THE REASON OF THE COLLAPSE OF AN ANCIENT KILN IN EGNAZIA FROM MINERALOGICAL AND THERMAL ANALYSIS OF CERAMIC FINDS

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Two kilns, one of which collapsed during firing cycle together with its entire pottery load, have been excavated at the Egnazia site in Southern Italy.

To understand the reason for the collapse, 'Broad Line' typology pottery finds were analysed by complementary analytical techniques. Analytical results not only suggest as cause of collapse sudden overheating in kiln due to uncontrolled increases in temperature, but also indicate a good technological cycle from the recovery of raw materials to the manufacturing and firing process, which tends to disprove the common assumption of non-professional production.

Keywords: *chemical characterisation, early medieval pottery, mineralogical composition, multivariate statistical analysis, thermal analysis*

Introduction

The examined finds come from Egnazia, one of the most important archaeological sites in Southern Italy, which was inhabited from the 16th Century BC up to the Middle Ages. During the Roman Empire and Late Antiquity the town had a central role in commercial trade between Rome and Brindisi, with the via Traiana, and between Italy and the Eastern Mediterranean Basin, via the harbour.

Recent excavation campaigns[*], which have been mainly aimed at investigating the organization of the town from the Roman Age up to its abandonment, suggest that Egnazia still had an important economic role during the First Middle Ages [1–3]. This hypothesis is strengthened by the new excavation finds, particularly with the valuable vases imported from Africa and Asia until the 6th Century AD, and the presence of two active kilns in the 5th and 6th Century AD, confirmed by the presence of early medieval lamp found in one of the kilns. This tends to confute two of the more common theories about Egnazia, the transformation of the town into a rural centre in Late Antiquity and its abandonment due to raids by the Goths (mid-6th Century AD) [1–4].

The north kiln A and the south kiln B were a part of a well organized workshop (Fig. 1), as attested by the presence of two other nearby rooms. One of the

Fig. 1 Plan of worshop area in the archaeological site of Egnazia. a – Kiln A; b – Kiln B; c – Tub for clay decantation; d – Wheel room; e – Woodshed

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Fig. 2 Typical examples of examined finds: a – Sample 1, amphora Type 1 with brown painted broad lines; b – Sample 3, amphora with red painted broad lines; c – Cooking Ware, lid Type 1; d – Cooking ware, bowl rim

rooms was probably used for modelling vases, as suggested by traces of a wheel, a tub for clay decantation and many tools for making pottery; the other was probably used as a woodshed. The workshop produced mainly small amphorae painted with red lines – 'Broad Line Ware' – and cooking pottery.

The presence of the entire load of 'Broad Line Ware' in kiln A [5] (Fig. 2) suggests that the firing process was interrupted. The evident signs of fire found in the destruction layers of the rooms of the workshop and the appearance of vases inside the kiln point to a catastrophic event outside the kiln, probably a fire starting from the woodshed. On the basis of chemical and morpho-mineralogical characterisation of materials, the aim of this research is to clarify the reasons for the kiln collapse.

An additional objective is to characterize the 'Broad Line Ware' typology that spread in Southern Italy between Late Antiquity and the Middle Ages, when the lack of demand for wares caused the breakdown in manufacturing and long distance trade and led to the re-emerge of local, simplified, non-professional production. 'Broad Line Ware' is generally irregular in throwing and finishing, and decorated with red lines, without a well defined motif. 'Broad Line Ware' first appears in Basilicata [6, 7], over time this ceramic typology becomes more 'fashionable' [8] and spreads all over Southern Italy. For this reason it is often considered the 'guide fossil' in the recognition of the Middle Ages in archaeological sites. In spite of its great importance to the history of Southern Italy, its morphological and compositional aspects have never been studied before and no production centre has been found. The discovery of the workshop in Egnazia offers us a chance to fill the gap in the study of this ceramic.

Experimental

Samples

The examined finds consists of 40 items presented in Table 1, either as fragments or unbroken artefacts.

30 samples are 'Broad Line Ware', consisting of two types of amphorae. The smaller amphorae have been categorised as Type 1, the bigger amphorae as Type 2 – with large and squashed ribbon handles, oval rims and globular forms.

In some samples from kiln A the painted lines appear brown or black.

Compared to other vases of this type, the Egnazia amphorae are characterised by an unusual feature. The red lines are painted with a standardized schema: two curved broad lines between the handles on the shoulder, one on the largest point of the body and others on the handles and on the rim. This characteristic suggests that the potter may have been linked to the older and more specialized methods of production typical of the Roman Period [9].

The 10 samples from kiln B consist of cooking ware – open shapes, lids, and different kinds of jug.

Methods

The fragments have been examined with complementary techniques, namely polarized-light optical microscopy (OM), scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), inductively coupled plasma-mass spectrometry (ICP-MS), thermal analysis (TG/DTA/ DDTA) and X-ray diffraction (PXRD). Multivariate statistical techniques have been used for treating compositional data.

Orthoscopic analysis was conducted on polished thin sections of fragments by optical microscopy and followed by SEM analysis of the same thin sections, previously metallized with a 30-μm-thick layer of graphite. A Leo Instruments Scanning Electronic Microscope EVO-50XVP was used. Microanalyses were conducted by using an Oxford-Link meter in EDS with Ge detector equipped with a 0.4-mm-thick super atmosphere thin window (SATW).

Each sample (about 100 mg) was ground (<100 μm) and dried for 6 h in a vacuum over calcium chloride, and was then submitted to thermoanalytical

Table 1 Analysed samples

Typology	Place of finding		Code	Description
Broad line ware	North kiln	prefurnium	1	amphora Type 1
			2	amphora Type 2
		cooking room	3	amphora Type 2
			4	amphora Type 1
			5	Handle Type 1
			6	Body
			7	Handle Type 2
			8	Body
			9	Body
			10	Body
			11	Body
			12	Body
			13	Body
			14	Handle Type 2
			15	Body
			16	Handle Type 2
			17	Body
			18	Body
			19	Rim Type 2
			20	Body
	A area		21	Handle Type 2
			22	Rim Type 2
			23	Handle Type 2
			24	Body
			25	Rim Type 2
	South kiln		26	Handle
			27	Body
			28	Body
			29	Handle
			30	Body
Cooking ware			31	Body
			32	Bowl rim
			33	lid
			34	Body
			35	Body
			36	Lid Type 1
			37	Bowl rim
			38	Lid Type 1
			39	Bowl rim
			40	Body

investigations at heating rates of 10°C min^{-1} in static air (Netzsch STA 409 apparatus).

Powder X-ray diffraction analyses were performed by using a Philips PV-1710 X-ray diffractometer (CuK_{α} radiation).

The chemical composition of the ceramic body was analysed by scraping off bulk ceramic matter from fractures already existing on fragments or from small visible points of inside or under the base museum artefacts after removing the outermost external contaminated layers. Weighted aliquots of about 100 mg of bulks were dissolved by acid with a solution of 37% HCl, 70% HNO_3 and 40% HF (Fluka trace selected for trace analysis reagents), in a 2:1:1 (*v*/*v*/*v*) ratio [10]. 10 elements (Al, Ca, Mg, Fe, Ti, Na, K, Cr, Sr, Ni) were quantified by ICP-MS (PerkinElmer Elan 9000 spectrometer). The entire analytical procedure was tested on standard clay material – certified sample 'Brick clay' Standard reference materials 679 (National Bureau of Standards). External calibration with matrix matching standards was employed for quantification and three replicate readings were performed on both standards and samples.

Results and discussion

OM and SEM-EDS analysis

'Broad Line Ware'

OM and SEM analyses on all pastes have revealed a fine texture with coarse flakes, mainly of carbonates, fossils and chamotte (Fig. 3). The percentage of skeleton was greater in handles than in both rims and

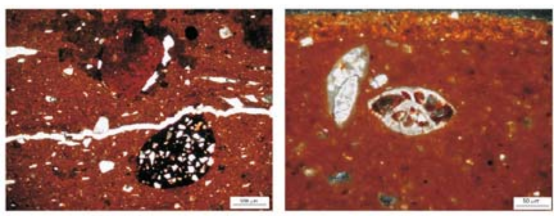

Fig. 3 Polars optical microscopy of fabric of shards 23 (left) and 3 (right, crossed), showing fine textured clay body with chamotte and fossils. A clay layer on the surface of sample 3 is also visible

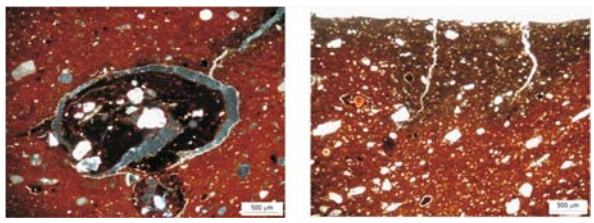

Fig. 4 Polars optical microscopy of shard 4 showing shrinkage area in the ceramic body (left, crossed) and fractures from surface (right)

walls. The orientation of micas and pores parallel to the wall of ceramic vessels have revealed the use of a potter's wheel.

Numerous micro-fractures and empty areas around fossil remains and chamotte were present in all samples found in the kiln A (Fig. 4) with the exception of samples 1 and 2. The presence of 'shrinkage' areas is indicative of a thermal shock that caused a marked contraction of the paste around fossils and chamotte during firing. Secondary calcite was widespread along shrinkage margins within pores or had substituted fossil shells. The same samples presented lower sintering grades and a greater amount of primary calcite with respect to samples found outside kiln A.

A 50–100 μm-thick clay layer, with a slightly finer texture and larger quantities of Al, Fe, K and lower quantities of Ca and Mg, with respect to the ceramic body, was present on the surface (Fig. 5). The absence of large inclusions and the chemistry composition of this layer suggests that a finer clay was employed in its production, while a coarser clay, richer in calcium compounds, could have been used for the ceramic body.

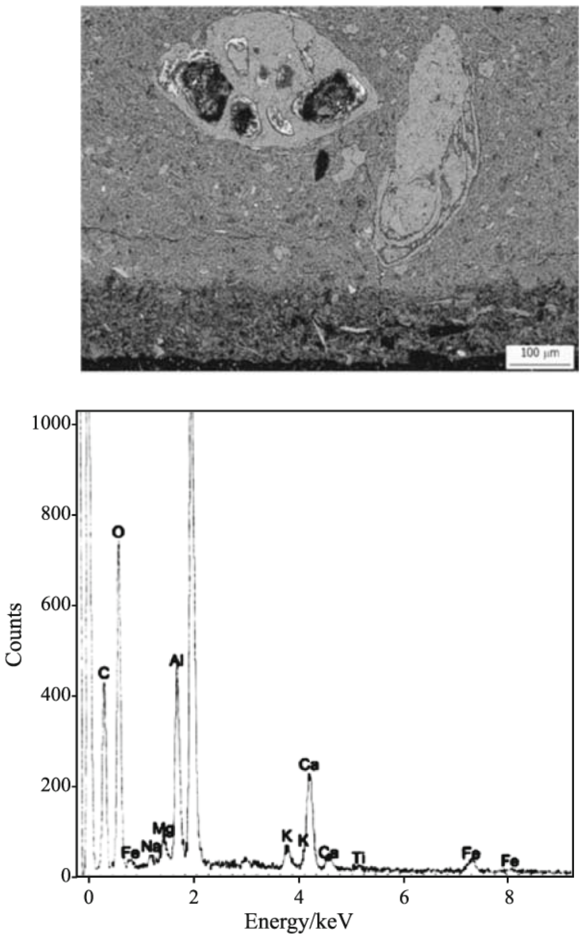

Fig. 5 SEM-BSE photomicrograph of the thin section of shard 3 highlighting, on the ceramic body, a 100 μm-thick layer with a slightly finer texture with respect to the ceramic body. The ED spectrum of this layer is lower

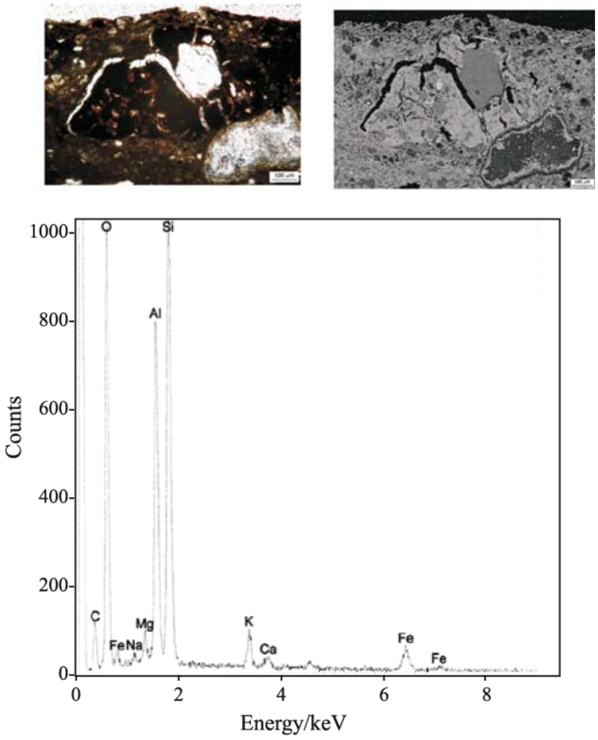

Fig. 6 Polars optical microscopy (left) and SEM-BSE photomicrograph (right) of the thin section of fragment 2, lumps of pigment are visible. ED spectrum of lumps of pigment

Decorations were applied before firing, as revealed by the penetration of chemical elements, which characterise the colouration materials, in the ceramic body. The high Al/Si value, high content of K, Fe and negligible amount of Ca, as highlighted by ED spectrum on a lump of pigment, is compatible with the use of the so called 'terre rosse' [11, 12], common to Apulia and widespread in the Egnazia site (Fig. 6). No chemical difference between red and black lines on vases in kiln A was revealed. Iron was responsible for both, since the red colouring associated with Fe(III) compounds is characteristic of an oxidizing firing atmosphere, and black, associated with Fe(II) compounds, of a reducing firing atmosphere. While these vases are part of the same load, it appears they were exposed to different firing atmospheres.

'Cooking pottery'

A fine texture, with remarkable amounts of iron oxides and mineral inclusions, almost all of quartz and feldspar, and a chemical composition which matches well the raw material 'terre rosse' were characteristics of the ceramic body of all fragments (Fig. 7).

Table 2 Ceramic body composition by ICP-MS

Sample	Element concentration										
	Mass%							ppm			
	Al	Ca	Mg	Fe	Ti	Na	K	Mn	Sr	Cr	Ni
1	7.48	8.46	1.77	3.64	0.35	1.07	2.17	483	297	131	69
2	6.78	9.61	1.44	3.53	0.35	1.15	2.28	645	302	118	60
3	5.88	7.60	1.66	3.18	0.30	1.15	2.13	500	215	85	51
4	6.88	10.5	1.11	3.50	0.33	1.00	1.91	599	303	120	65
5	6.54	10.6	1.63	3.24	0.33	0.93	1.95	677	268	113	120
6	6.80	12.2	1.18	3.43	0.36	1.04	2.38	830	339	112	59
7	6.67	10.8	1.40	3.38	0.32	0.99	2.10	616	320	108	53
8	6.27	7.99	1.62	3.17	0.32	1.09	2.11	573	254	98	58
9	6.74	11.0	1.66	3.43	0.32	1.11	2.29	493	312	106	59
10	6.79	11.2	1.59	3.41	0.32	0.97	2.18	629	312	109	63
11	6.15	8.30	1.70	4.11	0.31	1.07	2.18	735	285	101	112
12	7.16	11.2	1.74	3.57	0.34	1.11	2.18	790	298	100	54
13	6.66	10.5	1.59	3.41	0.33	1.19	2.29	583	297	97	55
14	7.04	9.01	1.30	3.49	0.36	1.17	2.53	697	323	122	55
15	6.14	7.72	0.98	3.68	0.29	0.85	2.19	908	134	109	106
16	7.94	10.2	1.24	3.95	0.38	0.99	2.38	775	282	127	63
17	7.12	9.41	1.36	3.64	0.34	1.15	2.24	556	326	128	55
18	6.42	10.4	1.43	3.14	0.31	1.04	1.89	519	302	107	49
19	6.92	9.85	1.44	3.46	0.36	1.10	2.22	634	279	113	50
20	7.25	7.76	1.21	3.68	0.32	1.08	2.27	747	254	94	59
21	7.96	9.04	0.96	4.05	0.36	1.09	2.21	840	270	115	50
22	6.91	11.8	1.13	3.44	0.33	0.94	2.08	661	331	99	57
23	7.20	8.95	0.83	3.69	0.32	0.92	1.95	853	260	108	53
24	7.39	10.3	1.12	3.94	0.34	0.90	2.20	733	353	119	53
25	6.22	11.7	0.90	3.17	0.30	0.92	2.01	555	328	90	44
26	6.53	10.8	1.00	3.31	0.33	1.01	2.23	654	294	96	57
27	6.13	11.1	0.94	3.05	0.36	1.23	2.44	758	282	97	44
28	6.12	10.1	0.86	3.35	0.28	0.94	2.07	644	241	91	43
29	6.21	10.2	0.92	3.10	0.33	1.15	2.34	649	347	93	43
30	6.56	10.1	1.03	3.16	0.25	1.01	2.11	683	288	93	44
31	8.70	1.87	0.59	4.52	0.45	0.28	2.31	770	134	82	46
32	8.36	2.06	0.60	4.45	0.36	0.39	2.05	598	121	86	46
33	9.05	1.80	0.63	4.76	0.38	0.33	2.10	630	123	93	45
34	7.57	1.91	0.55	4.47	0.46	0.38	2.10	602	124	89	45
35	8.84	2.11	0.63	4.54	0.39	0.30	2.23	527	163	86	46
36	8.76	2.54	0.62	4.51	0.38	0.34	2.11	703	149	99	45
37	9.51	1.96	0.73	4.98	0.45	0.63	2.22	650	112	81	46
38	8.69	1.91	0.67	4.64	0.47	0.42	2.22	580	127	93	46
39	9.02	2.21	0.66	4.98	0.47	0.58	2.50	678	135	89	45
40	8.77	2.47	0.59	4.37	0.38	0.72	1.99	623	128	85	46

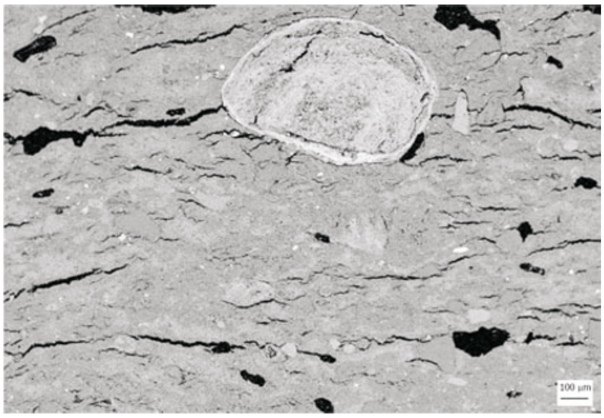

Fig. 7 SEM-BSE photomicrograph of the thin section of fragment 40 showing the fine texture of the ceramic body, iron oxides pisoid is present

Chemical analysis and statistical treatment of data

The results of chemical analysis by ICP-MS of the ceramic bodies, which are reported in Table 2, have been expressed as mass% for major and minor elements and as ppm ($\mu g\ g^{-1}$) for trace elements. To identify groups of objects distinguishable on the basis of their compositional features, compositional data have been processed with principal components analysis (PCA) and cluster analysis using the SCAN software package (Minitab) [13, 14].

Handle samples have been kept out of statistical treatment because of their markedly different petrographic characteristics, as highlighted by OM and SEM analyses.

The results of the multivariate statistical analysis, which are shown in Fig. 8, illustrate the scores plot onto the first three principal components subspace, which accounts for 82% of the total variance, and the loading plot of the different parameters. Two markedly distinct groups can be identified. The same figure shows the 95% isoprobability ellipsoids, whose surfaces define the boundary of the two clusters, A and B.

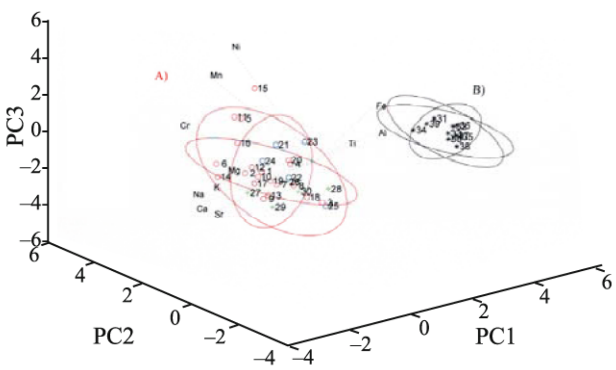

Fig. 8 Scores and loadings diagram for the first three principal components relating to finds examined. The accounted variance is 82% of the total variance. * – Cooking pottery; ○ – Broad Line Ware from kiln A; ○ – Broad Line Ware from area A; + – Broad Line Ware from kiln B

Cluster A includes all ‘Broad Line Ware’ artefacts, while cluster B includes all ‘Cooking pottery’.

Cluster A differs from B along PC1 principally due to the loadings relative to the Ca, Al, Fe, Na and K parameters. The fact that the two clusters appear to be connected to different raw materials and modes of production probably depends on the function of vases – whether contain drinking water as in the ‘Broad Line Ware’ or for cooking purposes as in the Cooking pottery.

Thermal and diffractometric analysis

PXRD and thermal analyses – TG, DTA and DDTA – on ‘Broad Line Ware’ samples, from both inside and outside kiln A, have been performed to ascertain the reason for collapse.

Thermoanalytical curves of all samples showed endothermic effects principally due to ‘moisture’ and ‘bound’ water below 250°C, to loss of water of hydrated oxides in the range 300–400°C, to dehydroxylation of clay minerals in the range 400–650°C and to decomposition of calcite at about 800°C [15–18].

Finds inside and outside kiln A differ in calcite and clay minerals contents, as highlighted by the thermal curves (Figs 9 and 10). Mass loss due to dehydroxylation of clay minerals and to decomposition of calcite for the analysed samples gives mean values of 1 and 4%, respectively for samples outside kiln, 5 and 9% for samples inside kiln, 2 and 7% for samples 1 and 2.

PXRD analysis has shown the presence of neo-formed mineralogical phases as diopsidic pyroxene, gehlenite and hematite, in samples outside kiln and only for samples 1 and 2 inside kiln (Figs 9 and 10), which suggests that these finds reached a temperature of about 950°C [19].

Both thermal and PXRD analysis suggest that temperatures for all other samples inside kiln were much lower.

The difference between samples 1 and 2 and all others inside kiln A indicates a marked lack of thermal homogeneity in the kiln, probably associated with an anomalous firing cycle.

Conclusions

The results obtained by the different analytical techniques on pottery from Egnazia provide interesting indications about technological-productive aspects and lead to important results from both the archaeo-

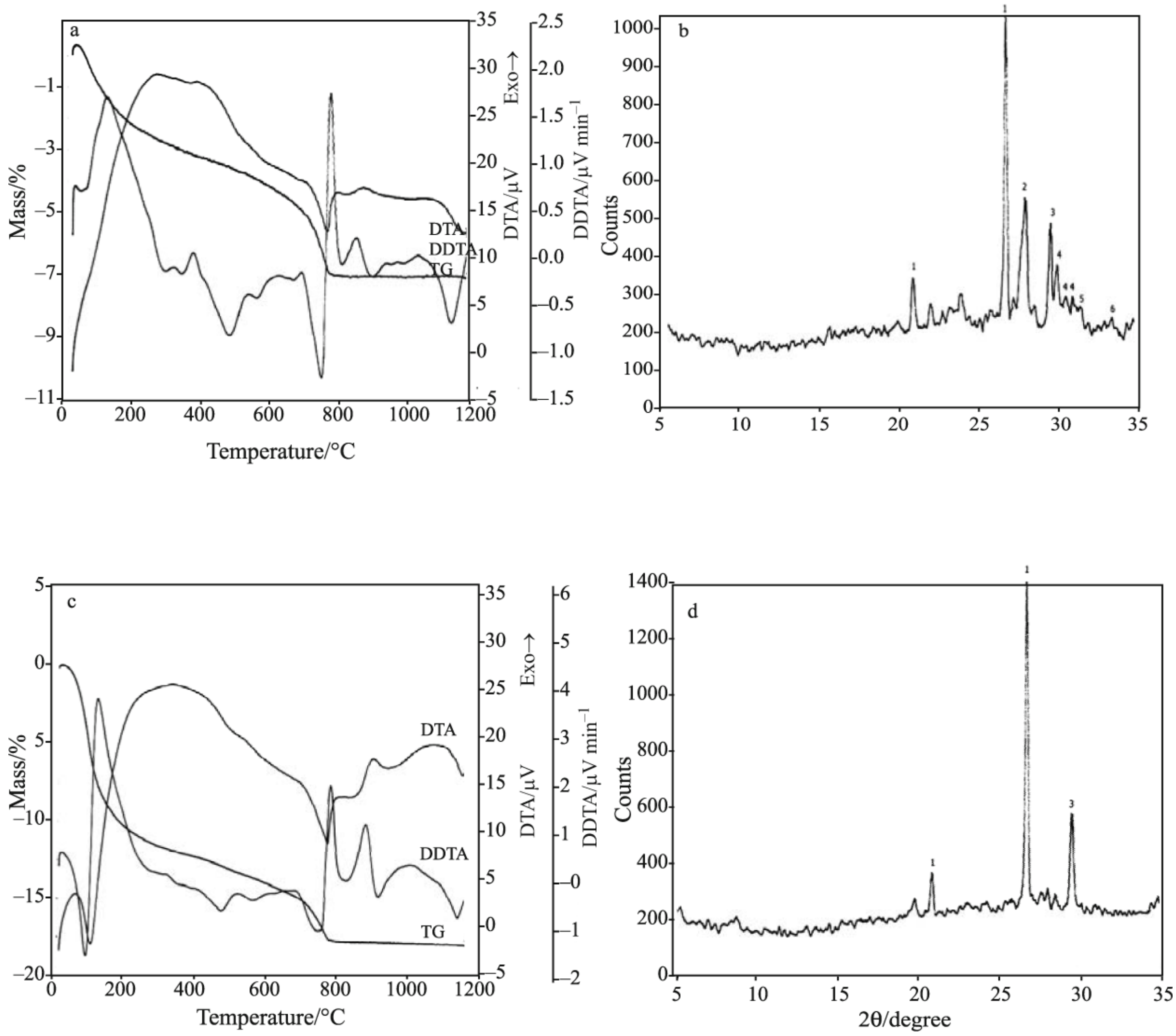

Fig. 9 Thermal curves of samples 1 and 3 (a, c). X-ray diffractograms of the same samples (b, d), showing peaks of the relative minerals: 1) quartz, 2) feldspar, 3) calcite, 4) pyroxene, 5) gehlenite, 6) hematite

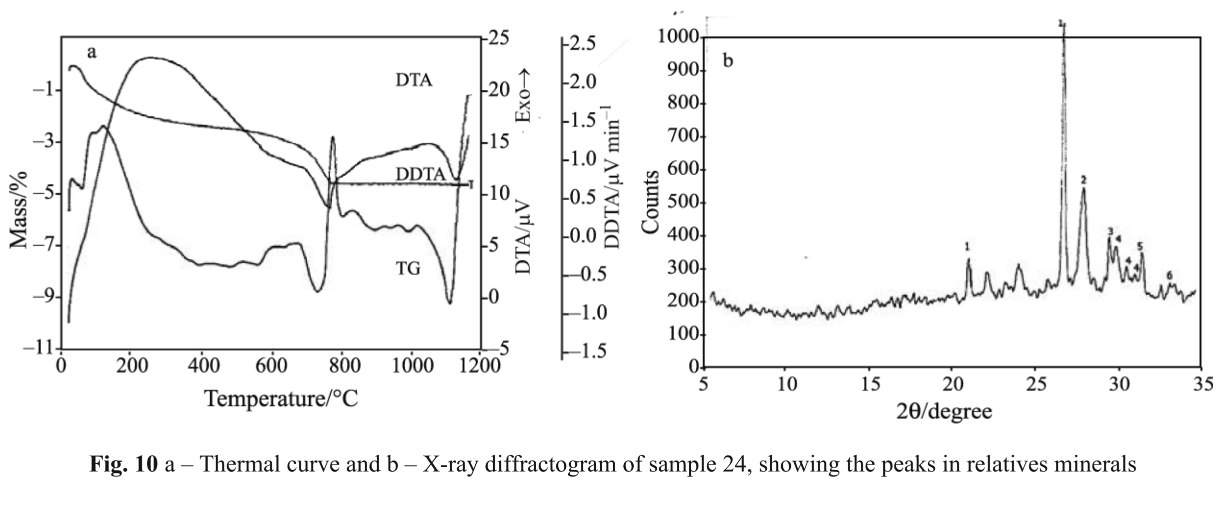

Fig. 10 a – Thermal curve and b – X-ray diffractogram of sample 24, showing the peaks in relatives minerals

metric and archaeological points of view, particularly for the characterisation of 'Broad Line Ware', one of the most important ceramic typologies for the Middle Ages in Southern Italy.

Mineralogical and micro-structural features suggest a good technological cycle from the recovery of raw materials to the manufacturing and firing process. This tends to disprove, at least for Egnazia finds, the common idea of less specialized production and supports the archaeological hypothesis, suggested by the decorative schema, of potters not unprofessional, but working within older Egnazia traditions. The most interesting results regard the explanation for the kiln collapse that allows us to exclude the possibility of a large fire outside the kiln. For all the ceramic bodies of artefacts found in kiln A, excluding samples 1 and 2, the low degree of vitrification, absence of newly formed minerals and the presence of primary calcite are indicative of temperatures lower than that of a fire.

The thermal shock suffered by vases can be explained by sudden overheating, as result of uncontrolled increases in temperature. A possible reason for the kiln collapse may have been the accumulation of combustion ash in the chimney holes of the cupola. Bad choice of fuel or introduction speed may also have led to incomplete combustion and smoke rich in ash. An ineffective draught may have caused higher temperatures and pressure leading to the disconnection and shearing of the cupola towards the prefurnium with the subsequent fall of samples 1 and 2 in the prefurnium. As the firing process went on, samples 1 and 2 reached higher temperatures. Once a slight draught had been established in the areas nearest the prefurnium, a reducing firing atmosphere was probably responsible for the black coloration of painted lines on the surface and greyish body of the vases found in the prefurnium (Fig. 2).

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