Microchemical Journal 134 (2017) 354–361

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

An analytical techniques pool to hit the target. A comprehensive examination on an Apulian red figured pottery collection

Lorena Carla Giannossa [a,1], Federica Giacobello [b], Italo Maria Muntoni [c], Rocco Laviano [d,1], Maria Cristina Caggiani [e], Fabrizio Mastrorocco [e], Giovanni Lagioia [a], Annarosa Mangone [e,*,1]

[a] Dipartimento di Economia, Management e Diritto dell'Impresa, Università Aldo Moro, Largo Abbazia Santa Scolastica 53, 70124 Bari, Italy
[b] Dipartimento dei Beni Culturali ed Ambientali, Università degli Studi di Milano, via Festa del perdono 7, 20121 Milano, Italy
[c] Soprintendenza per i Beni Archeologici della Puglia, via De Nittis 7, 71100 Foggia, Italy
[d] Dipartimento di Scienze della Terra e Geoambientali, Università Aldo Moro, via Orabona 4, 70126 Bari, Italy
[e] Dipartimento di Chimica, Università Aldo Moro, via Orabona 4, 70126 Bari, Italy

A R T I C L E I N F O

Article history:
Received 8 April 2017
Received in revised form 29 June 2017
Accepted 1 July 2017
Available online 8 July 2017

1. Introduction

The 19th century vases collections are an essential resource for the study and documentation of Apulian red-figured pottery: even though they cannot provide data concerning the stratigraphy and the excavations, they still constitute a primary source of knowledge. An important example is the pottery collection of Intesa Sanpaolo, kept at Gallerie d'Italia Leoni Montanari, Vicenza (Italy). It is a historic collection assembled at Ruvo di Puglia (Bari, Italy) by the archdeacon Giuseppe Caputi between 1830s and 1860s. It contains a relevant number of specimens of Apulian production, in excellent conservation conditions and all coming from the same finding area (Arena, Ruvo di Puglia).

These artworks, although entirely out of their original context of origin (however, allegedly, coming from the 6th–3rd century BC necropolis of ancient Central Peucetia), constitute an exceptional complex. This singularity arises from historical and documentary values - since the collection itself essentially came down to us intact-and also from artistic and archaeological ones [1]. It is well known that in ancient times - especially during the 5th and 4th centuries BC - Ruvo di Puglia was an important, deeply Hellenised Peucetian centre: figured and non-figured vases, emblems of social distinction and success, were used in the funeral rites and put among the grave goods accompanying the dead in the afterlife. The quantity of vases found in Ruvo brought about the hypothesis of its central role in pottery reception, request and production. In the earliest phase the Greek colonies Taranto and Metaponto produced the vases in their own workshops in continuity with the Attic Greek tradition, whereas for the last 40 years of the 4th century BC, a shift of production towards central (Peucetia) and northern (Daunia) Apulia has been hypothesized.

The specific archaeological aim of the analyses conducted on Intesa Sanpaolo collection is to investigate the pottery workshops that produced this class of vases, which traditionally were assigned to specific painters following only stylistic features, and to contribute to the identification of production areas. The attribution of the vases to the Apulian painters is assigned by the archaeologists according to stylistic criteria: the rendering of bodies, garments, objects, and other figurative details are characteristic of each painter. According to the chronology of the excavation evidence and the painting features changes in time, it is possible to establish a dating of painters and of their workshops.

The specific archaeometric goal is to prove that the combination of analytical techniques, besides the integration of archaeometric and archaeological results, constitute the optimal methodology for the study of archaeological heritage. In fact, the synergic approach allows to take advantage of each technique benefits and to overcome drawbacks and limits linked to the objective impossibility of an adequate sampling of the archaeological find, due to its preciousness and uniqueness. Only this combined approach allows to obtain a complete characterization of the find, including both compositional and structural information concerning bulk and surface, needed to answer archaeological

* Corresponding author.
E-mail address: annarosa.mangone@uniba.it (A. Mangone).
[1] Centro Interdipartimentale Laboratorio di Ricerca per la Diagnostica dei Beni Culturali, via Orabona 4, 70126 Bari.

http://dx.doi.org/10.1016/j.microc.2017.07.002
0026-265X/

questions, as production technology or provenance of raw materials. Also, differences and similarities between objects, emerging from such results, can help to discriminate specific workshops or artists. The same methodology would allow to recognize non-authentic parts linked to not recorded 19th century mimetic restorations. These specific aims are part of a comprehensive project exploring the technical and manufacturing features of Apulian red figure pottery, deeply studied from a stylistic-typological point of view thanks to its predominant role in Magna Graecia during the 5th and 4th centuries BC. Nevertheless, this class, up to now, has not been much subjected to archaeometric investigations mainly for two reasons: academics supported Trendall approach [2–4] on the footsteps of Beazley [5] expertise application to Attic figured pottery and this production technology did not cause instantly curiosity because it was automatically assumed to be the same as the Attic one.

The archaeometric investigations carried out up to now on this ceramic class mainly concerned pottery coming from private collections and few works relative to vases coming from archaeological sites. The entirety of available archaeometric data [6–18] is not at all sufficient to give a thorough idea of the technology employed of such a problematic and diversified ceramic class and to compare it with the Attic production. As concerns Ruvo di Puglia, despite the conspicuous number of vases excavated from the digs, only four (to the best of authors knowledge) were analyzed [6,10].

Furthermore, as regards the material brought to light during the 19th century, it is known that the most important pottery was restored following an “antiquarian type” of restoration, i.e. reconstruction and repainting, according to the mimetic taste of the time.

In this perspective, archaeometric investigations can also provide detailed directions on the 19th century restoration techniques, as previously occurred for figured vases of the National Archaeological Museum of Naples [10].

We believe that a deep knowledge of this class, not only from stylistic but also from technological and productive points of view, does not imply a mere local merit, considering that a high number of Apulian red figured vases, almost always lacking appropriate context data, is kept in the most important museums in the world.

2. Experimental

2.1. Samples

Red figured vases, covering the whole Apulian period, from Ancient to Late, were selected for this study (Table 1, Fig. 1). Two figured vases, among the oldest ones - referring to Ancient Apulian period -, were considered: a bell-shaped krater attributed to the Painter of Lecce 686 (V23) and a Panathenaic amphora attributed to the Painter of Karlsruhe B9 (V9), both linked to the numerous group of painters who follow style and manner of the Painter of Tarporley, traditionally in workshops inside the polis of Taranto. As regards the Middle Apulian Period [1], the Painter of Felton, present in Taranto around 370 BCE, represents an exponent of it and the pelike (V21) here analyzed is attributed to his group. A copious group of the studied figured vases is attributable to the Licurgo Painter [19], well documented in Northern Apulia, especially in Ruvo. It includes: four kraters, all representing mythological scenes (V10, V17, V18, V12) and a pelike with bridal scene (V15), while a hydria (V22) was attributable to the group of Ilioupersis and Licurgo Painters [19]. A second group of figured vases refers to the group of Varrese Painter, in whose group the Painter of *Nasi Camusi* also worked (his production could be moved closer to Peucetian centres): a Panathenaic amphora (V8) is attributable to the Painter of Ruvo 407/408, while two kraters with small columns (V11, V13) are attributed to the group of the Painter of Nasi Camusi and Varrese Painter; finally, a krater with funerary scenes (V16), attributable to the group of Painters of Gioia del Colle and Copenhagen 4223, and belonging to the end of Middle Apulian, was analyzed.

Concerning the productions traditionally allocated in the last 30 years of the 4th century BC and referable to the Late Apulian Period [1], we have analyzed two hydria (V14, V19). Both items present a funereal subject, with strong iconographic and stylistic affinities and attribution to the Workshop of Darius and the Underworld Painters by Lamburgo [20]. However, here it is considered (Table 1) a slightly older chronologically attribution: the Workshop of the Painter of Gioia del Colle. We also analyzed a volute krater (V7) and an oinochoe (V20-) attributed to the other relevant workshop that ruled the market

Table 1
List of the samples analyzed.

Code	Inventory number	Sampled area	Shape	Painter	Date (BC)	Cluster
V1	172	Powder from the foot	Amphora	Patera Painter	340–320	A
V2	123	Powder from the foot	Amphora	Patera Painter workshop	340–320	A
V3	179	Powder from the inside of the body	Crater	Trieste Civetta Group	330	A
V4	174	Powder from the foot	Long neckoinochoe	Patera Painter	340–320	A
V5	189	Splinter from the swan Powder from the foot	Crater	Patera Painter workshop	340–320	A
V6	175	Powder from the inside of the foot	Loutrophoros	Patera Painter workshop	340–320	A
V7	215	Powder from the inside of the body	Crater	Baltimore Painter	330–310	A
V7B	215	Fragment from the inside of the foot	Crater	Baltimore Painter	330–310	
V8	116	Splinter from the swan Powder from the foot	Amphora	Ruvo Painter 407/408	350–340	A
V9	82	Splinters in an envelope within the vase	Amphora	Karlsruhe PainterB9	380–360	B
V10	108	Powder from the body	Crater	Licurgo Painter	375–360	B
V11	123	Powder from the foot	Crater	Ginosa Painter	350–340	B
V12	111	Powder from the foot	Crater	Licurgo Painter	360–350	B
V13	124	Powder from the body	Crater	Roermond Painter	350–340	B
V14	141	Powder from the basis of the foot, splinters in an envelope within the vase	Hydria	Gioia del Colle workshop	350–320	B
V15	113	Powder from the foot	Pelike	Licurgo Painter	350	B
V16	133	Powder from the inside of the body	Crater	Gioia del Colle Painter workshop	350–340	B
V17	109	Powder from the body	Crater	Licurgo Painter	375–360	B
V18	110	Powder from the foot	Crater	Licurgo Painter	360–350	B
V19	142	Powder from the foot	Hydria	Gioia del Colle workshop	350–320	B
V20	221	Handles in an envelope	Oinochoe	Baltimore Painter workshop	330–320	
V21	86	Splinters in an envelope within the vase	Pelike	Felton Painter workshop	380–360	
V22	107	Fragment from the handle	Hydria	Workshop of Ilioupersis Painter and Licurgo Painter	360–350	
V23	80	Splinter from the border	Crater	Lecce Painter 686	380–370	

Fig. 1. Representative examples of the finds examined: a) krater V18, b) krater V7, c) krater V17, d) amphora V1, e) pelike V21, belonging to Collezione Intesa Sanpaolo. Photo credit: Archivio Attività Culturali, Intesa Sanpaolo.

of Ruvo, that of Baltimore. Lastly, we investigated a conspicuous figured group of objects attributed to the Painter of Patera [19] or his workshop, which notoriously shows common characteristics with that of Baltimore and which was placed in one of the most important Northern Apulian area. This group consists of a Panathenaic amphora (V1), a trefoil oinochoe (V4), a loutrophoros (V6), a vase with small columns (V3) and a volute krater (V5).

2.2. Experimental procedure

The sampling was subordinated to the safeguard of the integrity of the objects: their cultural importance lead to the removal of about 40 μg of ceramic body from hidden areas of the vases - inside or underneath them with an experimental procedure fine-tuned with the aim of preserving the archaeological findings without any damage. The sampled powders were mixed, homogenized and subjected to dissolution through acid attack [21,22]. The obtained solutions were analyzed by means of Inductively Coupled Plasma Mass Spectroscopy (ICP-MS Nexion 300 Perkin Elmer) quantifying 20 elements (Fe, Al, Mg, K, Ti, Ca, Mn, Ni, Cr, Ce, Ba, Zn, Na, Sr, Co, Pb, V, La, Sm, Nd).

The software package Minitab® was applied on compositional and standardized data to perform the multivariate statistical treatment. Statistical models, in case of ceramic items, are usually exploit to find clusters distinguishable per provenance [8,11,21], manufacturing process [12,14,22] or archaeological class [21,24].Firstly, we determined the concentration of 20 elements, then we applied PC analysis to the matrix composed by all the elements available, achieving a 55% explained variance diagram. Nevertheless, a more efficacious result was found employing statistical criterion of selecting features. It consists, for instance, in comparing the means and the variances of the different variables (concentration of 20 elements) before the PC treatment (e.g. the elements are eliminated when the mean is quite the same in each supposed class and/or the intra-class variance is high). The subset represented by the defined variables plus Pb and Ba - reported since they can provide useful indications concerning the restoration processes on the vases - was reported in Table 2.

For the intact vases, the investigation stopped with the chemical analysis of the ceramic body. For the damaged ones, we took slivers of few millimetres from already existing fractures to perform minero-petrographic analyses. When existing, small fragments belonged to the vase at the time of the purchase by Intesa Sanpaolo, but not integrated into the following restorations - V9, V14, V20 and V21, as reported by the archive documentation - were analyzed. Two different samples were taken from the vaseV7, one from the inside of the body (V7) and one from the foot (V7B), to verify if the latter was a successive addition, as suspected by archaeologists.

For the minero-petrographic analyses, thin sections (30 μm in thickness) were prepared after the inclusion of samples in epoxyresin [23]. The polarized light observations were conducted with the optical microscope Axioscop 40 - Carl Zeiss. The same thin sections, covered

Table 2
Chemical composition of the samples analyzed.

Sample	Fe	Al	Mg	K	Na	Ti	Ca	Mn	Ni	Cr	Sr	Pb	Ba
	(% w/w)							(ppm)					
V1	3.46	6.58	0.91	1.77	0.76	0.39	8.97	538	55	151	393	23	564
V2	3.37	6.05	0.88	1.47	0.70	0.37	8.14	517	49	141	359	18	423
V3	3.34	6.91	1.02	1.69	0.65	0.37	8.83	583	46	144	439	12	477
V4	3.74	7.68	1.13	1.90	0.67	0.42	7.10	548	48	144	417	62	511
V5	3.04	6.46	0.91	1.90	0.70	0.35	6.27	512	44	119	347	47	585
V6	3.49	7.69	1.10	2.12	0.65	0.41	7.06	570	48	138	393	130	477
V7	3.31	6.88	0.98	1.79	0.71	0.41	5.45	622	52	167	361	184	334
V7B	3.29	7.65	1.06	1.84	0.75	0.40	6.56	558	46	147	356	64	269
V8	3.08	6.80	1.00	1.55	0.66	0.36	6.42	530	43	136	392	64	505
V9	3.79	8.04	1.34	1.79	0.69	0.43	6.46	999	71	186	397	37	383
V10	4.23	6.98	1.23	1.59	0.70	0.47	7.08	809	69	162	434	127	571
V11	4.05	8.07	1.37	1.86	0.71	0.46	6.04	774	63	172	382	26	449
V12	4.26	8.35	1.28	1.71	0.70	0.45	5.25	962	61	153	406	18	671
V13	3.79	7.56	1.25	1.64	0.68	0.43	5.58	913	62	164	383	45	613
V14	4.41	9.43	1.40	1.77	0.67	0.51	5.05	938	61	161	376	53	451
V15	3.83	7.81	1.25	1.80	0.68	0.45	4.89	947	65	167	339	26	340
V16	4.78	8.30	1.40	2.11	0.76	0.52	5.48	933	69	171	372	371	465
V17	4.19	7.12	1.26	1.84	0.84	0.51	5.10	959	71	181	331	153	660
V18	3.72	7.01	1.06	2.23	0.67	0.42	4.98	718	63	157	353	27	441
V19	3.64	7.84	1.22	1.75	0.66	0.43	4.87	994	59	145	343	81	405
V20	3.23	6.90	1.15	1.37	0.70	0.37	8.22	524	44	135	397	705	221
V21	2.91	6.30	1.07	1.21	0.70	0.34	7.84	477	39	120	392	221	217

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 Atmosphere Thin Window©.

Powder X-ray diffraction analysis was 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.

Raman acquisitions were performed on the surfaces and on the polished cross/thin sections of the micro-samples (after OM and before SEM observations) using Xplora (Horiba Jobin-Yvon, France) spectrometer, equipped with YAG 532 and 638 and diode 785 nm lasers, associated to an Olympus (Japan) microscope.

3. Results and discussion

3.1. Chemical analysis through ICP-MS and statistical treatment of the data

The results obtained from the chemical analyses of the ceramic bodies are listed in Table 2.

The analysis of the data highlighted, for some samples, concentrations of Pb - and sometimes also of Ba -, much higher than the average. This result is certainly linked to the 19th century restoration actions. In these cases, the integrations/restorations were performed using a leaded coating in place of the typical black gloss [10], that certainly cannot be noticed with an autoptic exam. Moreover, the strong resemblance of the chemical compositions of samples V7and V7B allows to dispel the hypothesis of non-originality of the vase foot.

The chemical results were subjected to Principal Component Analysis and Cluster Analysis [25]. Pb and Ba were excluded from the treatment; sample V7B was not considered, since itis already represented by sample V7.

The scores and loadings diagram in the sub-space of the first three PCs is shown in Fig. 2.

The observation of the figure highlights two clearly distinct clusters: A and B.

The vases V1, V2, V3, V4, V5, V6, V7 and V8 are grouped in cluster A, while V9, V10, V11, V12, V13, V14, V15, V16, V17, V18 and V19 in cluster B. Cluster A, characterized by the negative PC1, includes all the objects attributed to the Patera, Baltimore and Trieste Civetta Group painters. Cluster B, characterized by the positive PC1, includes all the objects attributed to Lycurgus, Gioia del Colle, Karlsruhe B9, Roermond and Ginosa painters. Samples V20 and V21 have negative values of PC1, but are located outside cluster A.

The loadings analysis shows that the discrimination between the clusters along PC1 must be mainly attributed to a different content in Al, Fe, Ti, Ni and Cr in the ceramic bodies of the fragments. Apart from sample V8, the distribution of the samples into the two clusters seems to reflect a chronological difference: A and B gather the vases stylistically attributed to painters working in the Late (A), and Ancient and Middle (B) period.

To confirm, also on analytical bases, the Peucetian provenance of the studied vases, the statistical treatment was extended to the ceramic bodies of previously studied Apulian pottery coming from other Apulian sites [10–15]. Samples V20 and V21 were excluded from the data matrix since, being located outside the two clusters they could represent integrations made during the 19th century restoration. The obtained result is shown in Fig. 3a.

Fig. 3a highlights the presence of three clusters (C, D and E), cluster E is in turn divided into two sub-clusters (E1 and E2). Cluster C includes all the samples from Taranto (Arsenale site) and Egnazia (Western Necropolis tombs and Punta Penna Grossa). Cluster D groups the samples coming from Arpi (ONC28 tomb, 2005 tomb and Niobids tomb). Cluster E1 gathers the samples of cluster B of Vicenza, samples coming from Monte Sannace, Altamura, Conversano, krater inv.81667-the so called 'Vaso dell'Amazzonomachia' (N8) and the loutrophoros inv.82267 (N4) (stored in the National Archaeological Museum of Naples but coming from Ruvo di Puglia). Cluster E2 includes samples of cluster A of Vicenza and samples from Canosa.

It is interesting to underline that cluster A of Vicenza gathers the samples of Baltimore painter, who is thought to have worked in a Canosa workshop [27]. The results of the chemical analysis, highlighting a strong similarity between the samples of cluster A of Vicenza and those from Canosa, led to a research of analytical data concerning Canosan clay. To this purpose, the compositional data of Table 2 - relative to the Apulian red figured pottery samples of Peucetian and Canosan area - were processed by PC analysis together with published data relative to already analyzed [27] sub-appennine clays collected in proximity of Canosa (OF1-OF7). Also, samples V20 and V21, suspected to be 19th century integrations and previously excluded from the statistical treatment, were inserted in the data matrix to point out possible differences or similarities with the Canosan clay and to hypothesize if the integration were obtained with local raw materials.

The results of the treatment (Fig. 3b) show the formation of two clusters (F and G). Cluster F includes all the samples of the Peucetian area, samples N4, N8 and the samples of cluster B of Vicenza; cluster G gathers the samples of cluster A of Vicenza, samplesV20 and V21and the sub-appennine clays taken in the Canosan area. The slight compositional difference of the clays with respect to the red figured ceramic of cluster A could be explained due to the procedures of vases manufacturing in the workshops: refining of raw materials, firing conditions, etc.

3.2. Optical (OM), scanning electron microscopies (SEM-EDS) and powder X-ray diffraction (XRPD) analyses

3.2.1. Ceramic body

The optical and scanning electron microscopies was carried out on ceramic bodies of samples V8, V7, V5, V9, V21, V20, V22 and V14,

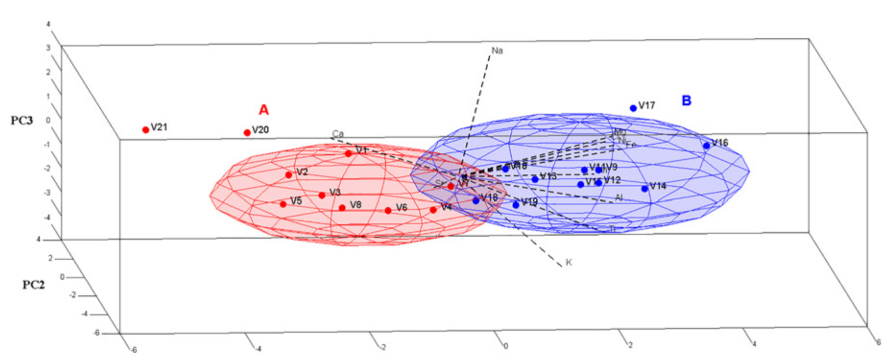

Fig. 2. Scores and loadings diagram for the first three principal components of the Apulian red figured pottery samples analyzed. The accounted variance is 83% of the total variance. 95% isoprobability ellipsoids, whose surfaces define the boundary of two clusters - A and B - are also reported.

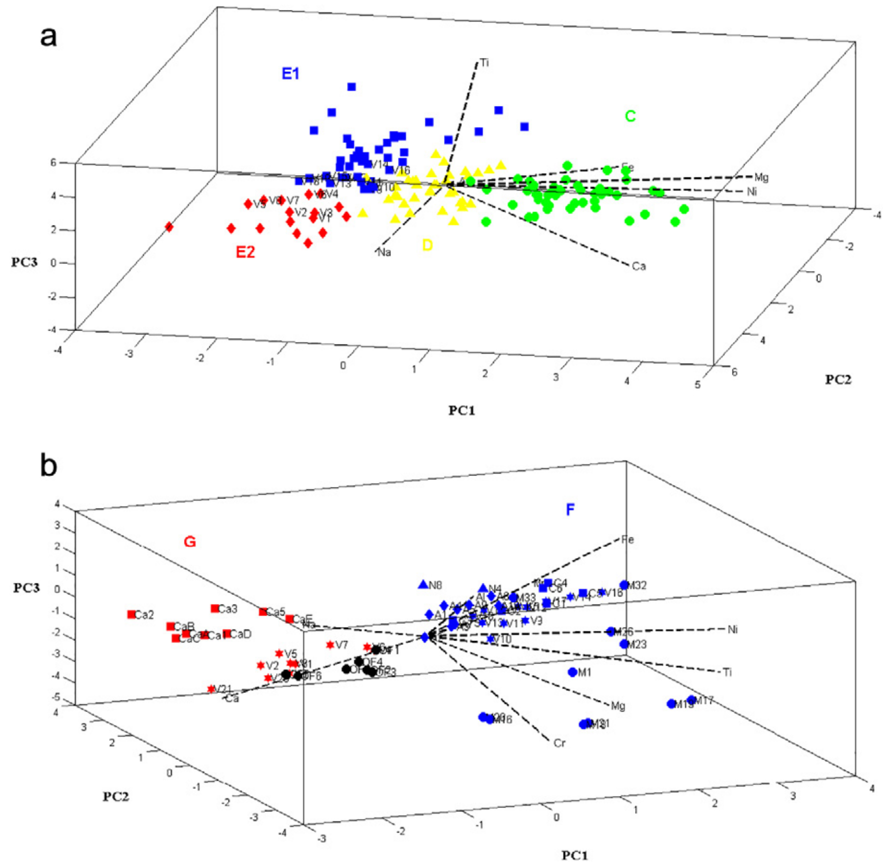

Fig. 3. Scores and loadings diagrams for the first three principal components of compositional data relative to: a) Vicenza samples and previously studied [10–15] Apulian pottery (samples from: ■ Monte Sannace (Gioia del colle), Conversano, Altamura, Ruvo (stored in MANN, Napoli) and cluster B from Vicenza; ◆ Canosa and cluster A from Vicenza, ▲ Arpi (Foggia), ● Taranto and Egnazia (Fasano)). Accounted variance is 70% of the total variance; b) samples of Peucetian and Canosan area and sub-appennine clays collected in proximity of Canosa [27]. Accounted variance is 73% of the total variance. ● Monte Sannace, ■ Conversano, ◆ Altamura, ▲ Ruvo (stored in MANN, Napoli), ★ Vicenza (cluster B), ■ Canosa, ★ Vicenza (cluster A), ● clay from Canosa.

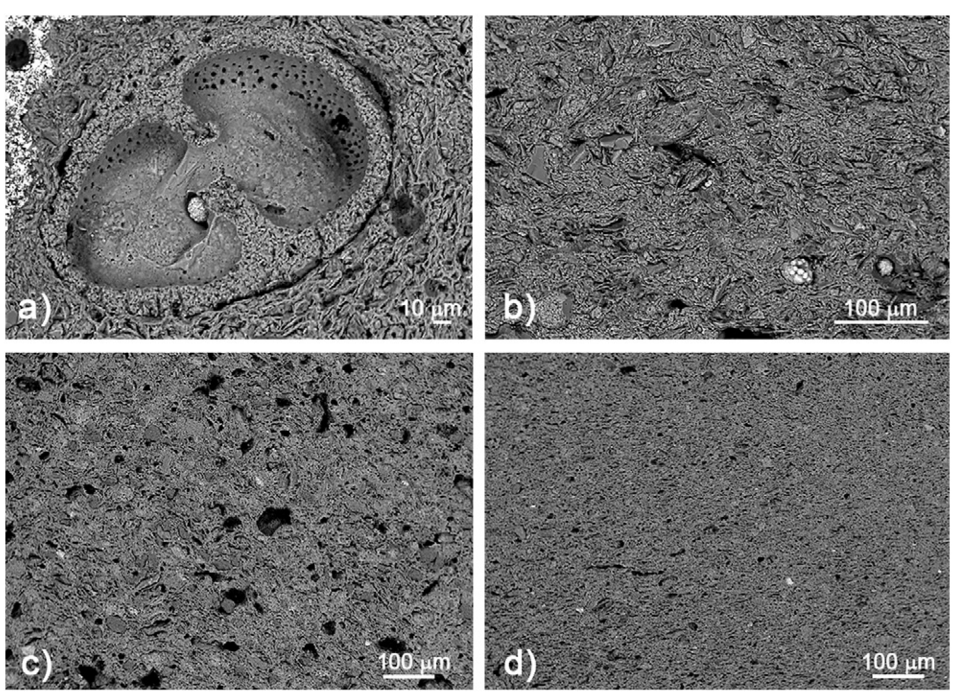

Fig. 4. SEM-BSD photomicrographs of a carbonatic fossil shell in V20 (a) and of V21 (b), V5 (c), V14 (d) ceramic bodies.

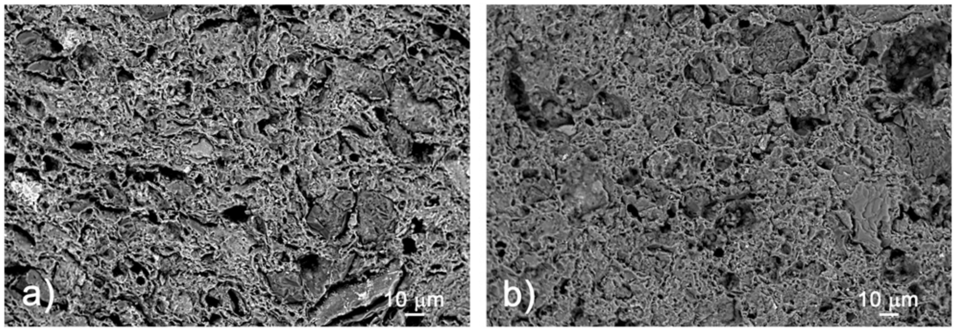

Fig. 5. SEM-BSD photomicrographs of V8 (a) and V17 (b) ceramic bodies.

bringing light on the peculiar features of the fragments belonging to the different clusters. First, the results of the minero-petrographic investigations allow to confirm the hints deriving from the chemical analyses for the samples V9, V14, V20 and V21 and to state that V9 and V14 are original, while V20 and V21 are not.

For both the latter samples, apart quartz, micas (mostly biotite), alkali feldspars, calcium phosphate, rutile and iron oxides, also big calcareous clasts, calcite and fossils are present in the ceramic body (Fig. 4a, b). The clay minerals are rich in Ca and the sintering level is extremely low (index of a low firing temperature and/or of a not sufficiently long firing duration).

3.2.1.1. Fragments belonging to cluster A. The ceramic body is medium-coarse (32-63 μm) silt grained with clasts of mainly quartz, micas (almost exclusively muscovite), alkali feldspars, iron oxides and hydroxides (Fig. 4c). The presence of secondary calcite at the edges of the pores can be observed by OM microscopy.

3.2.1.2. Fragments belonging to cluster B. The ceramic body is finer-grained (medium-fine silt-16–32 μm) with quartz, micas, (muscovite and biotite), alkali feldspars, iron oxides and hydroxides, rutile, ilmenite, calcium phosphate, sometimes plagioclase, pyroxene, zircons and occasionally rare earths phosphates (Fig. 4d).

The total absence of coarse-grained clasts suggests a refining of the clays employed. Phyllosilicates (micas and clay minerals) and pores are iso-orientated and parallel to the vase walls.

Clay sintering results good for the ceramic bodies of both clusters samples, slightly more advanced for cluster B samples, than for cluster A ones (Fig. 5).

Samples V22 and V23 ceramic bodies could not be sampled for the chemical analyses, but micro-chunks have been taken from the border and from the handle of the two vases respectively. Depending on the composition of clastic component, which shows the same minerals found for ceramic bodies of the samples of cluster B, it is reasonable to assume that both samples belong to cluster B, despite the grain a bit coarser of sample V22 (Fig. 6), in agreement with the stylistic attribution.

Concerning the raw materials, for samples of cluster A the chemical-compositional resemblance with the clays sampled in Canosa area (OF1–OF7) is parallel to the minero-compositional resemblance [27]. The SEM and XRPD (Table 3) analyses of the clastic component of the ceramic bodies of cluster A show a perfect compatibility and overlapping with the average composition of the sub-appennine clays. These samples in fact contain the same minerals as the sub-appennine clays, while there is no trace of the fragments of volcanic minerals belonging to the co-magmatic Roman province, characteristic of the eluvial and colluvial deposits widespread in the northern murgian area [27].

Sub-appennine clays [28–30] form the top of the plio-pleistocene sedimentary sequence of the Lucanian Basin, which is a paleo-geographic unit of the Bradanic trough. They outcrop all over the basin and are found as extensive deposits in the eastern belt of the Lucanian area, in the western margin of the Murge and along the Tavoliere di Foggia, in the Apulian area.

The clays are formed by clay minerals, quartz, feldspars and carbonates. Other accessory minerals, recognized by Optical Microscopy on sand fraction (>63 μm), are: muscovite and poorly crystallized iron oxides and hydroxides. The clay minerals are a mixture of illite (Ill), smectite (Sm, montmorillonite type), chlorite (Chl), kaolinite (Kln). Illite is 2 M polytype and it has Al^{3+} as the chief octahedral cation and almost solely K^{+} as interlayer cation; the degree of crystallinity (E) varies from 190 Å to 200 Å [31,32].Smectite is Mg + Fe rich and it has chiefly Ca^{2+} as interlayer cation (montmorillonite type); its degree of crystallinity is rather high. The crystallinity of kaolinite is rather low. The carbonates consist of calcite (organic and inorganic origin) and dolomite; the feldspars are represented by orthoclase, microcline and Na plagioclase.

As concern samples belonging to cluster A and B, the range of the equivalent firing temperatures (EFT) for the samples analyzed by XRPD was estimated according to the thermal stability ranges (appearance/disappearance of given phases) determined by experimental firings of Ca-rich clays found in the recent literature [27,34,35]. The presence, in all the samples, of the neo-formed phase gehlenite and pyroxenes (in different relative amount) suggests that their ceramic

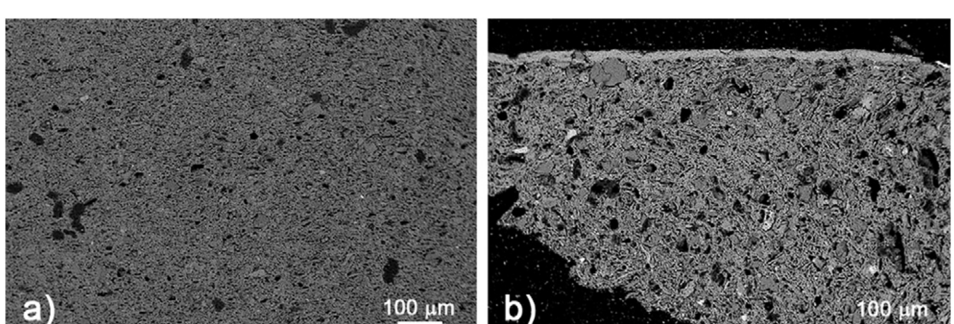

Fig. 6. SEM-BSD photomicrographs of V23 (a) and V22 (b) ceramic bodies.

Table 3
Semi-quantitative mineral content (XRPD) of the analyzed finds.

	Ms + Bt	Calcium phosphate	Qtz	Kfs	Pl	Cal	Px	Gh	Hem
V1	X		XXXXX	XX	X	XXX	XX	XX	X
V5	X		XXXXX	XX	X	XX	XX	XX	X
V8	X		XXXXX	XX	X	XX	XX	XX	X
V12			XXXXX	XXX	X		XX	TR	TR
V14		X	XXXXX	XXX	XX		XX	X	X
V15			XXXXX	XXXX	XX		XX		X
V16		X	XXXXX	XXXX	XX		XX	X	X
V18			XXXXX	XXXX	X		XX	TR	TR
V21	X		XXXXX	X	TR	XXXX			
V20	XX		XXXXX	X	TR	XXX			

Ms = muscovite; Bt = biothite; Qtz = quartz; Kfs = k-feldspar; Pl = plagioclase; Cal = calcite; Dol = dolomite Px = pyroxene; Gh = gehlenite; Hem = hematite [33].
Scale of relative abundance XXXXX very abundant, XXXX abundant, XXX good, XX present, X scarce, tr traces./absent.

bodies reached a temperature of 900–1000 °C, kept constant for long enough to complete the reaction of the clay minerals with calcite, forming a good quantity of the above-mentioned phases.

As concerns samples V20 and V21, the use of low firing temperature (<700 °C) and a brief firing time must be hypothesized. This result is in accordance with the information obtained from the SEM analysis (big dimensions of calcite clasts and calcareous fossils).

3.2.2. Surfaces

3.2.2.1. Black surfaces. Except samples V20 and V21, the black areas of all the samples show the constant presence, directly in contact with the ceramic body, of the black gloss typical of all the samples of Apulian red figured pottery analyzed up to now [9–12,14]. Its peculiarities are: the thickness (about 20 μm), the compactness (no pores), the sintering (very high) and the composition (richer in Al, Fe and K and poorer in Si and Ca with respect to the ceramic body). All these features are hints of the employ of a finer clay with respect to that of the body. Furthermore, the high sintering level of the black gloss slip must have been obtained lowering its melting point: this was probably done with the addition of plant ashes, illite and K-feldspars.

Peculiar cases are those emerged from the analysis of samples V5 and V14 surfaces, in which a Pb- and Ba-based coating can be seen over the black gloss (Fig. 7a): it must be interpreted as the result of a recovery intervention of the areas (where black gloss was no longer preserved) by means of an overpainting restoration, as typical of the restorations carried out at the beginning of the 19th century. This hypothesis is supported by the sharp contact between the layers and by the fact that lead has not penetrated in the underlying black gloss, features that also lead to think to a cold application. In detail, the analysis of this layer highlights the presence of lead, barium and strontium diffused in a carbon-based binding medium (Fig. 7a).

In samples V20and V21, instead, lead-based layers were used to imitate the black gloss (Fig. 7b, c).

For both samples, in the black areas two layers are present. The first, adjacent to the ceramic body, is made of Pb and Sb in a clayey matrix (V21), or is made of $CaSO_4$ (V20). The second contains Pb and $BaSO_4$ with traces of Sb (V21), or Pb, Al and K (V20): the presence of Al and K together suggests the use of potassium aluminate as Pb-binder.

3.2.2.2. Red surfaces. For all the samples analyzed, except V21, the red, on the surface in the areas without the black gloss, is simply the emerging ceramic body. In the case of V21 instead, these areas are covered with various layers analogous to the black ones of the same sample, with the addition of Hg and S in the external one (Fig. 8).

Investigations on these layers carried out with micro-Raman spectroscopy demonstrated that the presence of Hg is linked to the red sulphide cinnabar.

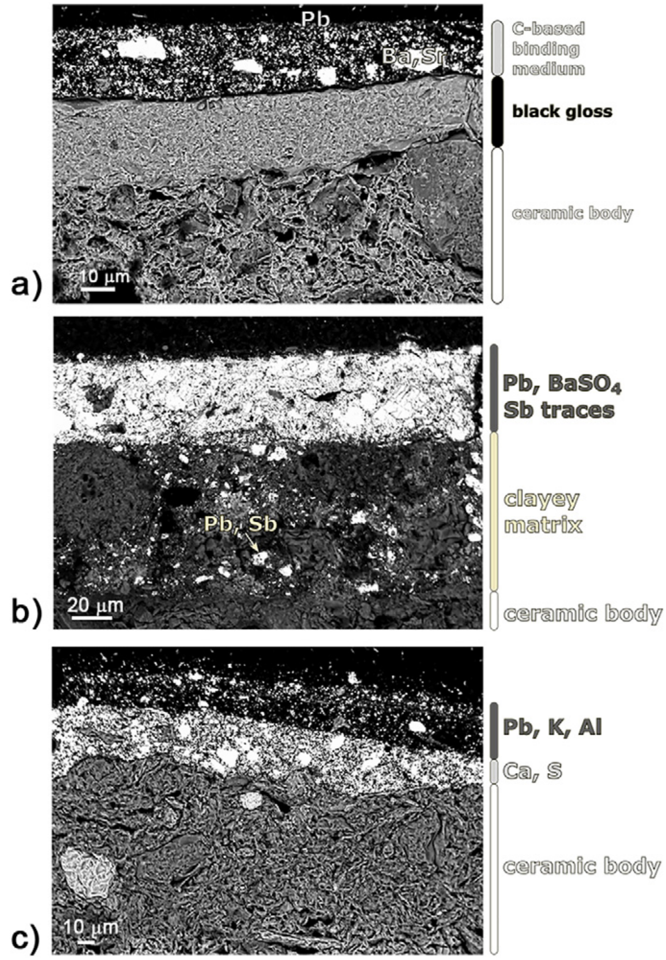

Fig. 7. SEM-BSD photomicrographs of the thin sections of sample V5 (a), V21(b) and V20 (c). Various overlapped painting integration layers are visible on top of the ceramic bodies and black gloss.

Therefore, also the results relative to surface highlight the non-originality of samples V20and V21.

4. Conclusions

The results obtained:

- Confirm the hypothesis of a fragmented local production for the Apulian red figured pottery [11,12,14,15].
- Highlight a more refined manufacture for theAncient and Middle Apulian Period vases (cluster B) comparing to Late Period ones. The manufacture involves the raw materials choice, the working

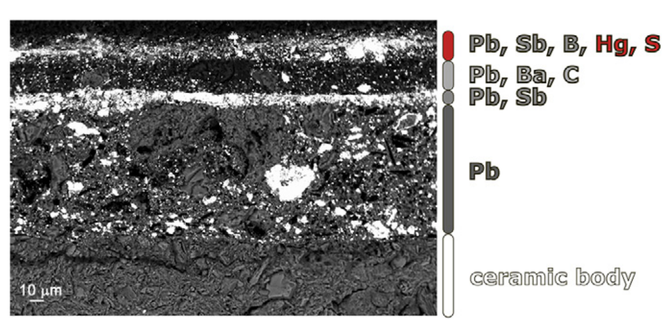

Fig. 8. SEM-BSD photomicrograph of the thin section of sample V21 in which various overlapped painting integration layers are visible on top of the ceramic body.

method and the shaping (the total absence of coarse-grain clasts suggests a process of purification of the clay, while the iso-orientation of micas and pores implies a careful smoothing) and the firing process (firing temperatures of 900–1000 °C and firing times longer than samples belonging to cluster A, as suggested by the higher sintering level). The better quality of the more ancient vases is in accordance with a less widespread production: in that period, they were mainly requested by the local aristocratic elite; furthermore, the connection with the Attic pottery was still strongly felt. After the half of the 4th century BC, a mass-scale increase of the demand brought to a serial production, with less attention both to the execution and to the figurative repertoire. The painter of Dario, able and innovator, was an exception.

- Indicate different supplying sources of the raw materials used to make the vases belonging to the two clusters (A and B), as suggested by their different chemical and mineralogical composition. In detail, the stronger chemical resemblance of Intesa Sanpaolo cluster A samples to those of Canosa and, above all, to the sub-appennine clays sampled in Canosa, could suggest an importation from that area of the entire vases or the raw materials only.
- Allow to discriminate the not original fragments both identifying integrations and restoration works and describing their composition and method of application. In fact, all the results of bulk and surface analyses (composition, microstructure, phases, etc.) in accordance indicate the non-originality of samples V20 and V21. It must be integration material of a 19th century restoration. The chemical and mineralogical resemblance with the sub-appennine clays of Canosa indicates that the restyling was carried out in loco.
- Provide information on 19th century restoration techniques of Apulian red figured vases.

The technological affinity of objects attributed to the same painter or to his workshop (e.g. Licurgo painter for cluster B and Patera painter for cluster A) is worth to be underlined. Also, a similarity is found for different painters or workshops, both in the case where a stylistic affinity had already been observed (e.g. Patera and Baltimore painters in cluster A) and in those where it had not (e.g. Nasi Camusi and Varrese painters groups, Gioia del Colle painter workshop).

The complex of the results obtained allows to retrace the whole history of the objects: features and raw materials sources, manufacturing process, not-documented restoration interventions, permitting to answer all the archaeological questions. This ultimate result has been obtained thanks to the employed analytical methodology based on a multi-technique approach and we believe that, besides the importance of the specific archaeometric results, it can give interesting hints about the analytical methodology to be employed for the study of pottery without context (i.e. artifacts in the most important museums and private collections, inside and outside Italy, or material coming from clandestine markets), that represent a substantial part of this ceramic class.

Acknowledgments

The authors would like to thank Intesa Sanpaolo for financial support and especially Michele Coppola (Manager of cultural Heritage Intesa Sanpaolo) and Laura Feliciotti (Coordinator of artistic Heritage), promoter of this scientific collaboration, Vincenzo Tiné, at the time Superintendent for Archaeological Heritage of Veneto, for having authorized this research.

References

[1] G. Sena Chiesa, F. Slavazzi, Ceramiche attiche e magno greche, Collezione Banca Intesa, Electa, Milano, 2006.
[2] A.D. Trendall, Handbook of Red Figure Vases of South Italy and Sicily, Thames-Hudson, London, 1989.
[3] A.D. Trendall, A. Cambitoglou, The Red-figured Vases of Apulia; Early and Middle Apulian I, Clarendon Press, Oxford, 1978.
[4] A.D. Trendall, A. Cambitoglou, The Red-figured Vases of Apulia; Late Apulian II, Clarendon Press, Oxford, 1982.
[5] J.D. Beazley, Attic Red-figure Vase-painters, Oxford University Press, Oxford, 1963.
[6] P. Graves, E. Robinson, M. Barbetti, Z. Yu, G. Bailey, R. Bird, Analysis of south Italian pottery by PIXE-PIGME, Meditarch 9 (10) (1997) 113–125.
[7] P. Mirti, M. Gulmini, A. Perardi, P. Davit, D. Elia, Technology of production of red figure pottery from Attic and southern Italian workshop, Anal. Bioanal. Chem. 380 (2004) 712–718.
[8] P. Mirti, M. Gulmini, M. Pace, D. Elia, The provenance of red-figure vases from Locri Epizephiri (Southern Italy): new evidence by chemical analysis, Archaeometry 46 (2) (2004) 183–200.
[9] P. Mirti, A. Perardi, M. Gulmini, M.C. Preacco, A scientific investigation on the provenance and technology of a black-figure amphora attributed to the Priam Group, Archaeometry 48 (1) (2006) 31–43.
[10] L.C. Giannossa, R. Laviano, F. Mastrorocco, G. Giannelli, I.M. Muntoni, A. Mangone, 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 (2016) 67–77.
[11] L.C. Giannossa, R.M. Mininni, R. Laviano, F. Mastrorocco, A. Mangone, M.C. Caggiani, An archaeometric approach to gain knowledge on technology and provenance of Apulian Red figured pottery From Taranto, Archaeol. Anthropol. Sci. (2016) http://dx.doi.org/10.1007/s12520-016-0345-9.
[12] A. Mangone, L.C. Giannossa, A. Ciancio, R. Laviano, A. Traini, Technological features of apulian red figured pottery, J. Archaeol. Sci. 35 (6) (2008) 1533–1541.
[13] A. Mangone, L.C. Giannossa, G. Colafemmina, R. Laviano, A. Traini, Use of various spectroscopy techniques to investigate raw materials and define processes in the overpainting of Apulian red figured pottery (4th century BC) from southern Italy, Microchem. J. 92 (2009) 97–102.
[14] A. Mangone, M.C. Caggiani, L.C. Giannossa, G. Eramo, V. Redavid, R. Laviano, Diversified production of red figured pottery in Apulia (Southern Italy) in the late period, J. Cult. Herit. 14 (2013) 82–88.
[15] A. Bitetto, A. Mangone, R.M. Mininni, L.C. Giannossa, A nonlinear principal component analysis to study archaeometric data, J. Chemom. 30 (7) (2016) 405–415.
[16] J. Thorn, M. Glascock, New evidence for Apulian red-figure production centres, Archaeometry 52 (2010) 777–795.
[17] E. Robinson, New Pixe-Pigme analyses for South Italian pottery, Mediterr. Archaeol. 26 (2013) 15–41.
[18] E. Robinson, Archaeometric analysis of Apulian and Lucanian red-figure pottery, in: T.H. Carpenter, K.M. Lynch, E.G.D. Robinson (Eds.), The Italic People of Ancient Apulia, New Evidence From Pottery for Workshops, Markets and Customs, Cambridge University Press, New York 2014, pp. 243–264.
[19] F. Giacobello, Aspetti produttivi delle Officine del Pittore dell'Ilioupersis e del Pittore della Patera, in: F. Giacobello (Ed.), Savoir-Faire antichi e moderni II. Pittori e officine ceramiche nell'Apulia di V e IV secolo a.C., Scalpendi, Milano, 2016.
[20] La ceramica attica in Apulia: una grande officina, i suoi pittori, un vaso famoso, in: C. Lamburgo, G. Sena Chiesa, F. Slavazzi (Eds.), Ceramiche attiche e magno greche, Collezione Banca Intesa, Electa, Milano 2006, pp. 44–93.
[21] A. Mangone, L.C. Giannossa, R. Laviano, C.S. Fioriello, A. Traini, 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 (2009) 214–221.
[22] A. Mangone, L.C. Giannossa, C. Laganara, R. Laviano, A. Traini, Manufacturing expedients in medieval ceramics in Apulia, J. Cult. Herit. 10 (1) (2009) 134–143.
[23] C. Giannotta, C. Laganara, R. Laviano, A. Mangone, A. Traini, Medieval Islamic-type pottery from Siponto (Italy): an integrated physical-chemical and mineralogical investigation, X-Ray Spectrom. 35 (6) (2006) 338–346.
[24] P. Bruno, M. Caselli, L. Curri, P. Favia, C. Laganara, A. Mangone, A. Traini, XPS, ICP and DPASV analysis of medieval pottery – statistical multivariate treatment of data, Fresenius J. Anal. Chem. 350 (3) (1994) 168–177.
[25] L.C. Giannossa, M. Acquaviva, G.E. De Benedetto, P. Acquafredda, R. Laviano, A. Mangone, Methodology of a combined approach: analytical techniques to identify the technology and raw materials used in thin-walled pottery from Herculaneum and Pompeii, Anal. Methods 6 (10) (2014) 3490–3499.
[27] G. Eramo, L.C. Giannossa, A. Rocco, A. Mangone, S.F. Graziano, R. Laviano, Oil lamps from the catacombs of Canosa (Apulia, fourth to sixth centuries AD): technological features and typological imitation, Archaeometry 56 (2014) 375–391.
[28] F. Balenzano, L. Dell'Anna, M. Di Pierro, Ricerche mineralogiche, chimiche e granulometriche su argille subappennine della Daunia (Puglia), Geologia Applicata e Idrogeologia 12 (1977) 33–54.
[29] L. Dell'Anna, R. Laviano, Mineralogical and chemical classification of Pleistocene clays from the Lucanian Basin (Southern Italy) for the use in the Italian tile industry, Appl. Clay Sci. 6 (1991) 233–243.
[30] M. Dondi, B. Fabbri, R. Laviano, Characteristics of the clays utilized in the bricks industry in Apulia and Basilicata (Southern Italy), Mineral. Petrogr. Acta 35 (1992) 181–191.
[31] H.S. Yoder, H.P. Eugster, Synthetic and natural muscovites, Geochim. Cosmochim. Acta 8 (1955) 225–280.
[32] J. Srodon, D.D. Eberl, Illite, in: S.W. Bailey (Ed.), Micas, Reviews in Mineralogy, vol. 13, Mineralogical Society of America, Washington, D.C. 1984, pp. 495–544.
[33] R. Kretz, Symbols for rock-forming minerals, Am. Mineral. 68 (1983) 277–279.
[34] M. Maggetti, C. Neururer, D. Ramseyer, Temperature evolution inside a pot during experimental surface (bonfire) firing, Appl. Clay Sci. 53 (3) (2011) 500–508.
[35] L. Maritan, L. Nodari, C. Mazzoli, A. Milano, U. Russo, Influence of firing conditions on ceramics products: experimental study on clay rich in organic matter, Appl. Clay Sci. 31 (1–2) (2006) 1–15.