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IS WHITE PIGMENT ON APPELES' PALETTE A TiO_2-RICH KAOLIN? NEW ANALYTICAL RESULTS ON THE CASE OF *MELIAN-EARTH*

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ABSTRACT

According to Theophrastus of Eressos (4th c. B.C.) Melian-earth was a very bright white color used by the painters of his era. Pliny the Elder described it as the white pigment of the famous painter Appeles (c. 352 - 308 BC). Earlier investigations on the island of Melos (Aegean Sea) have not identified the specific place of the extraction of this material, because of the unknown chemical character. In our new analytical data from excavations (Turkey, Italy, England) the presence of a TiO_2 phase in the white ground decoration of ceramics has been testified, especially after the meticulous exploration of the island of Melos with a new point of view. At the western side of the island Kaolin was found in the locality of Kontaros with 1% by weight TiO_2. Analytical results from the white layer of decoration of the white ground Lekythoi give us the same level of TiO_2. We propose that the famous white pigment well known as melian earth in antiquity could be a kind of natural *Titania* as impurity in the Kaolin.

KEYWORDS: pigment, TiO_2-rich kaolin, XRD, raman, Melian, Theophrastus

INTRODUCTION

The most ancient reference of Melian earth is made by Theophrastus of Eressos who has included it amongst other kinds of white earths in his text "On stones" (c.315 B.C.).

Subsequently, Pliny the Elder (1st c.A.D.) described this material and named it as *melimum*. Kaolin from the island of Melos kept the solution of the problem of the ancient melian earth. But the researches on the case of melian earth which were made until now, did not relate their results with the analytical data from the archaeological excavations. The material of melian earth could be found as something peculiar on an ancient artefact in accordance to our view. After that we have collected the results from many analytical works around the world with common characteristic the presence of TiO_2 in antiquity. Dioxide of titanium (TiO_2) according to bibliography is a modern pigment and dated after 1919. But all these new references proofed its presence in antiquity.

Presence of TiO_2 from World examples

The ancient city of Ainos (Enez), in the Northen Coast of the Aegean sea, has been described as one of the most important sites in Turkey. The excavations give us artefacts of 6th and 7th century B.C. The material was pottery fragments with pigment decoration. Among of these identified the mineral Anatase with micro-Raman spectroscopy (Akyuz et al. 2006). This is very important because this pigment was known as a modern invention of 1919.

In Italy another case arrived from the region of Tarquinia from Cerveteri. It was an Etruscan pottery panel with a depiction of a warrior. On the white ground identified the phase of Anatase (TiO2) in a body of Kaolin. So the bright white pigment was a Kaolin with anatase (Bordignon et al. 2007).

The most impressive find came from England. The finds are ceramic vessels with remains of pigments from a Romano British site near of Northampton. One vessel contains a white pigment which includes anatase. The most remarkable occurrence found in the vessel pigments is the presence of anatase a polymorph with rutile. It was the first time that anatase has been found among the pigments compositions used in the Roman Empire (Edwards et al. 2003).

Another application of white pigment with Anatase came also from England from a Romano British Villa at Easton Maudit dated ca 150 AD. The identification was made by Raman spectroscopy. This again is a unique contribution to current knowledge of ancient European pigment history, because the presence of this mineral has not hitherto been recognised fully in an ancient artist's palette (Edwards et al. 2006).

We have two cases from China, one from a Neolithic site (Yangshao) with painted pottery with anatase decoration which dated 4300-2800 BC (R. Clark et al 2007) and the other from Xishan site which it was for the first time that anatase was used to decorated ancient pottery (Jian Zuo 1999).

Another case comes from the other side of the Atlantic Ocean from the desert of Arizona. On ceramics of the civilization of Anasazi 700-900 AD decorated with anatase and the identification was made with Raman spectroscopy (Jana Striova 2006).

All these have something in common, the use of anatase since the 5th millen-

nium BC to 900 AD, in many places around the world: form China, Mediterranean coasts of Turkey, Greece, central Italy, Northern Europe, to the new word in the desert of Arizona in United States of America).

ANALYTICAL RESULTS

We studied the raw material which collected from the island of Melos from different places. We analysed our sample of kaoline from Kondaros with SEM/EDS analysis Table 1, XRD analysis (fig. 2) and Raman spectroscopy (fig. 3). The identification of a phase by using XRD needs 5% the presence of this phase, so we have 1-1.5 % of TiO_2 in our sample and it is out of this area. But Raman can identify the presence of TiO_2 of this minor level.

Table 1. SEM/EDS analysis of sample KND-3 from Kondaros of Melos Island. Elements in oxides % by wt. (total error <10% for major elements).

Na_2O	0,16
Al_2O_3	42,66
SiO_2	54,22
P_2O_5	0,38
SO_3	0,36
Cl_2O	0,53
K_2O	0,17
TiO_2	1,52
Total	100.00

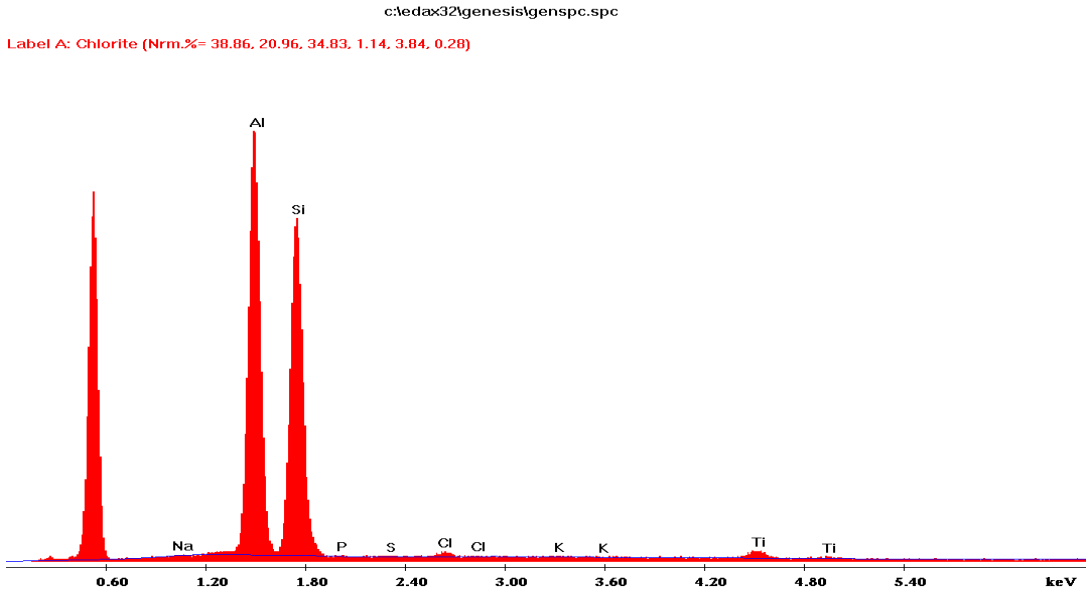

Fig.1: SEM spectra of samples KND-3 from the locality Kontaros at the western side of the island of Melos (Aegean Sea).

The sample from the site of Kondaros (KND-3) appears the characteristic peaks of Anatase at 243, 448, 609 cm-1. We have in comparison the spectra of pure Anatase which measured (fig. 4) with the same conditions with peaks at 242, 444, 608 cm-1.

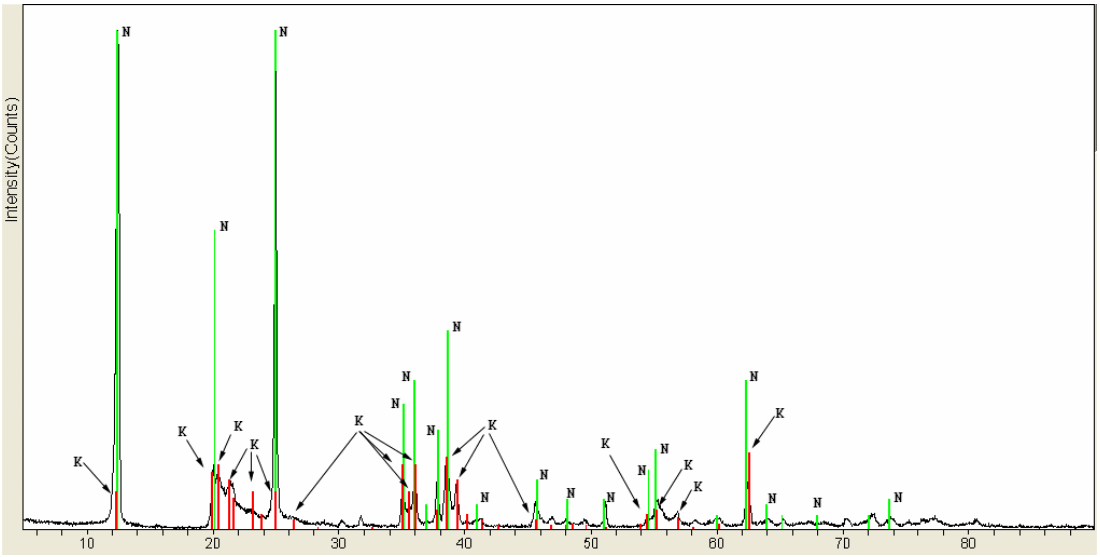

Fig.2: X-ray diffraction spectra of the sample KND-3. (K) Kaoline (12-0447 Kaolinite 1T (Aluminum Silicate Hydroxide) $Al_2Si_2O_5(OH)_4$) and (N) Nacrite (29-1488 Nacrite-1Md (Aluminum Silicate Hydroxide: $Al_2Si_2O_5(OH)_4$)

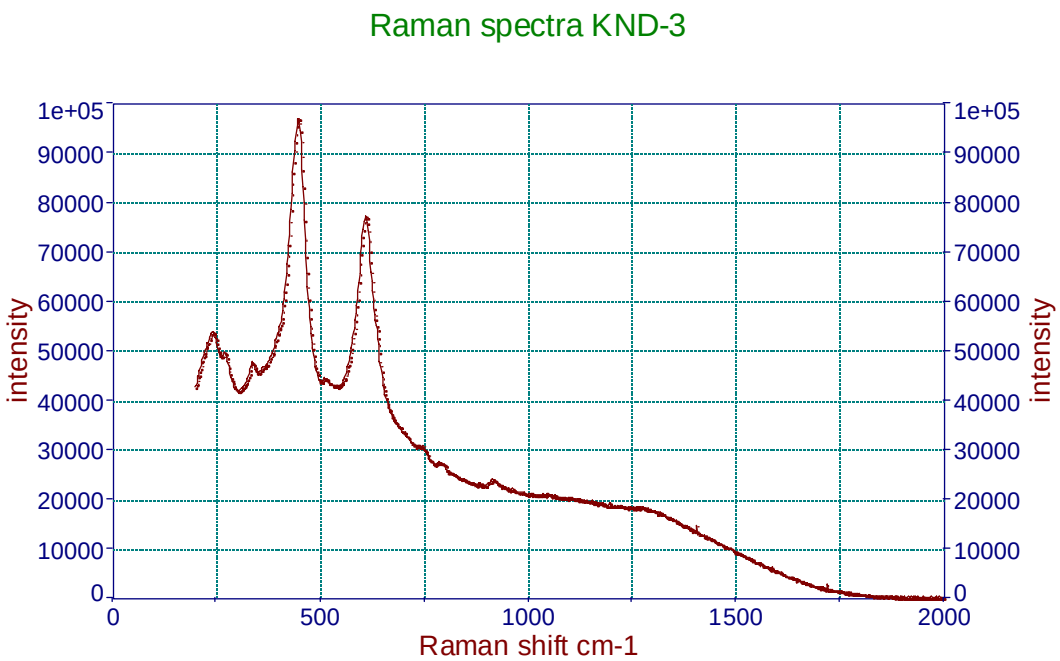

Fig.3: Raman spectra of the sample KND-3 with the peaks at 243, 448, 609 cm-1.

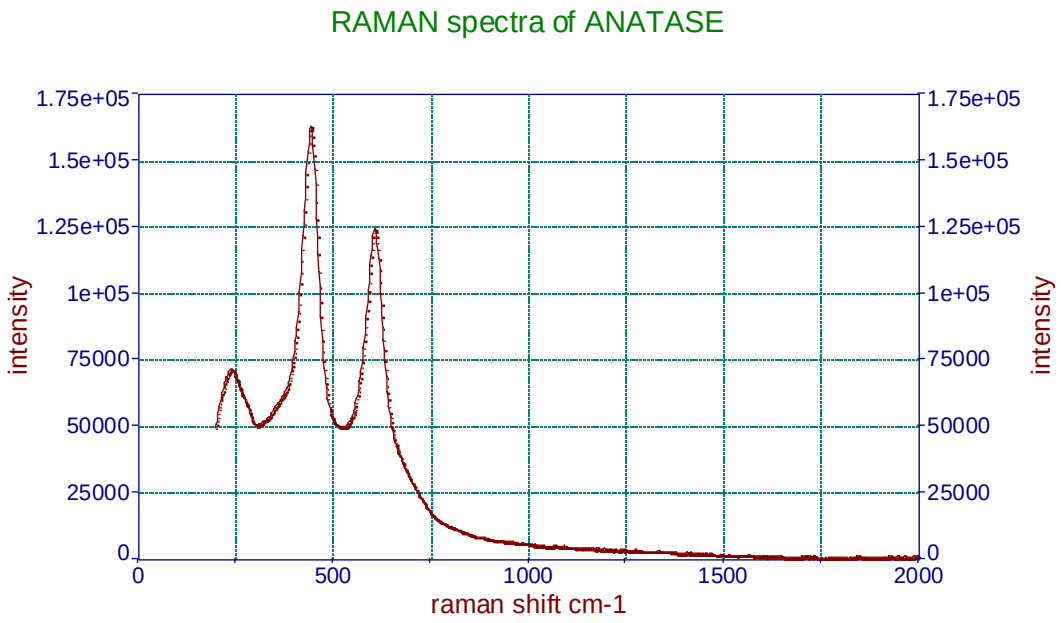

Fig.4 Raman spectra of pure Anatase (Kremer) with characteristic peaks of Anatase at 243, 444, 608 cm-1

CONCLUSIONS

The white of TiO_2 is a well known modern colorant since 1919. Since 2000 new finds from archaeological excavations around the world give us the opportunity to ask about the date of use of this material. The most significant find, came from England and was a clay pot (2nd cen. A.D.) which contains anatase with hematite too. The mineral anatase and rutile are two forms of TiO_2 and is something which is related to kaolin deposits. The level of TiO_2 in kaolin which used as white pigment from analyses around the world concentrated to 1% by weight. The presence of anatase as pigment in antiquity is proofed and the use of this material as dating element of artefacts is uncertain. The analytical results from white ground lekythoi for TiO_2 are around the level of 1%. This is agreed with the impurity of TiO_2 from the other places (Turkey, England, and Italy) and responded for the high whiteness of the specific pigment. The ancient writers and first of all Theophrastus mentioned the white earth from the Island of Melos as a white material very well for pigment. After him Pliny the Elder referred that the famous painter Apelles used the white material from Melos as his white pigment. On the Island of Melos the level of TiO_2 is higher in the west side and specially at Kontaros site, near of the cape Aspros Kavos. The meaning of the name of this cape related to the white color, because it means White Cape. We propose that the locality of Kontaros could be the place of extraction of the white pigment from melos in antiquity because in agreement with the chemical profile of the white ground Lekythoi.

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REFERENCES

Akyuz, S., Akyuz, T., Basaran, S., Bolcal, C., Gulec, A., (2007) FT-IR and micro-Raman spectroscopic study of decorated potteries from VI and VII century BC, excavated in ancient Ainos-Turkey, *Journal of Molecular Structure* 834-836, 150-153.

Bordignon, F., Postorino, P., Dore, P., (2007) In search of Etruscan colours-A spectroscopic study of a painted terracotta Slab from Ceri. *Archaeometry* 49,1, 87-100.

Boreadis, G. (1953) On the sediments of kaolin at the site of Kontaros (Melos Isl.) Greek Geological Society, vol.1, 157-180, (in Greek).

Brown, L.K., Clark H.J.R., (2002) Analysis of pigmentary materials on Vinland map and tartar relation by Raman microscopy, *Analytical Chemistry* 74, 3658-3661.

Caley Richards (1956) Theophrastus on stones, Ohio Univ. Press.

Clark, R.H., Wang, Q., Correia, A., (2007) Can the Raman spectrum of anatase in artwork and archaeology be used for dating purposes? Identification by Raman microscopy of anatase in decorative coatings on Neolithic (Yangshao) pottery from Henan, China, Journal of archaeological Science 34, 1787-1793.

Edwards, H.G., Hassan N.F., Middleton, P.S., (2006) Anatase-a pigment in ancient artwork or a modern usurper? *Anal. Bioanal Chem.* 348(6), 1356-1365.

Edwards, H.G.M., Middleton P.S., Jorge Villar, S.E., et al., (2003) Romano-British wallpaintigs II: Raman spectroscopic analysis of two villa sites at Nether Heyford, Northants. *Analytica Chem. Acta* 484, 211-221.

Edwards, H.G.M., Oliveira, L.F.C., Middleton, P., et al. (2002) Romano-British wallpainting fragments: a spectroscopic analysis. The Analyst 127, 277-281.

Laver, M. (1997) Titanium dioxide whites, Artist' pigments-A handbook of their history and characteristics, Vol. 3 (ed. Fitzhugh El.) National Gallery of Art, Washington, Oxford Univ. press., 295-355.

Photos-Jones E., Hall A.J., and Atkinson J.A. (1998) *The industrial minerals of Melos in Antiquity: Alunite and Sulphur*. The Silber and Barytes Mining Company: Athens. Public information on pamphlet published in Greek and English.

Photos-Jones E., J.A. Atkinson, A. J. Hall, A. Cottier and G. Sanders (1999) The Aghia Kyriaki, Melos period in the Aegean, *Annual of the British School at Athens*, 94, 377-413.

Pliny the Elder *Historia Naturalis* Book 35

Striova, J., Lofrumento, C., Zoppi, A., Castellucci, E.M.,(2006) Prehistoric Anasazi ceramics studied by micro-Raman spectroscopy *Journal of Raman Spectroscopy* 37, 1139-1145.

Zuo, J., Xu, C., Wang, CH.,Yushi, Z., (1999) Identification of the Pigment in painted pottery from Xishan site by Raman Microscopy, *Journal of Raman Spectroscopy* 30, 1053-1055.