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A WHITER SHADE OF VASE: DISCOVERING THE WHITE COLORS OF AN ANCIENT APULIAN KRATER THROUGH XRPD AND RAMAN SPECTROSCOPY

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ABSTRACT

Raman spectroscopy and X-Ray Powder Diffraction were applied in order to characterize the materials used for the manufacturing of an ancient, decorated vase of Apulian manufacturing in 4th century B.C. In this case study, three small fragments from one vase were sampled from pictorial areas in black and white. X-Ray Diffraction on a powdered sample was applied to characterize the composition of ceramic: the analysis allowed the identification of quartz, plagioclase and diopside and consequent hypotheses about the production process. The pictorial decorations in black and white were analysed through Raman spectroscopy. While the pigment constituting the dark areas was identified as maghemite γ-Fe_2O_3, an iron oxide with spinel structure, which suggests a maghemization oxidative process, in the white decoration it was possible to individuate the presence of both anatase -an allotropic phase of titanium oxide- and α-alumina. The application of alumina as pigment results peculiar and it represents a new knowledge advancement, which is worth of further studies. The combination of anatase and alumina suggested hypotheses about the origin of the starting materials for the white decorations, with reference to the manufacturing period and area. This set of data resulted in new information about the Apulian vase production, enriching the knowledge about a less popular pottery typology and opening new perspectives about commercial and cultural exchanges.

KEYWORDS: Apulian Krater, Raman spectroscopy, XRD, alumina, titanium dioxide, white pigments

1. INTRODUCTION

The common idea in the collective imagination about ancient decorated pottery usually corresponds to black- and red-figured Attic and Corinthian vases, produced after the 7th century B.C. and obtained through a multi-step firing process, which is actually not completely known and still under investigation (Balachandran, 2019; Cianchetta et al., 2016; Cianchetta et al., 2015; Iordanidis et al., 2011; Muşkara et al., 2021; Noble, 1960). However, reducing the ancient palette to red and black is oversimplifying, because the use of several colors is attested in order to produce particular decorations. For instance, a warm beige tone was used in particular for the production of black-figured *skyphoi*, obtained according to literature by mixing small amount of black to white slip, while a higher content of black glaze and the consequent firing allowed achieving gray hues. Moreover, the use of additional colors - blue, green, purple- applied after firing is reported, even if their fading, due to the conservation history, is addressed as the principal cause for their rare occurrence. A particular mention must be devoted to the presence of the white color, which was used for some details (e.g.: feminine faces), which was painted over black glazes and then subjected to firing (Noble, 1960). However, the manufacturing technique is not clear, and different materials could be used for the realization of parts of this color. If the oldest literary sources cite the use of a white slip, which would be constituted by a kaolinite-rich clay (Cuomo di Caprio, 2007; Noble, 1960), some recent studies identified the presence of alumina in Attic and Hellenistic vases (Pérez et al., 2004; Ulubey et al., 2008): in order to explain these findings, the hypothesis of thermal treatment of Greek bauxite was suggested (Pérez et al., 2004). However, the actual data are limited in order to have a clear perspective about the real relevance of alumina as pigment and about the know methodologies to achieve this compound from the available starting materials.

In this field, an important aspect which should be deepened is represented by the manufacturing methods for Apulian vases, which represents a production started in 4th century B.C. in Apulian centers and which grew in importance in the later centuries. The study of Apulian vase manufacturing is still limited from an archaeometric point of view, as it occurs with other typologies of pottery objects, whose chemical composition has been studied only in recent times (Belfiore et al., 2021; Šegvić et al., 2016): the main studies date back to last fifteen years and interestingly focused on the characterization of chosen materials and production methods, in order to highlight the main similarities and differences with the traditional Greek production of Attic vases (Giannossa et al., 2017; Mangone et al., 2009; Thorn et al., 2010; Muskara and Kalayci, 2021).

In this study, the object of interest was an Apulian vase, dated to the initial production of 4th century B.C. and manufactured in Campania. The decorations of these objects present several white areas, which, from a stratigraphic point of view, were painted above a black glaze. The focus of this study was the characterization of coloured materials used for decorative purposes on this vase, to collect new data about Apulian pottery manufacturing and to evidence and to extend our knowledge with reference to the better-known Attic production. The obtained diagnostic results accomplished the goal providing new data for the characterization of the production process and, with reference to new materials identified, for the comprehension of exchanges and trades with the Greek culture.

2. MATERIALS AND METHODS

2.1. *Samples*

The krater vase (temporary inventory number: 6638-T.462; H: 56 cm; W: 52 cm) was collected in an excavation in Caudium necropolis (Montesarchio area, near Benevento) dated back to 5th-4th century B.C.; according to the ritual traditions, kraters were placed between the deceased legs. The excavation included 3000 tombs and it led to the recovery of 400 kraters. The vases were subjected to a preliminary conservation treatment in 2011; a new intervention has been started in 2020, to remove encrustations and soil not completely expelled in the previous treatment, according to the principles of conservative archaeological restoration.

The vase (Supplementary Materials, Fig. 1) presents a red-figured decoration, with several areas in black and details in white; some decorations in yellow are present. Religious scenes and mythologic episodes are represented, along with geometrical decorations. The ceramic body is brown; the black parts appear as a metallic glaze, while the white and yellow details seem brush painted. From the optical analysis, it is not evident if these parts were realized with an organic binder, or they were subjected to firing. Three fragments from the vase were sampled: two were taken from white areas on the vase (Fig. 1), while a third one was an erratic. This last sample presented a black glaze and, above, a white layer. This third sample was collected for the diagnostic campaign because it was found very close to the vase and, in the tomb, there was no other pottery object which the sample could come from, so it was considered useful for the analysis and preferred to a further sampling with reference to the micro-invasively principles.

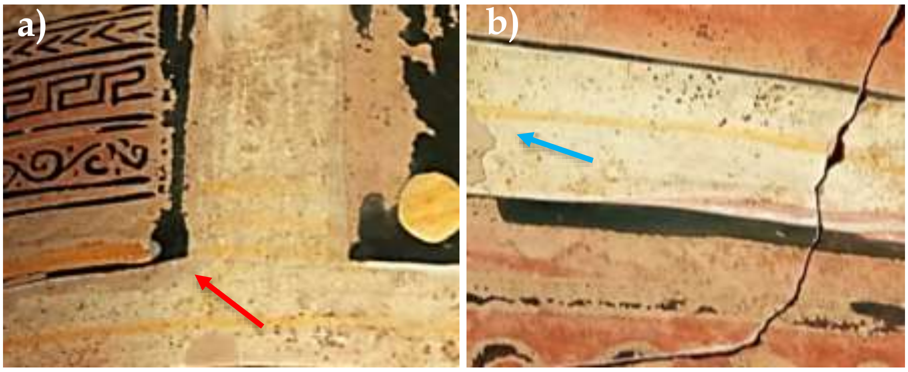

Figure 1: Sampling areas a) for the first and b) the second samples.

2.2. *X-RAY powder diffraction*

X-Ray Powder Diffraction (XRPD) was applied to analyse the mineralogical composition of the ceramic body. A few mg were finely ground in an agate mortar and analysed using a Bruker D8 focus diffractometer with Cu Kα radiation, operating at 40 kV and 30 mA. Spectrum was collected from 3° to 60° 2θ, with a scan step of 0.02° 2θ and 2s per step as counting time. Data processing was performed using XPowderX© software and semi-quantitative analysis was based on the "Reference Intensity Ration Method".

2.3. *Raman Spectroscopy*

For the Raman analysis of samples, a Horiba Jobin-Yvon HR-Evolution micro-Raman setup, equipped with a 633 nm laser and a motorized XY Mapping Stage, was used. Experimental acquisition conditions were changed according to the characteristic of the samples, minimizing the risk of material damage under the laser probe. Raman analysis was performed directly on the samples to characterize the different pigments, selected on the base of their optical differences. Raman spectrum assignations were confirmed by comparison with standards and literature data. Raman spectra were acquired in the range 20-2000 cm^{-1} (two measurements for every point in the ranges 20-1200 and 1050-2000 cm^{-1}); for some samples, also a spectrum in the range 3200-3900 cm^{-1} was acquired to individuate organic materials from their C-H stretching modes. Spectra were calibrated through Neon emission, and they were processed through subtraction of a polynomial background; only in few cases, a smoothing processing was applied (Savitzky-Golay; number of points ≤ 15), in order to minimize noise effects. Origin was used as data analysis software.

3. RESULTS

3.1. *X-RAY Powder Diffraction*

XRPD spectrum shows that the ceramic body was mainly composed of quartz and feldspar. Minor amount of clinopyroxene and traces of olivine (Fig. 2).

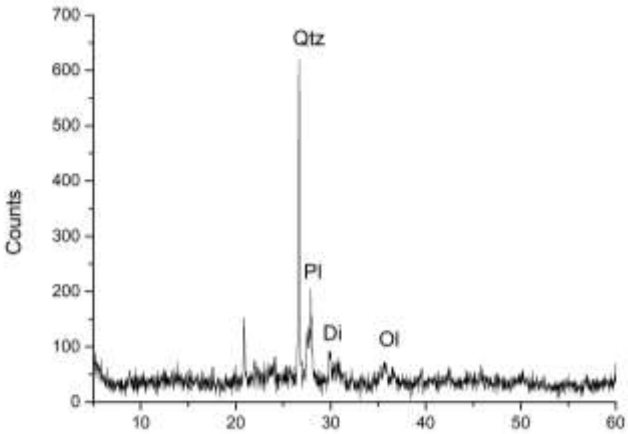

Figure 2: XRPD pattern of the ceramic body (Qtz:quartz; Pl:plagioclase; Di: diopside; Ol: olivine).

3.2. *Raman Analysis*

The Raman spectra acquired in the three samples present a general coherence in terms of spectral features for the black and white areas.

For the first ones, two broad bands are observable at 118 and 182 cm^{-1} with a characteristic double shape and a shoulder at 220 cm^{-1}. At higher wavenumbers, signals at 290, 345 (very broad and weak), 405 and 503 cm^{-1} can be distinguished, while the most intense feature is represented by a band at 680 cm^{-1} with a clear shoulder at 727 cm^{-1}. Moreover, in one of the spectra two sharp peaks at 126 and 466 cm^{-1} (the most intense) are evident, along with another band at 196 cm^{-1} overlapping with the previous one at 182 cm^{-1}, while two minor signals are observable at 355 and 395 cm^{-1} (Fig. 3).

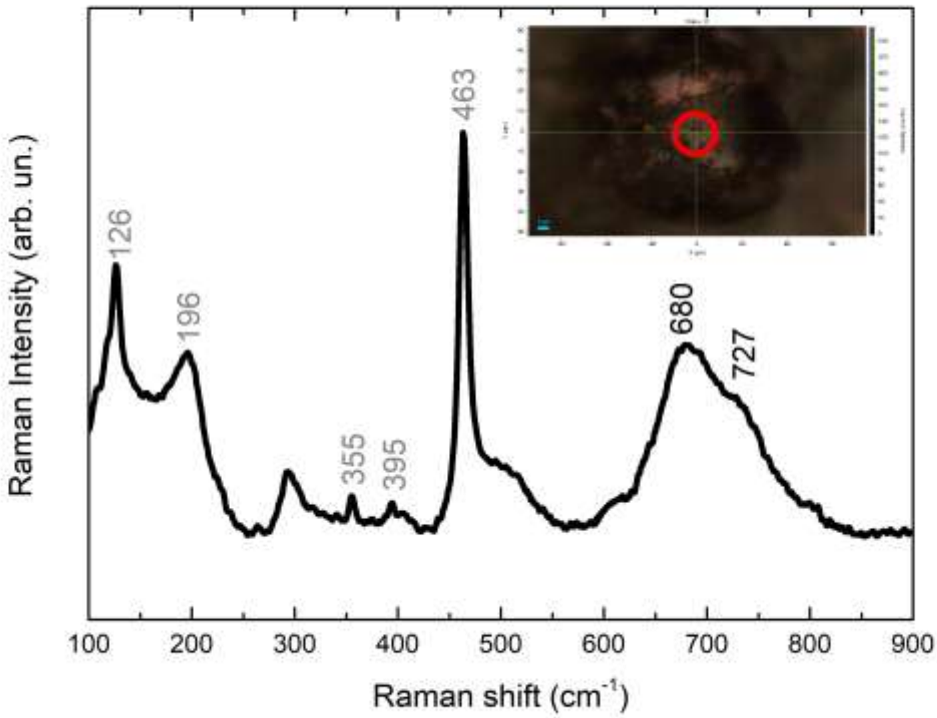

Figure 3: Raman spectrum obtained for a brown-black particle (spectrum acquisition area evidenced by red circle in the inset); typical Raman shift wavenumbers of maghemite are highlighted in black numerals, while the quartz analogues are evidenced in grey numerals.

In the white areas, all the corresponding spectra present a characteristic peak at 143 cm^{-1}, which is associated to very low intensity bands at 183, 393, 514 and 638 cm^{-1} (Fig. 4) in all the spectra with the highest signal/noise ratio. At higher wavenumbers, in all the spectra signals at 1368 and 1396 cm^{-1} are observable (Fig. 5). Furthermore, in most the spectra the same signals at around 122, 350, 389, 460 cm^{-1}, observed in black area analogue described above, are present. Finally, in one spectrum, a signal at 1178 cm^{-1} can be individuated.

It is important to highlight that, in the white areas, some isolated red particles appear. The Raman spectra acquired in their correspondence show two intense signals at 220 and 290 cm^{-1}, while other broader bands can be individuated at 405, 500, 604, and 660 cm^{-1}. In one of these spectra, the above-mentioned peaks at 120 and 460 cm^{-1} are observable with minor intensity in comparison to these dominant peaks, while in another spectrum signals at 118 and 155 cm^{-1} appear with the same intensity.

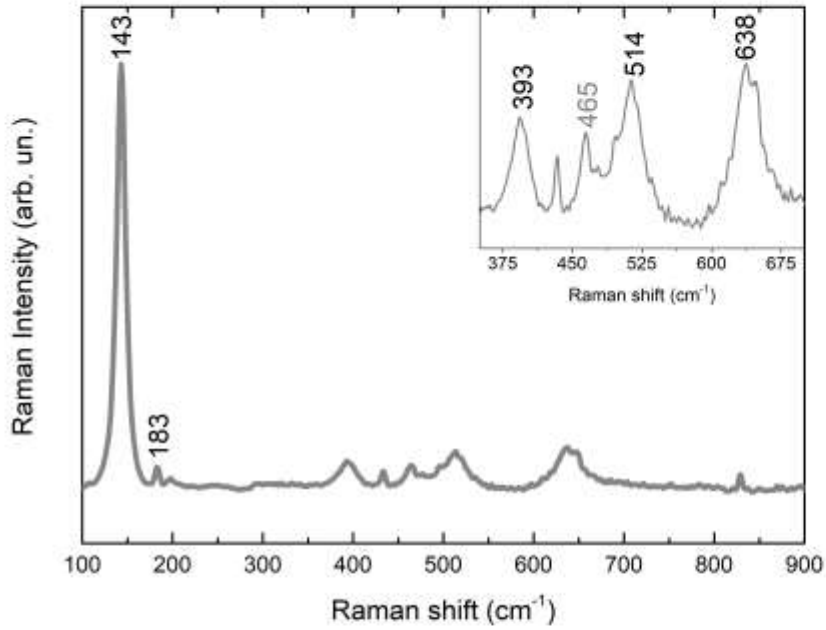

Figure 4: Raman spectrum (zoom inset) obtained for the white layer; typical Raman shift wavenumbers of anatase are highlighted in black numerals, while signals of quartz are evidenced in grey numerals.

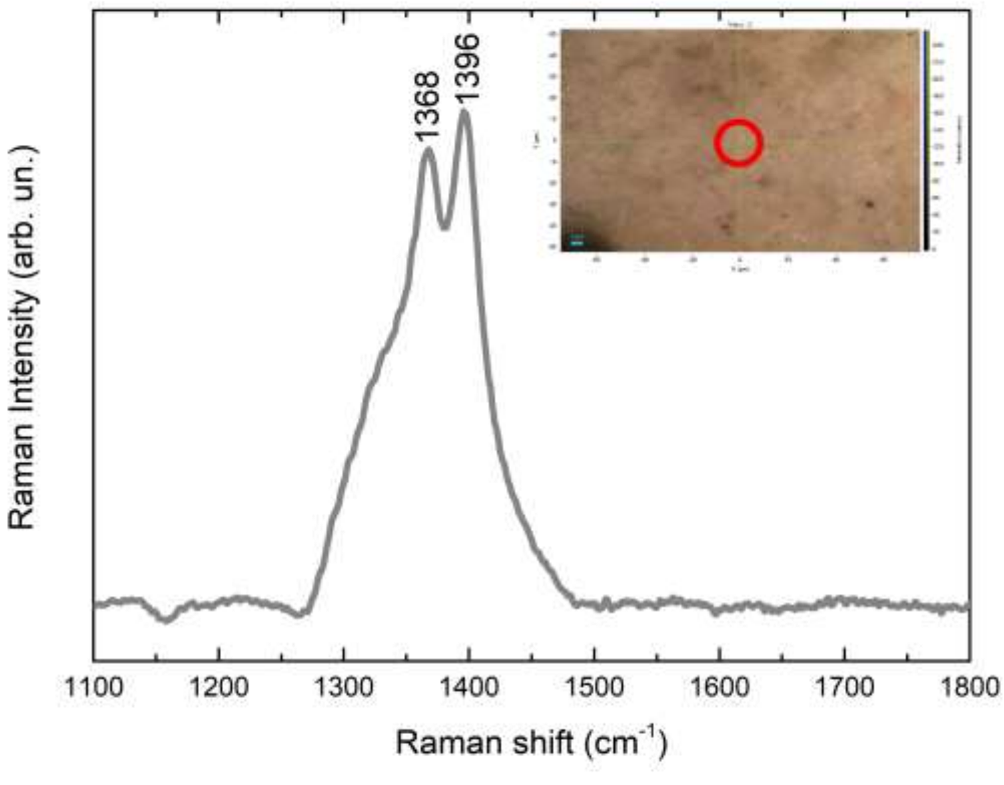

Figure 5: Raman spectrum obtained for the white layer (spectrum acquisition area evidenced by red circle in the inset); typical Raman shift wavenumbers of a-alumina are highlighted in black numerals.

4. DISCUSSION

The sample analyses show a fine-grained paste with colour ranging from pale-red to red. The total absence of coarse inclusions suggests a refining of the clay employed in the production.

Concerning firing temperature, the presence of neo-formed phases, such as pyroxenes, and the absence of calcite, strongly suggests a high sintering temperature kept constant for a time enough for completing the reactions. Indeed, calcite can be completely destabilized within a wide temperature range between 750 and 850-900 °C, whereas neo-formed clinopyroxenes can be found between 900 and 1200 °C (Dondi et al., 1998).

The formation of diopside in the ceramics can be hypothesized as the results of continuous reactions such as (Luettge & Metz, 1991; Duminuco et al., 1996; Duminuco et al., 1998; Rathossi et al., 2010):

illite+calcite+quartz→K-feldspar+gehlenite+quartz+H_2O+CO_2
gehlenite+quartz→diopside+anorthite

or
dolomite+quartz →diopside+CO_2
$2SiO_2 + CaMg(CO_3)_2 \rightarrow CaMgSi_2O_6 + 2CO_2$

at the presence of dolomite in the starting raw material.

The reconstruction of the starting raw material composition is a challenge due to the complete reactions occurring during firing. However, the neo-formed minerals identified allow us to hypothesize a calcareous refined clay that is compatible with the sub-Apennine clays in the area.

The composition of the pigmented areas is representative of different materials according to their colour. In the black areas, characteristic features of iron oxides are observable: In particular, the signals at 345, 405, 503, 680, and 727 cm^{-1} would be attributable to the presence of maghemite γ-Fe_2O_3, where the low intensity signals at 220, and 290 cm^{-1} could be attributable to small amounts of hematite (de Faria et al., 1997; Hanesch, 2009). It is fundamental to mention that the main band of magnetite is at 667 cm^{-1}, so it could be not visible because overlapping with the maghemite one. The intense signal at 463 cm^{-1}, observed only in one among the acquired spectra, would be indicative of the presence of quartz, along with the minor peaks at 126, 355, 395 cm^{-1} and the over-lapping band around 196 cm^{-1} (Bordignon et al., 2008; Krishnamurti, 1958; Raškovska et al., 2010; RRUFF Raman spectrum of quartz). The observed species represent characteristic compounds identified in decorations and glazes in ancient pottery. For instance, the presence of maghemite is reported, in combination with hercynite, in some Attic vase samples studied by Bente et al. (Bente et al., 2013): the authors addressed as surprising the high content of maghemite in comparison to magnetite, which was not identified by means of the approach they selected. The dominance of maghemite in comparison to magnetite was considered unusual for several reasons. In general, magnetite and hercynite (Fe^{2+} compounds) are considered the main chromophores for black ceramics, while maghemite, in association to hematite (both Fe^{3+} compounds), is considered characteristic of red areas (Cianchetta et al., 2016; Cianchetta et al., 2015a; Cianchetta et al., 2015b). Moreover, maghemite is usually addressed metastable in comparison to hematite over 350 °C. About this last objection, it is important to highlight that the grain size of maghemite could be the main factor to take into account for its stabilization: nanocrystal of maghemite could preserve their structure, with consequent stabilization at higher temperatures (Ye et al., 1998). Moreover, the occurrence of mixed phases of these iron compounds was reported in reconstructions of the firing processes and they are correlated to the combinations of temperature in the oxidative steps of decoration manufacturing (Cianchetta et al., 2016). The first critical factor is more difficult to answer: although maghemite could be present in black areas according to literature, the absence of hercynite prevents justifying their colour. The intense band at 182 cm^{-1} could suggest the presence of hercynite, while its band at 750 cm^{-1} would be not visible because of the close maghemite band at 727 cm^{-1} (Ospitali et al., 2005; Vu et al., 2021), but this hypothesis is not supported by any other data. However, it is important to highlight that there is a general lack of deepened studies about the Raman characterization of hercynite, so further studies with other techniques are necessary in order to be sure of its absence in the dark parts. Moreover, with reference to the three-step firing process usually used to explain the manufacturing of Attic vases, a high conversion of magnetite and hercynite to maghemite in the second oxidative step a process referred as "maghemization"- could be responsible for a higher content of this spinel (Cianchetta et al., 2015a). Consequently, further analyses are necessary to better individuate the principal chromophores in dark parts.

About the white areas, it is possible to identify several species. The signals at 143, 183, 393, 514 and 638 cm^{-1} are indicative of the presence of titanium dioxide in anatase form (Burgio et al., 2001; RRUFF Raman spectrum of anatase), which was identified in several archaeological vases as a component of white areas

(Bersani et al., 2016; Bordignon et al., 2007; Bordignon et al., 2008). The sharp peaks at 1367 and 1395 cm^{-1}, instead, are indicative of α-Al_2O_3 (Bersani et al., 2016), even if they are not real Raman signals but photoluminescence bands of Cr^{3+} ions, present in this species. The presence of γ-alumina, according to the literature, should be confirmed by a broad band centered at 1270 cm^{-1}, which is not evident in our case (Pérez et al., 2004). Finally, the peaks at 126, 355, 395, 463 cm^{-1} are indicative of quartz particles, while those one observed in the spectra acquired in correspondence of the red particles are assigned to hematite. The composition of the white areas presents a correspondence with their analogues on Greek vases produced between the 5th and 4th Century BC and on Hellenistic pottery from the 3th century from Anatolia (Pérez et al., 2004; Ulubey et al., 2008). In particular, in one of this study (Pérez et al., 2004) it is hypothesized that original Greek bauxite could be thermally decomposed at temperature over 500 °C to obtain both the alumina allotropes. Following this interpretation, the absence of γ-alumina in the analysed samples could be indicative of a starting material richer in diaspore than in boehmite: the first one is subjected to direct transition to α-Al_2O_3, while the second is subjected to a first transition to γ-Al_2O_3 and then, over 1100 °C, this species is converted to the α-form. Probably, the production of alumina from bauxite was not achieved at high temperatures, because otherwise the present anatase, a typical minor component of bauxite, would have transformed into its stable analogue, rutile (Hanaor et al., 2011; Shannon et al., 1948). However, the use of anatase/rutile amount as firing thermometers was called into question in some recent studies, so this aspect cannot be considered totally discriminating. Another interesting factor to be mentioned is represented by the presence of bauxite quarries in South Italy, which could confirm the avail-ability of this material for the pottery manufacturing: for instance, a bauxite mine is present in Cusano Mutri, close to Benevento (Prete et al., 2002), even if no main information is available about its exploitation in antiquity. Further studies should be addressed in order to deepen the use and the provenance of painting materials for this typology of objects.

5. CONCLUSIONS

In this study, the composition of the body and both the black and white painted area in an ancient Apulian vase was studied through the combination of X-Ray Powder Diffraction and Raman spectroscopy. While the pottery resulted constituted by a refined clay, confirming the good quality of the ceramic, Raman spectroscopy provided information on the used pigments. The presence of maghemite suggests a maghemization process, which converted black spinel into maghemite conferring a warmer tone to the black areas, but further analyses should be addressed in order to identify minor amounts of magnetite and hercynite. About the white color, the presence of alumina and anatase suggest suggests the production of the white pigment from bauxite. This discovery links the manufacturing of Apulian vase in Italy to Greek pottery tradition, opening new perspectives in reconstructing the production techniques of this typology of artist objects. Finally, further studies should be addressed to individuate the sources of used materials, especially regarding the bauxite processing, and to clarify aspects related to their provenance and market.

AUTHOR CONTRIBUTIONS

Conceptualization, A.C. and L.M.; methodology, A.C., I.S. and L.M; formal analysis, L.M.; investigation, A.C.; resources, G.M.; data curation, A.C. and L.M; writing - original draft preparation, A.C., G.M., L.M; writing - review and editing, A.C., L.M., G.F.; supervision, R.C, P.P., G.F.; project administration, G.F. All authors have read and agreed to the published version of the manuscript.

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