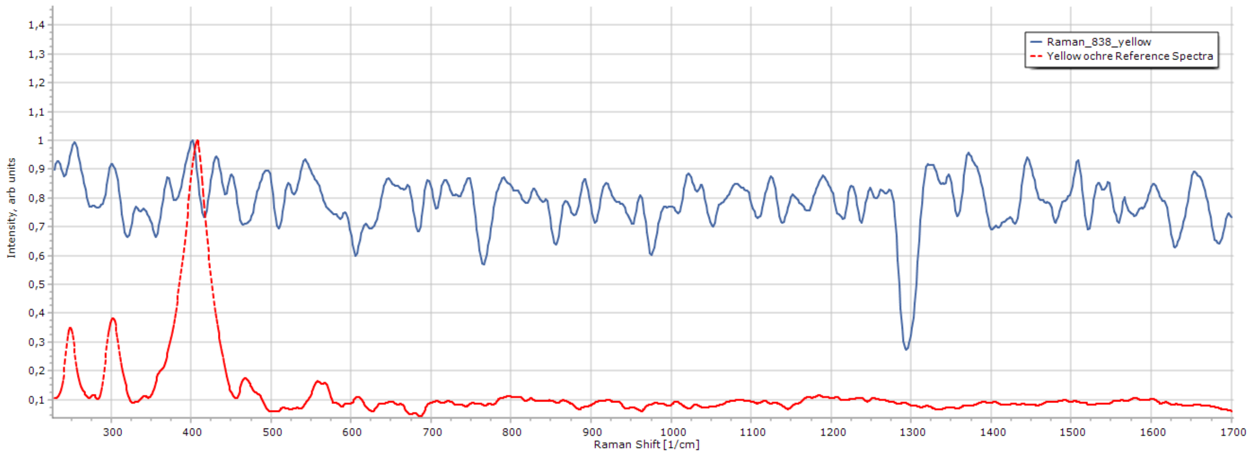


Figure 8. Raman spectra of No 838 measurement along with reference spectra

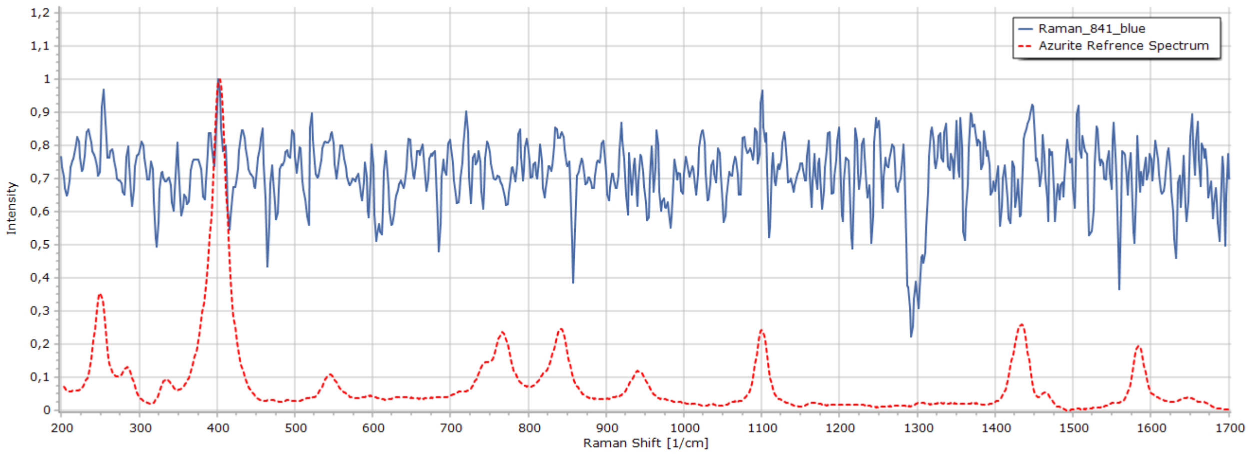


Figure 9. Raman spectra of No 841 measurement along with reference spectra

Table 2. Summarizing overview of the results from XRF and Raman employed along with the founded pigments.

Entry number of measuring point	Color (visual observation)	Major Elements from XRF qualitative Analysis	Pigments identified with Raman
822,823, 824, 825, 826, 829, 830, 840	Red	Ca, Fe	Red ochre (Goethite / Iron Oxide)
		Hg	Vermilion
827, 828, 844	Black	Ca, Fe	Ivory Black
832, 835, 836, 837, 847	White	Ca	Gypsum
		Pb	Lead White
834, 841, 842, 843	Blue	Cu	Azurite
		Ca, Cu	Egyptian Blue
831, 833, 838	Yellow	Ca, Fe	Yellow ochre

4. CONCLUSIONS

Through the present study, we were given the opportunity to deal with the remarkable archaeological material found in the Delphi Museum and to apply novel techniques for the determination of pigments that have been used for coloring them.

Summarizing the results from the analytical techniques employed in this work it may be conclude that lead white (“psymithion”) was used for the white colour and in some cases Gypsum, yellow ochre (“Ghoethite”/Iron Oxide) was used for yellow color, red ochre (“Kea’s Miltos”) and vermilion (“cinnabar”) for red, azurite and egyptian blue for blue colouring and finally for black the carbon black (known as ivory black).

All the above-mentioned results of this study are in full accordance with similar research results for the main color pallet in archaic and Classic Period and reinforce the belief of rich color sculptures during that period of history.

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REFERENCES

Amandry P. (1981) Chronique delphique. *Bulletin de Correspondence Hellenique*, Vol. 105, No 2, pp. 673-769

Alfeld, M, Mulliez, M, Martinez, P, Cain, K, Jockey, P and Walter, P. (2017) The Eye of the Medusa: XRF Imaging Reveals Unknown Traces of Antique Polychromy *Anal. Chem.* 2017, 89, 1493−1500 DOI: 10.1021/acs.analchem.6b03179.

Aubert, M., Brumm, A., Ramli, M., Sutikna, T., Saptomo, E. W., Hakim, B., Morwood, M. J, Van den Bergh, G. D., Kinsley, L., Dosseto, A. (2014) Pleistocene cave art from Sulawesi, Indonesia, *Nature*, Vol.514, pp. 223–227.

Bell I., Clark R.J.H., Gibbs P.J., (1997), Raman spectroscopic library of naturaland synthetic pigments (pre- ≈ 1850 AD), Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,53, 12, 2159-2179

Bersani D., Madariaga, J.M. (2012) Applications of Raman spectroscopy in art and archaeology, Journal of Raman Spectroscopy, vol. 43, issue 11, pp. 1523-1528

Boardman J. (1982), Greek Plastic. Archaic Period, by Eva Semantoni-Bournia, Kardamitsa Publications, Athens

Bratitsi, M, Liritzis, I, Alexopoulou, A, Makris, D (2019) Visualising underpainted layers via spectroscopic techniques: a brief review of case studies. *SCIENTIFIC CULTURE*, Vol. 5, No. 3, (2019), pp. 55-68. DOI:10.5281/zenodo.3340112.

Brekoulaki X (2008), On Multicolor in Ancient Greek Architecture and Sculpture: Between Reality and Vision, Lithos. Conservation Workshop, Thessaloniki (in Greek)

Brecoulaki, H. (2014). "Precious colours" in Ancient Greek polychromy and painting : material aspects and symbolic values. Revue archéologique, 57(1), 3-35

Brinkamann V.(1994), Die friese des siphnierschatzhauses, Biering & Brinkamann, Munchen

Brinkmann V., (2007) Research on the Color of Ancient Sculptures & Colors and Painting Techniques. In Multicolored Gods. Colors in Ancient Sculptures, Exhibition Catalog, National Archaeological Museum, Athens, pp. 15-22 & 193-197.

Caggiani, M.C., Cosentino, A., Mangone A., (2016), Pigments Checker version 3.0, a handy set for conservation scientists: A free online Raman spectra database, Microchemical Journal 129, 123–132,

Clark, R.J.H., Franks, M.L. (1975) The resonance Raman spectrum of ultramarine blue. *Chem. Phys. Lett*. 34, 69-72.

Despinis G and Kaltsas N. (2014), National Archaeological Museum. List of Sculptures I.1. Sculptures of archaic times from the 7th century to 480 BC Text, Issued by the Archaeological Resources and Expropriations Fund, Athens

Ferraro, J. R.,Nakamoto K.,Brown C. W. (2003), Introductory Raman Spectroscopy,2nd edition, Academic Press

Gasanova, S., Pagès- Camagna, S., Andrioti, M., Lemasson, Q., Brunel, L., Doublet, C., and Hermon, S. (2017) Polychromy Analysis on Cypriot Archaic Statues by Non- and Micro-Invasive Analytical Techniques. Archaeometry, 59: 528– 546. doi: 10.1111/arcm.12257.

Kakoulli I. (2010), "Painting Techniques and Materials of the Late Classical and Hellenistic Period: An Overview of Technical Literature" in Archaeological Studies, vol. edited by I. Lyritzis & N. Zacharias, Athens

Katsaros Th. (2009), Chromatology of Theophrastus from Eressos: Analyses - identification and contribution to the works of cultural heritage, PhD thesis, University of the Aegean (In Greek).

Katsaros Th. (2012), Pigments - Composition and Origin. In Archaic Colors, ed. Acropolis Museum, Athens, pp. 18-23

Katsaros, T, Liritzis, I and Laskaris, N (2009) Is White pigment on Appele's palette a TiO2-rich kaolin? New experimental and analytical study, *Mediterranean Archaeology & Archaeometry* Vol.9, No.1, pp. 29-35.

Kopczynski, N, de Viguerie, L , Neri, E , Nasr, N (2017) Polychromy in Africa Proconsularis: investigating Roman statues using X-ray fluorescence spectroscopy. *Antiquity*, Vol.91, No. 355, pp. 139-154

Mohamed Moustafa, Medhat Abd Allah, Ramy Magdy, Ahmed Abdrabou, Islam Shaheen, Hussein M. Kamal (2017) Analytical study and conservation processes of scribe box from Old Kingdom. SCIENTIFIC CULTURE, Vol. 3, No 3, pp. 13-24. DOI: 10.5281/zenodo.840011

Østergaard, J.S (2009)(Editor) Ny Carlsberg Glyptotek & the Copenhagen Polychromy Network, Tracking Colour. The polychromy of Greek and Roman sculpture in the Ny Carlsberg Glyptotek, Preliminary Report 1.98 p.

Siddall, R (2018) Mineral Pigments in Archaeology: Their Analysis and the Range of Available Materials. *Minerals,* 8, 201, pp. 1-35. doi:10.3390/min8050201.

Smilgies D-M, , Powers, J.A, Bilderback D.A, and Thorne, R.E (2012) Dual-detector X-ray fluorescence imaging of ancient artifacts with surface relief *J Synchrotron Radiat.*; 19(Pt 4): 547–550.

Stieber M.(2010), The Poetics of Appearance in the Attic Korai, University of Texas Press

Tiverios, M and Tsiafakis, D (eds.)(2002) *Color in ancient Greece*. Proceedings of the Conference: The Role of Color in Ancient Greek Art and Architecture (700-31 B.C.), Thessaloniki, Aristotle University of Thessaloniki & Lambrakis Research Foundation, Thessaloniki, ISBN: 960-243-520-8.

Vlassopoulou Ch., (2012) "History of Multicolor Research in Sculpture" in Ancient Colors, ed. Acropolis Museum, Athens, pp. 8-9

Vandenabeele, P., (2004), Raman spectroscopy in art and archaeology*, Journal of Raman Spectroscopy*, vol. 35, issue 89, pp. 607-609.