Contribution of mineralogical and analytical techniques to investigate provenance and technologies of Hellenistic pottery from Arpi (SouthernItaly)

Lorena Carla Giannossa[a,1], Italo Maria Muntoni[b], Rocco Laviano[c,1], Annarosa Mangone[d,*,1]

[a] Dipartimento di Economia, Management e Diritto dell'Impresa, Università Aldo Moro, Largo Abbazia Santa Scolastica 53, 70124 Bari, Italy
[b] Soprintendenza per i Beni Archeologici della Puglia, Via De Nittis 7, 71100 Foggia, Italy
[c] Dipartimento di Scienze della Terra e Geoambientali, Università Aldo Moro, via Orabona 4, 70126 Bari, Italy
[d] Dipartimento di Chimica, Università Aldo Moro, via Orabona 4, 70126 Bari, Italy

1. Introduction

Arpi, on the Tavoliere delle Puglie, is one of the largest indigenous Daunian settlements and dates back to the early Iron Age, that is to the 8th century BC. The structure would have been that typical of Daunian settlements with groups of huts, tombs close by and open areas in which agricultural and husbandry activities took place. The settlement was delimited by an *agger* of about 13 km in length, composed of earth piled up from a ditch dug in front of it. The *agger* probably dates to the 6th century BC and encloses and area of over 1000 ha. From the 4th century on – during the Hellenistic era – the settlement underwent profound changes as the culture opened up to the Greek and, in particular, Macedonian worlds. This process was further stimulated by the arrival of King Alexander I of Epirus in 333 BCE. Archaeological research has involved the excavation of several houses and many tombs and has revealed the existence of a wealthy Hellenised local aristocracy, which supported the development of local craft activities. In particular, the production of various forms of ceramic vessel was important. These include Apulian painted vases, red figure ware, wares with banded decoration, black-glazed ware that was often painted in the Gnathia style and tempera-decorated wares (Mazzei, 2010, 2015 with previous bibliographic reference).

While the collection of ceramics from Arpi is extremely rich and varied, the archaeometric data on these wares is extremely sparse. Such data could help provide analytic support for ideas about the operationof specialised artisanal workshops working at a high level of both technical and artistic refinement.

The analyzed finds come from a rich "grotticella" tomb located along the Celone river dating back to the second half of the 4th century BC and excavated in 2005, during a joint mission by the Soprintendenza Archeologica della Puglia and the University of Salento, Dipartimentodi Beni Culturali - Laboratorio di Topografia antica e Fotogrammetria (LabTAF), in Arpi (Foggia, Italy).

The undisturbed tomb contains the remains of two men and a woman and also 91 objects. These grave goods are mainly ceramic, but there are also metallic armaments, including two bronze belts, a spear and an iron javelin.

The ceramics are of different classes - unpainted, band decorated,red figure, Gnathia, black gloss and unfired pottery (painted in black with overpainting in red, white and yellow).

The tomb vault collapsed in ancient times causing the fragmentation of many of the vases, but at the same time preserving them.

A passageway (*dromos*), with six steps at its end (length about 3 m, width 1.20 m), leads into the entrance of the tomb, closed by a lime- stone slab.

Beyond the entrance there is another step. On the right and on the left of this, two symmetrical polychrome "spool" supports were placed. On these, two painted unfired vases, with *appliques* with a female figure, were located.

The objective of this paper is to study ceramic grave goods, aiming to highlight differences in raw materials and production technology used in the making of objects of different classes, but which are coevaland come from the same context.

This work is part of a comprehensive project exploring the technical and manufacturing features of Apulian Hellenistic pottery, with particular attention being given to the interconnection between various ceramic classes from a technological-productive point of view. From an archaeometric perspective, although Apulian Hellenistic pottery has been widely studied from a stylistic-typological viewpoint, it has largely not been subject to archaeometric investigation. Studies which have been carried out up to now have focused principally on red figure pottery, mainly coming from private and museum collections, and as such we have little or no information about the provenance of the pottery which has often been subject to restoration of an "antiquarian nature", with reconstruction and repainting (Giannossa et al., 2009, 2016, 2017a, 2017b; Mangone et al., 2008, 2013; Grave et al., 1997;

Table 1
Analyzed samples: pottery (a) and clay (b).

a

Ceramic class	Code	Inventory number	Vase shapes
Red figure	Ar2	FG 48529	Bell Krater
	Ar3	FG 48530	*Lebes gamico*
	Ar9	FG 48537	Bell Krater
	Ar23	FG 48549	*Pelike*
	Ar8A	FG 48535	Little Olla's lid
	Ar8B	FG 48536	Little Olla
	Ar50A	FG 48576	Little Olla
	Ar50B	FG 48577	Little Olla's lid
Unpainted	Ar18	FG 48545	Olla
	Ar49	FG 48575	*Lopas*
Band-decorated	Ar33	FG 48559	Bell Krater
	Ar57	FG 48584	Olpe
	Ar20	FG 48547	Bell Krater
Gnathia	Ar24	FG 48550	*Skyphos*
Unfired	Ar34	FG 48560	Krater?
	Ar37	FG 48563	Krater?
	Ar61	FG 48588	Krater?
	ArS.N.		Krater

b

Sample	Coordinate UTM WGS 84	
	Easting	Northing
cl1	530607	4599532
cl2	568680	4561582
cl3	524579	4599834
cl4	551828	4602320
cl5	557980	4570902
cl6	554614	4569363
cl7	558169	4572417
cl8	546103	4571777
cl9	568375	4568565
cl10	536212	4600941
cl11	512341	4620901
cl12	556275	4578407
cl13	537725	4588649
cl14	558313	4588198
cl15	546832	4578426

Thorn and Glascock, 2010; Robinson, 2013, 2014a, 2014b). Only few finds coming from archaeological sites have been analyzed, so that the available archaeometric data is in no way sufficient to provide a thor- ough idea of the technology employed. It is our belief that considering the large number of Apulian Hellenistic vases housed in some of theworld's most important museums, a deep knowledge of the technolo- gical aspects involved in the production of this pottery will be of great interest to many.

2. Material and methods

2.1. Samples

Eighteen Hellenistic ceramic finds, representative of the different ceramic classes, were selected -Apulian red figured (n = 8), band de- corated (n = 3), Gnathia (n = 1), unpainted (n = 2) and unfired pot- tery (n = 4) (painted in black with overpainting in red, white and yellow)-. The pots selected for the analysis are displayed in Table 1a. Some examples representative of the ware analyzed are illustrated in Fig. 1. Geological clay samples were collected from major river valleys throughout the Tavoliere delle Puglie (Fig. 2, Table 1b).

2.2. Techniques

To obtain the chemical composition of both ceramic pastes and clays, about 40 mg of ceramic body from hidden areas of the vases -inside or underneath them- were sampled. The experimental procedure was fine-tuned with the aim of preserving the archaeological findings without any damage. The powders were mixed, homogenized and subjected to dissolution through acid attack (mixture of 37% HCl, 70% HNO_3 and 40% HF 1:4:5 (v/v/v) ratio (Fluka trace selected for trace analysis reagents), using a controlled microwave technique (Milestone Start D (FKV) microwave oven)) (Mangone et al., 2009a). The obtained solutions were analyzed by Inductively Coupled Plasma Mass Spectro- scopy (ICP-MS Nexion 300 Perkin Elmer). The entire analytical proce- dure was tested on standard clay material -"Brick clay" standard re- ference materials 679 (National Bureau of Standards)-. External calibration with matrix matching standards was employed for quanti- fication and five replicate readings were performed on both standards and samples. Indium was used as internal standard (25 ppb). ICP-MS analysis parameters are reported in Table 2.

The software package Minitab® was applied on compositional and standardized data to perform the multivariate statistical treatment.

For the intact vases, the investigation stopped with the chemical analysis of the ceramic body. For the fragmented ones, we took slivers of few millimetres from already existing fractures to perform petro- graphic analyses. For the petrographic analyses, thin sections (30 μm in thickness) were prepared after the inclusion of samples in epoxy resin (Mangone et al., 2009b). The polarized light observations were con- ducted with the optical microscope Axioscop 40 - Carl Zeiss. The same thin sections, covered with a 30 nm graphite layer, were subjected to Scanning Electron Microscopy observations (SEM-EDS) (microscope EVO-50XVP LEO). Microanalyses were achieved with an X-max(80 mm^2) Silicon drift Oxford detector supplied with a Super Atmo- sphere Thin Window©: the analyzed area was 200 μm × 150 μm. Powder X-ray diffraction analyses of both ceramic pastes and clays were carried out with a Philips X'Pert Pro X-Ray diffractometer, employing as working conditions: CuKα Ni filtered radiation, 40 kV and 40 mA of power supply, divergence slit 1°, anti-scatter slit 0.5°, receiving slit 0.2 mm, scan speed of 0.5° (2θ) per minute. A semiquantitative eva- luation of the mineralogical composition of clays (within the < 2 mm fraction) was obtained by applying the analytical methods of Schultz (1964) and Shaw et al. (1971), modified by Laviano (1987).

3. Results

3.1. Ceramic bodies: chemical and mineralogical composition

a) Hellenistic ceramic

The chemical compositional data of the analyzed finds' ceramic bodies are reported in Table 3a.

From an analysis of the data in Table 2a, a large compositional si- milarity between samples Ar8a and Ar8b, Ar 50a and Ar50b is evident. These are the pot and lid of a little olla and kylix respectively, therefore surely made using the same raw materials, but however subjected to a slightly different manufacturing process. This suggests that objects made with the same raw materials, even if subject to a different man- ufacturing process, maintain a compositional chemical similarity.

The compositional data were subjected to multivariate statistical treatment, using principal component and cluster analysis. The aim was to collect knowledge concerning provenance (Giannossa et al., 2017b; Giannotta et al., 2006), manufacturing process (Eramo et al., 2014; Mangone et al., 2009c, 2013; Bitetto et al., 2016) and archaeological class (Mangone et al., 2009a) by grouping together objects depending on their chemical composition.

The diagram of the scores and the loading of the ceramic bodies of the finds analyzed in the sub space of the first three principal compo- nents (PCs) is shown in Fig. 3.

Two distinct groups -A and B- can be recognized. In particular, the scores of cluster A samples, grouping together all the red figure samples

Fig. 1. Representative examples of the finds examined. a) red figure lebes Ar3, b) red figure olpe Ar23, c) Gnathia skyphos Ar24, d) unpainted olla Ar18, e) band-decorated olpe Ar57, f) band-decorated krater Ar33. (photo SABAP FG).

with the exception of Ar23-, are spread along positive PC1 values, principally due to the loading relative to the Ca parameter. However, the scores of samples belonging to cluster B, grouping all the other ceramic classes samples, along with the red figure sample Ar23, are spread along negative PC1 values.

Diversities among samples from the two clusters can be recognized also in type, amount and size of minerals in their paste.

The ceramic bodies of the cluster A samples, made using calcareous clayey raw materials, are very similar both in mineralogical composition and sintering degree (Fig. 4, Table 4). Predominant clusts are quartz, feldspars, micas -biotite and muscovites-, plagioclases, iron oxides and hydroxides, rutile, ilmenite, less frequent calcium phosphate crystals, zircons and garnets, as well as newly formed pyroxenes and gehlenite, developed during firing. The grain-size varies, in a narrow range, from very fine (4–16 μm) to medium-coarse silt (16–62 μm) (Shepard, 1954). Micas, clay mineral sand pores are iso-oriented and parallel to the vase walls. The sintering degree is very high.

On the contrary, the cluster B samples are very different in mineralogical composition (Fig. 4, Table 4). In addition to quartz, K-feldspars, hydroxyapatite, calcite, micas and plagioclases, which are common to all samples, we find also Ca rich micas in sample Ar33, well-rounded limestone in sample Ar57 and Mg-calcite and albite in sample Ar18. As regards sample Ar18, the massive presence of phyllosilicates, mainly micas (muscovite and biotite) is most unusual (Table 4). Sample Ar49's paste is very different from that of other samples in cluster B (Fig. 4). It appears to be extremely rich in quartz sand grains. Pores are large, elongated in shape and well iso-oriented. The paste structure suggests the use of raw materials coming from alluvium or eluvial deposits, characterized by the presence of "red earth", quartz and calcite, due to superficial erosion. These mineralogical-structural-grain size differences makes it a unique piece, comparable in composition and raw materials with samples coming from the area south of Bari (Mangone et al., 2009a).

The grain size of the B cluster samples varies from the fine silt of sample Ar33 to fine sand (< 250 μm) for sample Ar49 (medium silt for Ar20, very fine sand (< 125 μm) for both samples Ar57 and Ar18 (the

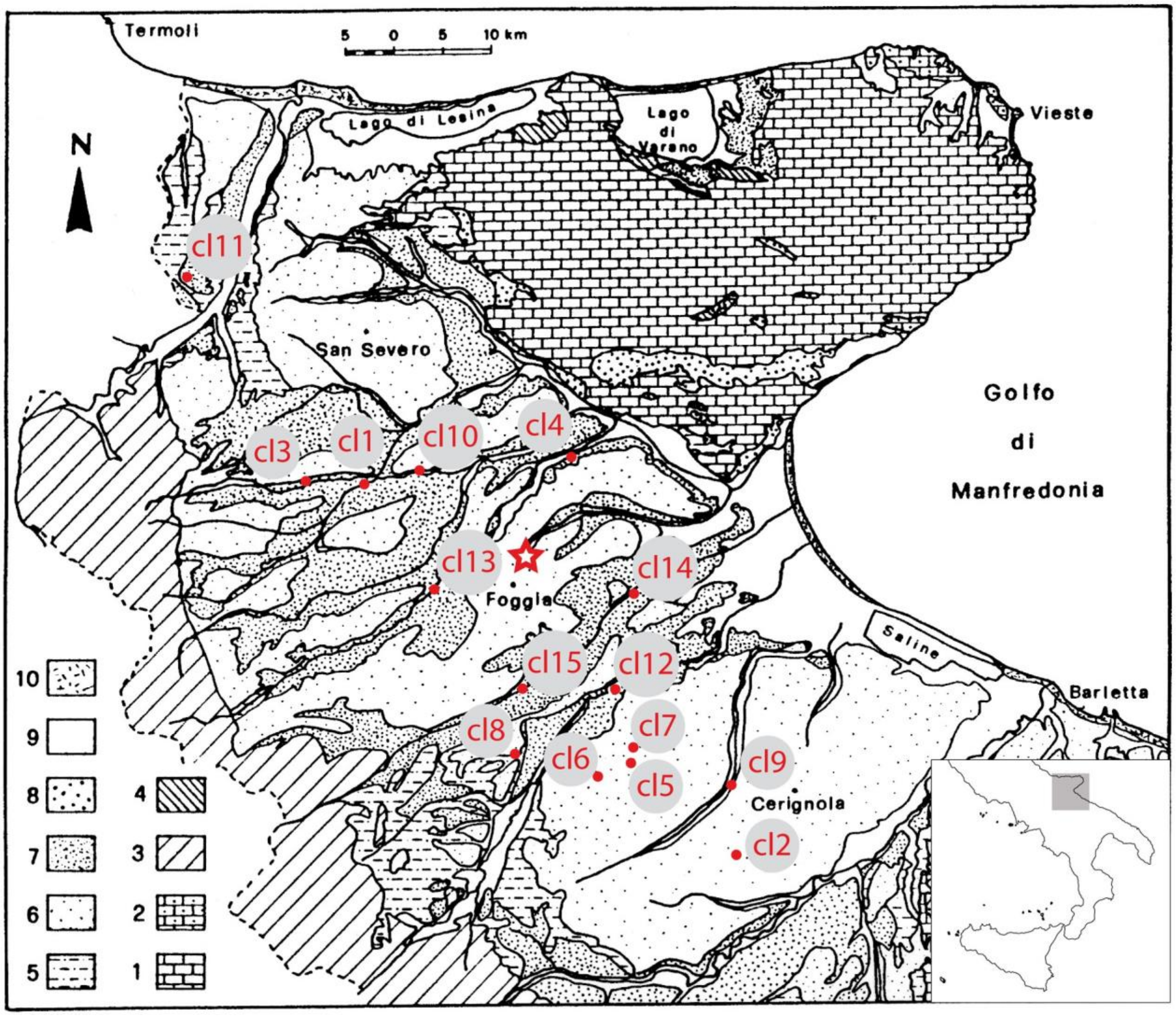

Fig. 2. Localisation of the archaeological site of Arpi (star), and of the fifteen analyzed clay samples. Legend: 1. Mesozoic bedrock; 2. Eocenic calcarenites; 3. Apenninic Chain Units (from pre-to late orogenic); 4. Miocenic calcarenites; 5. Bradano Units (Pliocene-Lower Pleistocene); 6. Terraced marine deposits (Upper- Middle Pleistocene); 7. Terraced alluvial deposits (Upper Pleistocene); 8. Talus breccias and eluvial deposits (Holocene); 9. Alluvial and lacustrine deposits (Holocene); 10. Beach and coastal dunes (Holocene).

Table 2
Typical operating conditions for ICP–MS analyses.

Nebulizer gas flow	1,2 l min^{-1}
Auxiliary gas flow	1,2 l min^{-1}
Plasma gas flow	18 l min^{-1}
ICP RF power	1600 W
Analogue stage voltage	−2000 V
Pulse stage voltage	1300 V
Discriminator threshold	12
Deflector voltage	−12 V
Quadrupole rod offset	0
Cell Entrance voltage	−5V
Cell Exit Voltage	−5V
Cell rod offset	−12
Peristaltic pump speed	−20 rpm

latter with rare clusts of fine sand (< 250 μm))). The sintering degree, very low for sample Ar18 and medium for both samples Ar49 and Ar57, is very high for both samples Ar33 and Ar20.

Even though samples Ar23 and Ar24 belong to ceramic classes which are very similar in terms of raw materials used and production technology -i.e. red figure and Gnathia pottery respectively- they are markedly different, not only in chemical but also in mineralogical composition when compared to the samples belonging to cluster A. Their pastes -with medium-coarse silt grain size- are richer in micas and less sintered. In sample Ar23's paste, it is interesting to point out the presence of Al and Al-Cu fragments; similar fragments have already been highlighted in red figure ceramic finds, presumably from Ruvo di Puglia (Fig. 5). This discovery is unique, and to our knowledge, there is nothing similar to it in other sites and in other ceramic classes.

From the XRPD data of Table 4 -where the sintering degree, according to the samples' mineralogical features is also reported- interesting manufacturing information can be obtained, deducing the equivalent firing temperatures (EFT) (Tite, 1995; Maggetti, 1982; Maggetti et al., 2011; Maritan et al., 2006). The EFT is 550 °C forsample Ar18, in the range between 900 and 1000 °C for samples Ar20, Ar33 and Ar57 and between 950 and 1050 °C for samples Ar3, Ar9 and Ar50.

As far as both samples Ar49 and Ar57 are concerned, the sintering degree of the paste is not very clear due to the lower presence of the clay fraction (< 4 μm) compared to the other samples.

The presence of micas not completely destroyed in sample Ar3, despite the extremely high EFT value, is surely due to the greater size of the crystals present in the samples's paste (often over 50 μm) when compared to the other samples of the same cluster, so that longer times for the complete destruction of micas would have been required.

Table 3
Chemical composition of the samples analyzed: Hellenistic pottery (a), unfired pottery (b) and clay (c).

a

Sample	(w/w %)						(μg g⁻¹)		
	Al	Fe	K	Mg	Ca	Ti	Ni	Sr	Mn
Ar2	10.00	4.82	3.41	1.38	11.03	0.37	70	71	1183
Ar3	8.18	4.42	3.47	1.69	11.84	0.49	73	101	1089
Ar9	10.75	4.93	2.90	1.47	9.52	0.42	31	85	807
Ar23	8.82	3.92	2.85	1.33	14.20	0.39	15	57	658
Ar8A	10.07	5.17	2.64	1.44	6.51	0.39	49	139	774
Ar8B	9.84	4.93	2.80	1.27	4.95	0.41	52	141	763
Ar50A	9.56	4.87	2.88	1.25	5.36	0.34	52	131	873
Ar50B	9.62	4.65	2.87	1.35	6.15	0.25	53	134	881
Arpi18	7.86	4.51	2.53	1.12	7.52	0.25	36	98	581
Ar33	9.09	4.05	2.41	1.24	10.03	0.24	38	137	700
Ar49	7.28	3.25	2.25	1.02	8.58	0.26	33	66	876
Ar57	7.24	3.54	2.57	1.07	13.29	0.47	41	110	658
Ar20	9.38	3.98	2.68	1.31	11.76	0.37	21	59	748
Ar24	9.01	3.79	2.82	1.27	13.27	0.45	16	59	644

b

Sample	(w/w %)						(μg g⁻¹)		
	Al	Fe	K	Mg	Ca	Ti	Ni	Sr	Mn
Ar34	6.12	2.97	1.87	1.15	16.59	0.25	34	86	618
Ar37	6.24	3.09	2.18	1.21	18.25	0.24	35	88	619
Ar61	6.18	3.04	2.28	1.22	17.97	0.26	31	83	583
ArS N	5.99	2.94	1.91	1.23	16.42	0.23	33	84	561

c

Sample	(w/w %)						(μg g⁻¹)			
	Al	Fe	K	Mg	Ca	Ti	Ni	Sr	Cr	Mn
cl1	5,91	2,85	3,40	0,95	10,97	0,32	36	372	72	994
cl2	6,78	2,83	4,87	0,80	7,22	0,28	20	246	42	995
cl3	3,73	1,71	2,39	0,88	22,85	0,18	17	333	39	495
cl4	5,40	2,22	3,94	0,92	9,65	0,24	28	291	60	601
cl5	7,90	2,98	5,39	0,93	2,13	0,33	20	280	46	1032
cl6	7,15	2,57	4,69	0,86	4,35	0,33	25	117	76	486
cl7	8,43	3,26	5,84	1,01	2,86	0,34	23	272	51	1142
cl8	6,37	2,77	4,91	0,86	6,67	0,28	23	321	63	852
cl9	6,95	3,15	4,53	0,84	6,01	0,30	22	277	52	948
cl10	5,39	2,66	3,17	0,90	11,54	0,29	29	363	67	777
cl11	7,07	2,94	4,98	0,83	4,87	0,30	28	277	58	1070
cl12	8,20	4,07	3,76	1,09	8,04	0,41	40	307	61	1211
cl13	4,85	2,50	2,86	0,83	15,06	0,25	29	545	52	935
cl14	5,33	2,67	2,64	0,91	15,24	0,27	27	613	68	518
cl15	5,37	2,95	3,02	0,77	15,48	0,27	35	634	154	1261

b) Unfired pottery

The study of unfired vases is extremely important from a scientific point of view, because it provides the most evident way to closely correlate the material with which the vases were made with the raw material used, since these are not modified by manufacturing processes.

Several matters have to be considered to locate clayey raw materials in the case of ceramic finds: the manufacturing process, the probable merging of different clays, the deliberate adding of tempers (sand, plant fibers, broken pottery, etc.), the unavoidable minero-petrographic alteration of the final paste at the end of the entire production process (forming, firing, painting, glazing, etc.). The chemical compositional data of the pastes in the unfired vases are reported in Table 3b, their mineralogical composition in Table 4.

As can be inferred from Table 4, the vases are made of marly clay, rich in fossils and large clusts of calcite, dolomite, quartz, alkali feldspars, micas (biotites and muscovite), albite, plagioclase and hydroxyapatite (Fig. 6, Table 4).

Some of these minerals are not present in Table 4 as they are highlighted through SEM-EDS.

These are accessory minerals, which can be usually used as markers of clayey sedimentary basins. They are present in small quantities and so their presence does not influence the average chemical composition of the ceramic body. However, the presence of a certain mineral makes it possible to identify a specific sedimentary deposit or exclude that this deposit was used.

The perfect recognizability (well-defined XRD spectrum by their diffraction peaks) of the individual clay minerals, as well as the absence of neoformed phases and sintering, confirms the archaeological hypothesis that they were not fired - firing even at low temperatures would have at least caused the collapse or transformation of some of the identified clay minerals (i.e. smectite and kaolinite)-.

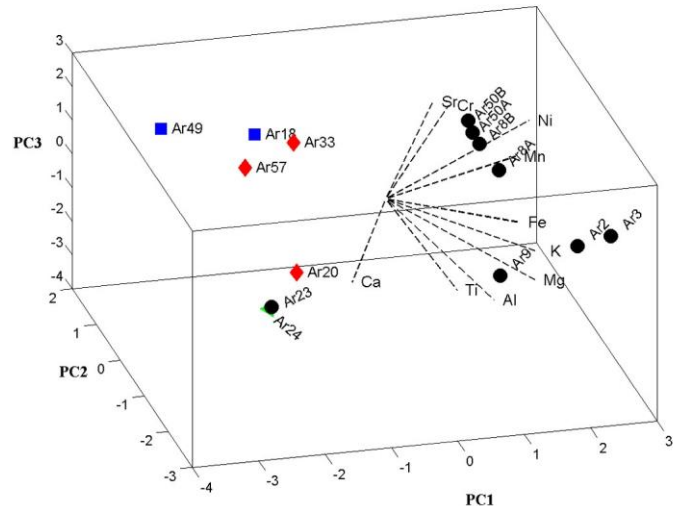

Fig. 3. Scores and loadings diagram for the first three principal components of the ceramic bodies of the analyzed samples. The accounted variance is 83% of the total variance (red figure unpainted band decorated Gnathia pot- tery). Unfired samples -Ar34, Ar37, Ar61 and ArSN- were not included.

c) Geological clays

To distinguish possible sources of ancient raw materials and assign individual finds to their geological origins, the chemical data relative to geological clay samples collected from major river valleys throughout the Tavoliere delle Puglie (Table 3c) were analyzed. The chemical data relative to geological clays and unfired pots (Table 3b) were compared.

In Fig. 7, the dendrogram obtained through HCA analysis of the chemical data of clays and unfired pottery samples is shown. It highlights that the unfired pottery items are more similar in composition to clays collected in the area closest to the Arpi necropolis -i.e. Candelaro complex (cl1, cl4, cl10, cl13)- than to other clays. A close link between unfired samples and Candelaro complex clay can also be recognized in the mineralogical composition (Tables 4 and 5). Both the phyllosilicate components (Clay Material C.M.), (illite and muscovite), and the non-phyllosilicate components (calcite and feldspars) -the latter in both the alkaline and plagioclase components-, and mostly quartz, are present in the same quantities in the two groups of samples.

Both the phyllosilicate (C.M.), specifically illite and muscovite, and non-phyllosilicate component, calcite and feldspars -both in the alka- line and plagioclase components-, and even more quartz, indeed, are comparable in amount in the two groups of samples.

The fact that clay 3 is very different to the other clays, highlighted in Fig. 7, is due primarily to the abundance of calcite (Table 5), therefore classifying it as marl, and as such an unsuitable material for

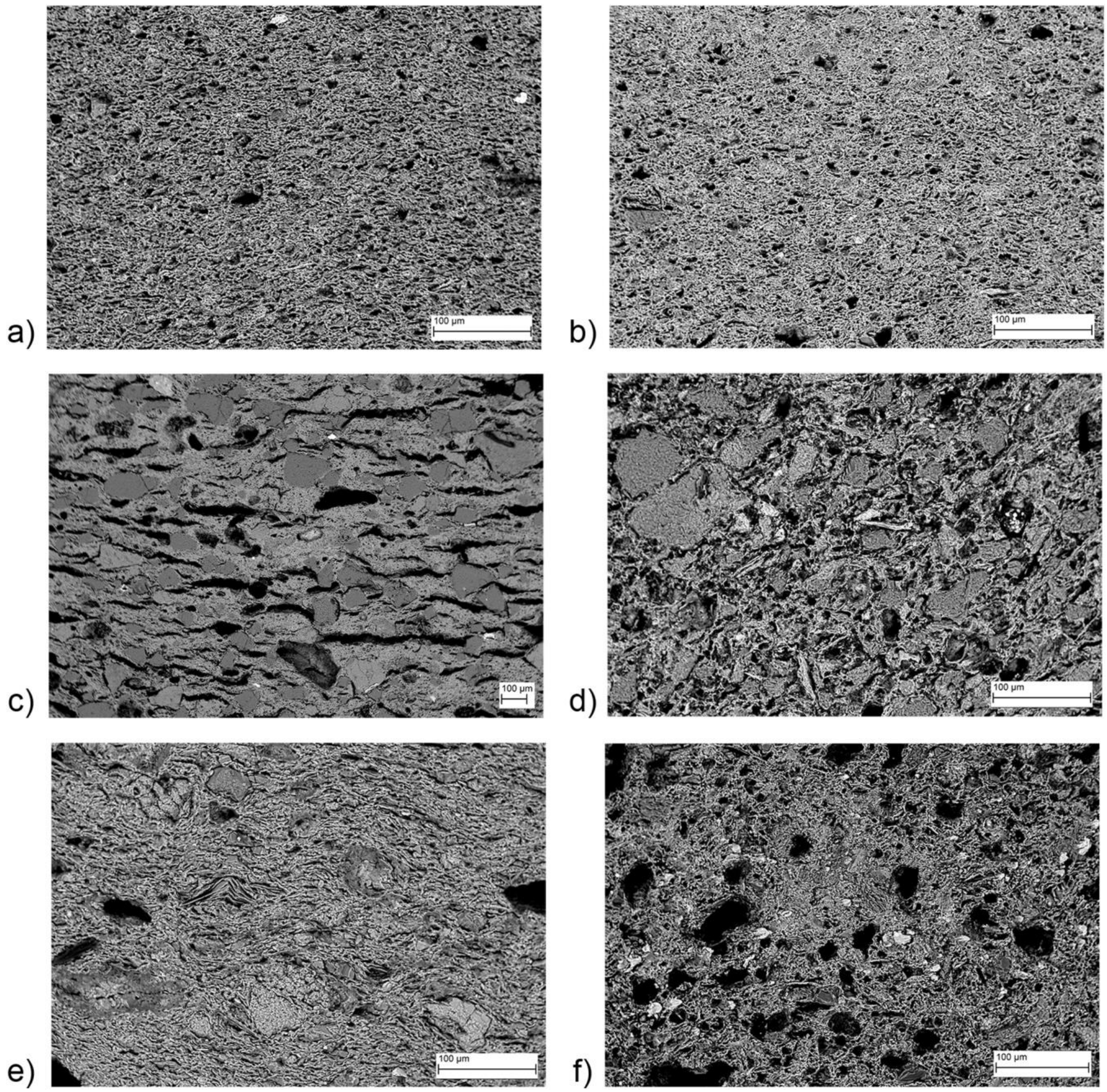

Fig. 4. SEM-BSE photomicrographs highlighting the different texture of the ceramic body of vases belonging to cluster A and B respectively. [a) Ar9, b) Ar33, c) Ar49, d) Ar57, e) Ar18, f) Ar23].

the manufacturing of pottery. All the other materials, with the exception of samples cl5 and cl7 which are clays s.s., are classifiable as marly clays.

3.2. Coatings: chemical and mineralogical composition

a) Hellenistic ceramic
   1 Black

In the black surface areas, a compact and highly vitrified layer -on average 20 μm thick-, was highlighted. Its composition, particularly regarding the Al, Fe, K and Ca contents, is different for both red figure and Gnathia samples when compared to band-decorated ones. For the former, both structural and compositional characteristics are very similar to those of all the samples of the same ceramic classes found in Apulia and so far analyzed (Mangone et al., 2008, 2009b, 2013; Giannossa et al., 2016, 2017a, 2017b).

For band-decorated vases, some areas of the gloss appear red. For these, SEM analysis showed a lower degree of sintering and a greater amount of Al, Fe, Ca and a lower amount of K and Si than in the black areas. An inadequate addition of flux and/or a poor mixing of raw materials, aggravated -in the case of samples Ar49 and Ar57- by lower firing temperatures or shorter firing times could have been the cause of the reoxidation of the gloss.

2 White

For all the analyzed samples, the white overpaintings were realized with a raw material based on kaolinite mixed with low-melting matters, such as feldspars. The same raw material was found on all the vases of the same period coming from Apulia with white overpaintings, so far as analyzed (Giannossa et al., 2009; De Benedetto et al., 2011).

Table 4
Semi-quantitative mineral content by XRPD of representative samples and estimated maximum firing temperature (EFT).

	Ms + Bt	Qtz	Cal	Kfs	Pl	Px	Gh	Hem	EFT (°C)	Sintering
Ar3	X	XXXXX	XXX	XXX	XX	XXX	tr	tr	950–1050	H
Ar9	tr	XXXXX	tr	XXX	X	XX	/	X	950–1050	H
Ar50	tr	XXXXX	tr	XXX	XX	XX	/	tr	950–1050	H
Ar20	X	XXXXX	XX	XXX	X	XX	XX	X	900–1000	H
Ar33	X	XXXXX	X	XXX	XX	XX	XX	tr	900–1000	H
Ar18	XXX	XXXX	XX	X	tr	/	/	/	550	VL
Ar 23	/	XXXXX	XX	XXX	X	XX	XX	tr	900–1000	H
Ar 24	tr	XXXXX	XX	XXX	X	XX	XXX	tr	900–1000	H
Ar 49	/	XXXXX	X	XXX	tr	X	tr	tr	800–900	M
Ar 57	X	XXXXX	XX	XXX	X	tr	X	tr	900–1000	M

Sample	Sm	Ill + Ms	Kln	Chl	C.M.	Qtz	Cal	Pl	Kfs
Ar SN	2	23	8	8	41	18	22	4	15
Ar 34	2	18	11	10	41	20	30	1	8
Ar 37	5	24	5	9	43	19	28	1	9
Ar 61	tr	24	13	11	48	18	23	2	9

Key: Sm = smectite; Ill = illite; Ms = muscovite; Bt = biotite; Kln = kaolinite; Chl = chlorite; C.M. = Clay mineral; Qtz = quartz; Cal = calcite; Pl = plagioclase; Kfs = k-feldsparPx = pyroxene (diopside), Gh = gehlenite, Hem = hematite (Kretz, 1983). EFT, equivalent firing temperature.
tr, traces; X-XXXXX, relative abundance. Sintering degrees: H, high; M, medium: VL, very low.

b) Unfired pottery
1 Black, red and yellow overpaintings

For the unfired vessels it was impossible to exploit the different ox- red states of Fe compounds in order to obtain black, red and yellow, and so it was necessary to apply different pigments in the black, red and yellow areas to obtain the desired colours.

In Table 6 the chemical composition by EDS of the different co- loured areas are reported. Results are compatible with the use of Fe- based clayey material for all the pigments, added with Mn in the black areas. The Fe based clayey material in the red and yellow areas, al- though compositionally very similar, is structurally different.

The traces of Mn evidenced in the red areas could be due to a contamination during the manufacturing process or a deliberate addi- tion of small amounts of Mn oxides to obtain a darker red colour. It is interesting to underline the presence of S in all the pigments' raw ma- terials and its absence in the relative vase's paste. Its presence could be due to pyrite, commonly present as an accessory phase in Fe-deposits.

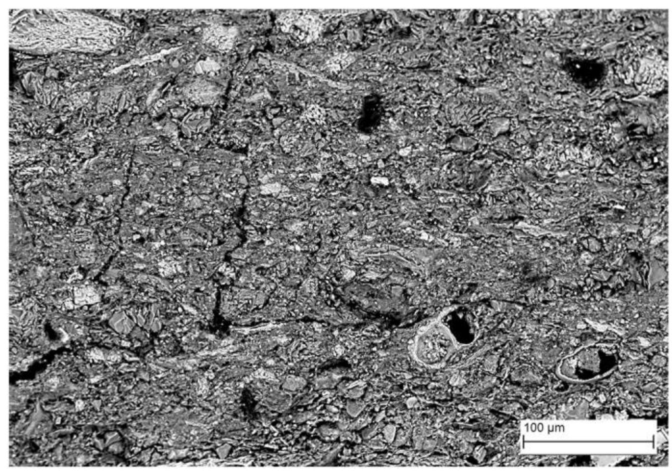

Fig. 6. SEM-BSE photomicrograph highlighting the texture of the ceramic body of Ar37 sample.

4. Conclusions

The obtained results show the use of different raw materials and production technologies for the realization of vases belonging to the different ceramic classes, but which are coeval and come from the same context.

In particular, a very accurate manufacturing process is clearly

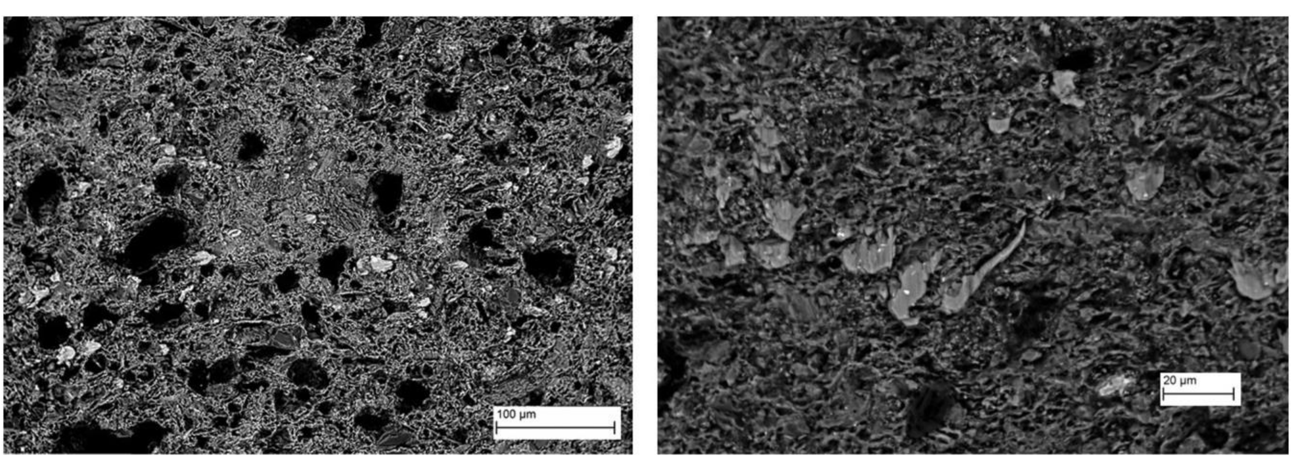

Fig. 5. SEM-BSE photomicrographs highlighting the presence of Al and Al-Cu fragments (light grey) in the pastes of Ar23 sample (left) and in the krater called “dell'Amazzonomachia” stored in the National Archaeological Museum of Naples (MANN).

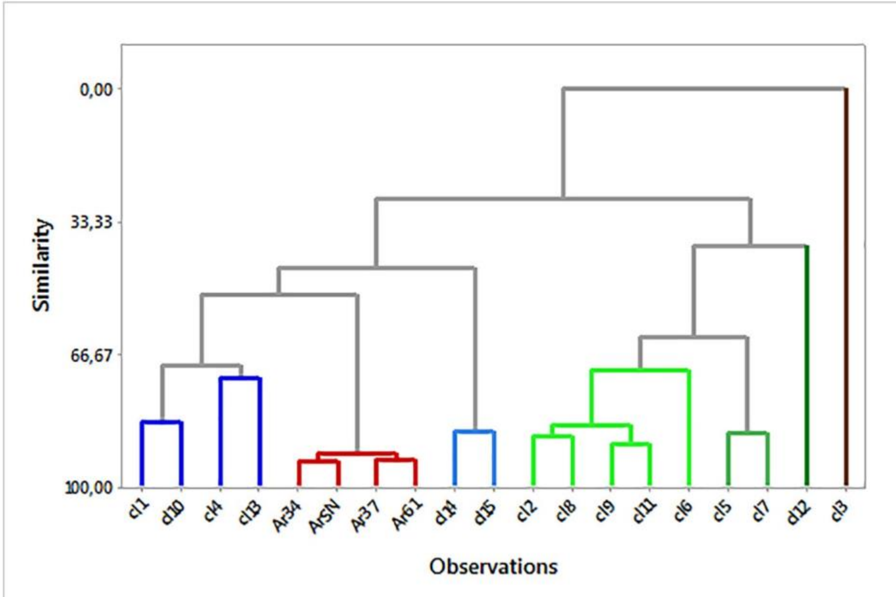

Fig. 7. Hierarchical cluster analysis dendrogram (complete linkage method, Manhattan distance, autoscaled variables) of compositional data relative to unfired pottery samples and clays collected in Tavoliere delle Puglie.

Table 5
Semi-quantitative mineral content by XRPD of clays collected throughout the Tavoliere delle Puglie.

Sample	Sm	Ill + Ms	Kln	Chl	C.M.	Qtz	Cal	Pl	Kfs
cl1	6	31	6	3	46	17	26	1	10
cl2	4	43	5	3	55	14	16	1	14
cl3	4	26	3	1	34	9	47	1	9
cl4	3	36	5	2	46	13	25	1	15
cl5	4	47	4	3	58	22	5	3	12
cl6	9	29	8	2	48	29	10	2	11
cl7	3	45	4	2	54	21	6	3	16
cl8	2	42	5	2	51	16	18	2	13
cl9	3	38	5	2	48	24	15	1	12
cl10	9	27	4	3	43	19	27	2	9
cl11	4	39	7	2	52	18	15	3	12
cl12	8	31	11	5	55	16	17	3	9
cl13	8	23	8	4	43	18	31	1	7
cl14	5	20	8	3	36	20	38	1	5
cl15	8	19	8	2	37	19	36	1	7

Key: Sm = smectite; Ill = illite; Ms = muscovite; Kln = kaolinite;Chl = chlorite; C.M. = Clay mineral Qtz = quartz; Cal = calcite; Pl = plagioclase; Kfs = k-feldspar (Kretz, 1983).

shown in the production stages of red-figure pottery: a careful selection and purification of raw materials -as suggested by the paste size grain (4–62 μm) and by the parallel orientation of micas and pores on the vase wall- a firing at high temperatures, maintained for a long time -as suggested by both the high level of sintering and the remarkable pre- sence of newly formed minerals-.

As concerns the pots of the other wares, except in the case of samples Ar20 and Ar33, the manufacturing process was less accurate -as suggested by the coarser grain size (always > 62 μm, reaching sand size for the Ar49 and Ar57 samples), by the absence of iso-orientation of micas and pores and by a firing at lower temperatures, for shorter times -as suggested by both the lower level of sintering and the presence of newly formed minerals-. A deliberately rough manufacturing process characterizes the manufacture of sample Ar18 -sand grain size, very low sintering degree and absence of newly formed minerals-.

The different levels of accuracy in the production strategy are clearly connected to the different value of the wares in question and for what purpose the pots were intended.

Regarding unfired vases, as would be expected, local clays closest to the Arpi site were used. These data confirm for the first time through the use of archaeometric data that there existed a local production of pottery in the city of Arpi. The manufacturing process was quick and inaccurate, as can be seen by the presence of a large number of fossils in their pastes, which allow us to exclude any process of clay purification. The raw materials used to paint the surfaces are based on Fe oxide with the addition of Mn for the black colour.

All the results indicate that Apulian potters operating in Magna Grecia during the 4th century BC had an excellent knowledge of pottery making, and that they made a considered selection of raw materials to be used, choosing the most suitable technological process for the pro- duction of the vase, depending on the market value, importance and what the pottery was intended for. Moreover, the potters were perfectly aware that they could use, Mn and Fe oxides for the realization of red and black on the same vase, therefore their employment of the “Attic” process was deliberate and destined to create more refined pottery such as the red figure and Gnathia pots.

Table 6
Microprobe analysis of black, yellow and red overpaintings (analyzed area: 20 μm× 15 μm).

Sample	(w/w %)								
	Na_2O	SO_3	Al_2O_3	FeO	MgO	CaO	TiO_2	SiO_2	MnO
Black	0.77 ± 0.17	1.33 ± 019	9.94 ± 0.25	30.04 ± 0.39	2.17 ± 0.18	3.05 ± 0.14	0	26.26 ± 0.28	26.44 ± 0.37
Red	0.69 ± 0.15	2.05 ± 023	14.87 ± 0.32	40.98 ± 0.6	0.58 ± 0.14	3.59 ± 0.2	0.82 ± 0.22	35.41 ± 0.51	1.01 ± 0.26
Yellow	0.62 ± 0.1	0.68 ± 0.13	12.89 ± 0.19	43.16 ± 0.37	2.32 ± 0.11	4.58 ± 0.13	0.47 ± 0.14	35.28 ± 0.32	0
Unpainted	0.9 ± 0.08	0	17.45 ± 0.2		2.88 ± 0.1	14.51 ± 0.19	0.95 ± 0.15	56.59 ± 0.36	0

Acknowledgments

The authors would like to thank Dr. C. Alexander of McDonald Institute for Archaeological Research (University of Cambridge) to provide clays samples and all information about them.

References

Bitetto, A., Mangone, A., Mininni, R.M., Giannossa, L.C., 2016. A nonlinear principal component analysis to study archaeometric data. J. Chemom. 30 (7), 405–415.
De Benedetto, G.E., Nicolì, S., Pennetta, A., Rizzo, D., Sabbatini, L., Mangone, A., 2011. An integrated spectroscopic approach to investigate pigments and engobes on pre-Roman pottery. J. Raman Spectrosc. 42, 1317–1323.
Eramo, G., Giannossa, L.C., Rocco, A., Mangone, A., Graziano, S.F., Laviano, R., 2014. Oil lamps from the catacombs of Canosa (Apulia, fourth to siXth centuries AD): technological features and typological imitation. Archaeometry 56, 375–391.
Giannossa, L.C., Colafemmina, G., Laviano, R., Traini, A., 2009. Use of various spectroscopy techniques to investigate raw materials and define processes in the over-painting of Apulian red figured pottery (4th century BC) from southern Italy. Microchem. J. 92, 97–102.
Giannossa, L.C., Laviano, R., Mastrorocco, F., Giannelli, G., Muntoni, I.M., Mangone, A., 2016. A pottery jigsaw puzzle: distinguish true and false pieces in two Apulian red figured vases by a poli-technique action plan. Appl. Phys. A Mater. Sci. Process. 122 (2), 68–78.
Giannossa, L.C., Giacobello, F., Muntoni, I.M., Laviano, R., Caggiani, M.C., Mastrorocco, F., Lagioia, G., Mangone, A., 2017a. An analytical techniques pool to hit the target. A comprehensive examination on an Apulian red figured pottery collection. Microchem. J. 134, 354–361.
Giannossa, L.C., Mininni, R.M., Laviano, R., Mastrorocco, F., Mangone, A., Caggiani, M.C., 2017b. An archaeometric approach to gain knowledge on technology and provenance of Apulian red figured pottery from Taranto. Archaeol. Anthropol. Sci. 9 (6), 1125–1135.
Giannotta, C., Laganara, C., Laviano, R., Mangone, A., Traini, A., 2006. Medieval Islamic type pottery from Siponto (Italy): an integrated physical-chemical and mineralogical investigation. X-Ray Spectrom. 35, 338–346.
Grave, P., Robinson, E., Barbetti, M., Yu, Z., Bailey, G., Bird, R., 1997. Analysis of South Italian pottery by PIXE-PIGME. Meditarch 9 (10), 113–125.
Kretz, R., 1983. Symbols for rock-forming minerals. Am. Mineral. 68, 277–279.
Laviano, R., 1987. Analisi mineralogica quantitativa di argille mediante diffrattometria di raggi X. In: Proceedings Procedure di analisi di materiali argillosi, ENEA S. Teresa, Lerici (Sp), 1-2/Giugno/1987, Ed. ENEA-Roma, pp. 215–234.
Maggetti, M., 1982. Phase analysis and its significance for technology and origin. In: Olin, G.S., Franklin, A.D. (Eds.), Archeological Ceramics. Smithsonian Institution Press, Washington, DC, pp. 121–133.
Maggetti, M., Neururer, C., Ramseyer, D., 2011. Temperature evolution inside a pot during experimental surface(bonfire) firing. Appl. Clay Sci. 53, 500–508.
Mangone, A., Giannossa, L.C., Ciancio, A., Laviano, R., Traini, A., 2008. Technological features of Apulian Red figured pottery. J. Archaeol. Sci. 35 (6), 1533–1541.
Mangone, A., Giannossa, L.C., Laviano, R., Fioriello, C.S., Traini, A., 2009a. Late Roman lamps from Egnatia: from imports to local production. Investigations by various analytical techniques to the correct classification of archaeological finds and delineation of technological features. Microchem. J. 91, 214–221.
Mangone, A., Giannossa, L.C., Eramo, G., Laviano, R., Fioriello, C.S., Redavid, V., Traini, A., 2009b. Technological features of Gnathia pottery. X-Ray Spectrom. 38, 386–393.
Mangone, A., Giannossa, L.C., Laganara, C., Laviano, R., Traini, A., 2009c. Manufacturing expedients in medieval ceramics in Apulia. J. Cult. Herit. 10 (1), 134–143.
Mangone, A., Caggiani, M.C., Giannossa, L.C., Eramo, G., Redavid, V., Laviano, R., 2013. Diversified production of red figured pottery in Apulia (Southern Italy) in the late period. J. Cult. Herit. 14, 82–88.
Maritan, L., Nodari, L., Mazzoli, C., Milano, A., Russo, U., 2006. Influence of firing conditions on ceramic products: experimental study on clay rich in organic matter. Appl. Clay Sci. 31, 1–15.
Mazzei, M., 2010. I Dauni. Archeologia dal IX al V secolo a. C. Claudio Grenzi, Foggia.
Mazzei, M., 2015. I Dauni. Archeologia dal IV al I secolo a. C. Claudio Grenzi, Foggia.
Robinson, E., 2013. New PiXe-Pigme analyses for South Italian pottery. Mediterr. Archaeol. 26, 15–41.
Robinson, E., 2014a. Archaeometric analysis of Apulian and Lucanian red-figure pottery. In: Carpenter, T.H., Lynch, K.M., Robinson, E.G.D. (Eds.), The Italic People of Ancient Apulia: New Evidence From Pottery for Workshops, Markets and Customs. Cambridge University Press, New York, pp. 243–264.
Robinson, E., 2014b. The early phases of Apulian red figure. In: Schierup, S., Sabetai, V. (Eds.), The Regional Production of Red-figure Pottery: Greece, Magna Graecia and Etruria. Aarhus University Press, Aarhus, pp. 217–233.
Schultz, L.G., 1964. Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. In: U. S. Geol. Sur. Prof. Pap. 391-C, pp. 1–31.
Shaw, D.B., Stevenson, R.G., Weaver, C.E., Bradley, W.F., 1971. Interpretation of X-ray diffraction data. In: Carver, R.E. (Ed.), Procedures in Sedimentary Petrology. Wiley, New York, pp. 554–557.
Shepard, F.P., 1954. Nomenclature based on sand-silt-clay ratios. J. Sediment. Res. 24 (3), 151–158.
Thorn, J., Glascock, M., 2010. New evidence for Apulian red-figure production centres. Archaeometry 52, 777–795.
Tite, M.S., 1995. Firing temperature determinations how and why? Kungliga Vitterhets Historie Och Antikvitets Akademien Konferenser 34, 37–42.