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Thermochimica Acta 321 (1998) 167–174

thermochimica
acta

Study and characterization by thermoanalysis of statues and fictile finds of different historical and prehistoric ages

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Received 10 March 1997; accepted 12 April 1998

Abstract

Several general instrumental methods (in particular, those involving thermal analyses – TG, DTA and TMA) were used to analyze a number of terracotta materials from different periods (prehistoric, Roman, Renaissance). The information obtained enabled factors related to certain evolutionary trends in terracotta technology to be identified. Considerable importance was attached to determining characteristics providing information regarding several terracotta processing and production technologies in the various historical periods and geographical areas considered. The parameters best suited to this type of investigation were also investigated and identified. © 1998 Elsevier Science B.V.

Keywords: Fictile finds; Different ages; Characterization; Thermoanalysis; Firing temperature

1. Introduction

Fictile samples of different ages were subjected to systematic instrumental chemical analysis, i.e. thermomechanical analyses (TMA and DTMA), thermogravimetric analyses (TG and DTG), differential thermal analysis (DTA), porosimetric analysis, X-ray diffractometry, plasma emission spectroscopy (ICP) and infrared analysis (IR). The instrumental analysis performed on several terracotta materials from different periods (prehistoric, Roman, Renaissance) yielded information concerning their composition and, to some extent, also the different levels of technical capability attained by the craftsmen.

In addition, it was possible to draw interesting conclusions concerning the suitability of different analytical instrumental techniques used to characterize the fictile material, to solve certain technical problems, to verify typological and historical assumptions and to check the historical evolution of the production technology of terracotta finds.

2. Samples analyzed

The analyzed samples were as follows: prehistoric terracotta material from an archaeological excavation carried out on the Libyan Tadrart Acacus mountains, dating to between 5000 B.C. and 8000 B.C., several terracotta statues from the fictile complex of Ariccia (Rome), dating to II–III centuries B.C., fictile fragments of architectonic terracotta material ascribable to two pediment decorations (named 'A' and 'B', respectively) from the Civitella in Chieti dump, dating to I–II centuries B.C. and, lastly, several pot shards from the excavation of the Rome "Chancery" dating to the

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PII: S0040-6031(98)00456-0

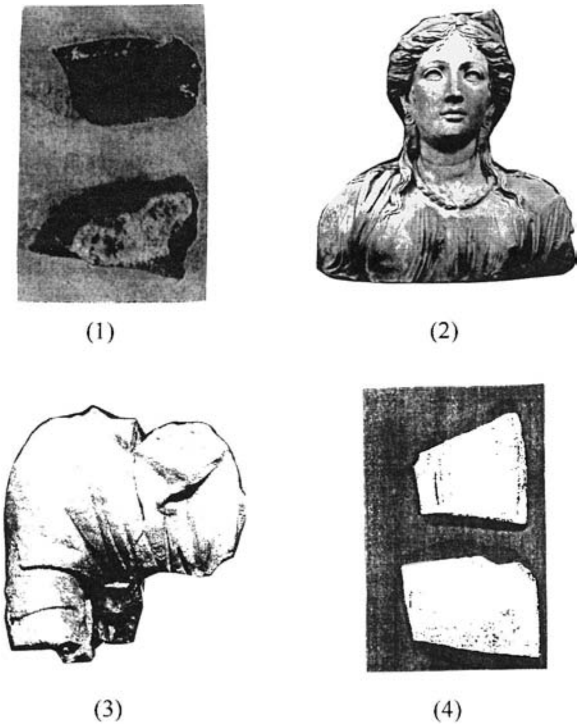

Fig. 1. Typical finds belonging to four groups of samples studied in this research. (1) Sample of prehistoric terracotta from Libyan Tadrart Acacus; (2) fictile statue from Ariccia (II–III centuries B.C.); (3) fictile statue of gable from Civitella in Chieti (I–II centuries B.C.); (4) sample of pottery from excavation of the Rome "Chancery" (XV–XVI A.D.).

XV–XVI centuries A.D. Typical finds from each of the four sites mentioned above are shown in Fig. 1.

3. Experimental and methods

Generally, the terracotta samples, with the exception of porosimetric analysis, were first ground into a homogeneous powder for the purpose of analysis [1].

The thermogravimetric analyses were performed using a Mettler TG 50 thermobalance connected to a TC 10 A microprocessor and a Swiss matrix printer, or using a Du Pont 951 thermogravimetric analyzer. The differential thermal analyses were carried out using a Du Pont apparatus (DTA cell); both Du Pont instruments were coupled to a Du Pont thermal analyst 2000 system.

The experiments were carried out in static and dynamic air and at a heating rate of 10°C min^{-1} .

The thermomechanical tests were performed on a Mettler TMA 40 thermomechanical analyzer coupled to a TC 10 A microprocessor and a Swiss matrix printer. In this type of analysis the powdered samples were subjected, above all, to an isothermal (25°C) recompaction process, using the TMA apparatus and the method described in previous researches [1–3]. At the end of this process the samples were subjected to thermomechanical scanning between 25° and 1000°C at a heating rate of 8°C min^{-1}, in static air conditions and with a constant, applied load of 0.05 N.

X-ray diffraction tests were performed on a PAD III Seifert automatic powder diffractometer, using CuK_α radiation (λ=1.54 Å).

IR spectrophotometric analysis was carried out using a Perkin–Elmer model 882 infrared spectrophotometer with direct dispersion of the powder comprising the sample as KBr pellets.

Tests to evaluate the pore size distribution in the samples were performed, using a Carlo Erba series 200 mercury porosimeter. Lastly, the plasma emission spectroscopy analysis was performed using a Jobin–Yvon type III sequential plasma I.C.P.

4. Results and discussion

As stated in Section 1, we systematically subjected terracotta samples from various sites to instrumental analysis. Although the finds examined so far are somewhat heterogeneous and come from only a small number of sites (four different sites, in practice), it may nevertheless be observed that they come from very different periods, ranging from prehistoric times to the Renaissance. The aim was, therefore, to use the results of the analysis to gather any evidence of the probable evolution of the production techniques over the centuries. Our data must therefore be interpreted as being only of preliminary significance. They will no doubt be added to or modified as the number of sites and historical periods investigated by ourselves and other researchers increases.

The equivalent firing temperatures estimated on the basis of thermal analysis [4] and, particularly, the 'shrinkage temperature' [5,6] obtained from the thermomechanical curves (Fig. 2) are shown in Table 1.

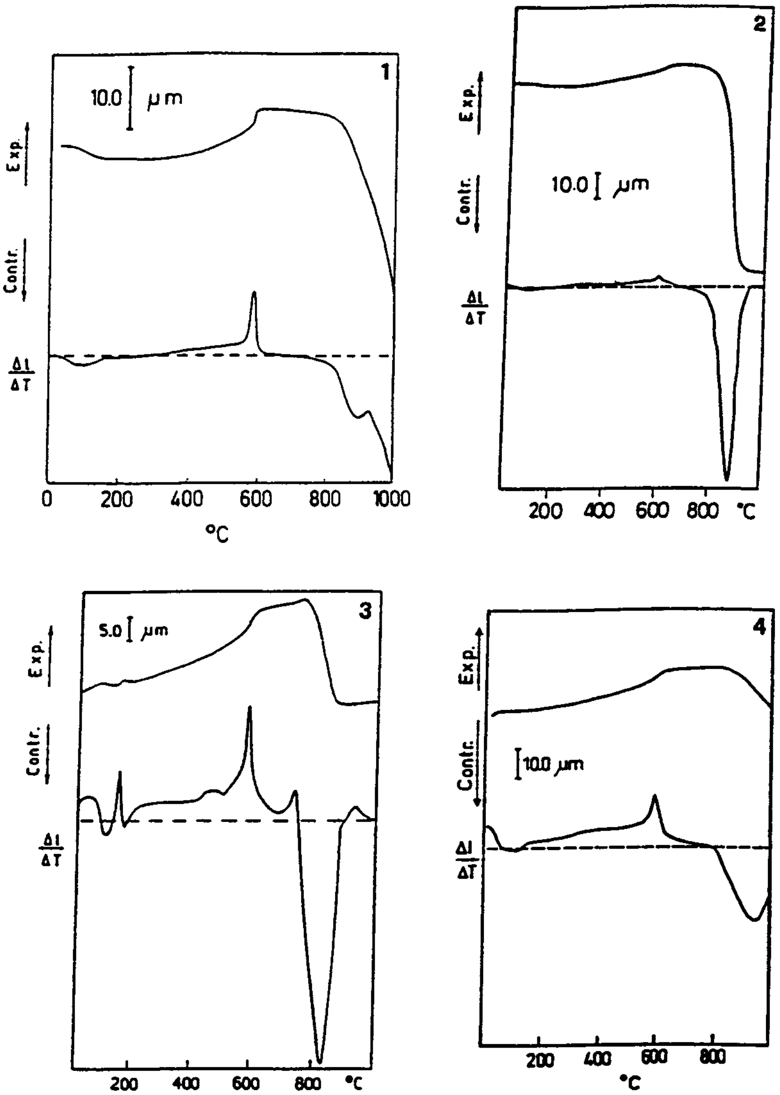

Fig. 2. Typical TMA and DTMA curves for the characterization of terracotta samples. Static air, heating rate 8°C $\min^{-1}$; applied constant load 0.05 N. (1) Sample of prehistoric terracotta from Libyan Tadrart Acacus; (2) sample of a fictile statue from Ariccia (Rome) (II–III centuries B.C.); (3) sample of a fictile gable from Civitella in Chieti (I–II centuries B.C.); and (4) sample of the pottery from excavation of the Rome "Chancery" (XV–XVI A.D.).

It is apparent that the equivalent firing temperature of the prehistoric finds is considerably lower than that of the earliest Italian terracotta examined (Roman period) and, of course, of the Renaissance pottery. This should be indicative of an evolving production technology.

Also the porosimetric curves (Fig. 3) seem to confirm this evolutionary trend [7]. For instance, while the Libyan Tadrart finds are characterized by a pore volume distribution covering practically the entire measuring instrument range, which is indicative of the presence of evenly distributed pores with widely differing radii (37–75 000 Å), the fictile statues of Civitella in Chieti and, to an even greater extent, the Renaissance pottery, have a pore volume distribution limited to a much smaller size range: ca. 65%

Table 1
Firing temperature of samples analyzed

Samples	Period	Equivalent firing temperature (°C) [a]
Libyan Tadrart Acacus	Prehistoric	600–650
Ariccia	II–III centuries B.C.	650–750
Chieti	I–II centuries B.C.	740–770
Renaissance pottery	XV—XVI centuries A.D.	750–770

[a] ‘Equivalent firing temperature’, found on the basis of the experimental value of the ‘shrinkage temperature’.

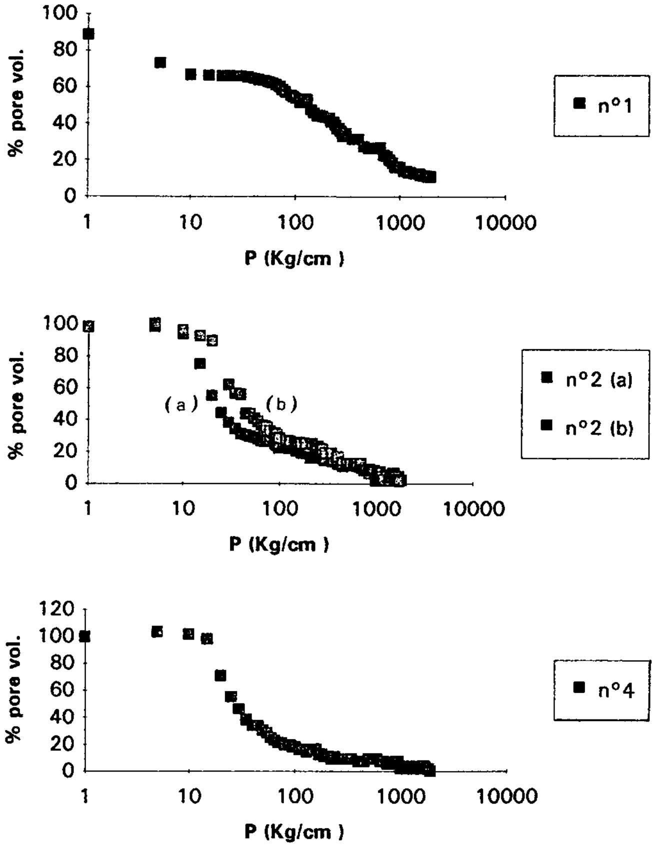

Fig. 3. Typical porosimetric curves (spread function vs. pressure (P)) for the characterization of terracotta samples. (1) Sample of prehistoric terracotta from Libyan Tadrart Acacus; (2) samples of the fictile gables from Civitella in Chieti (I-II centuries B.C.): (a), gable ‘A’, and (b), gable ‘B’; (4) samples of the pottery from excavation of the Rome “Chancery” (XV–XVI A.D.).

of the total volume for the Chieti finds and ca. 80% of the Renaissance pottery consist of pores with a radius of between 5000–1000 Å and 5000–750 Å, respectively. Such an even distribution is probably indicative of high quality productive technology [8], even taking into account the heterogeneity of the artifacts.

An analysis of the experimental data obtained for the Ariccia [1] and Chieti [9] terracottas reveals significant differences in the production of the two areas despite the relatively small difference in age and their geographical and historical proximity, even though the statues were manufactured for more or less the same purposes (votive statues or to represent

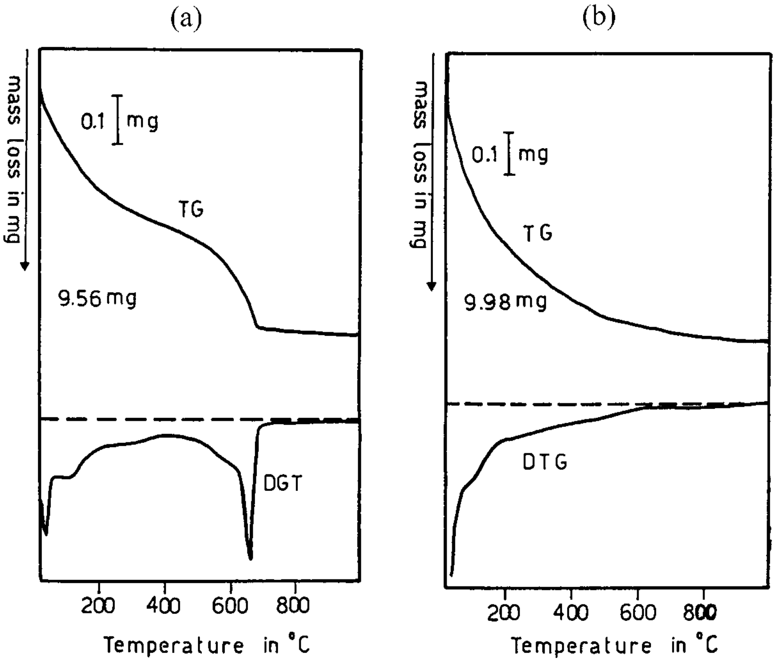

Fig. 4. Typical TG and DTG curves for the characterization of terracotta samples of fictile statues from Ariccia (Rome) (II–III centuries B.C.). Sample (a) belonging to the upper part and sample (b) from the lower part of fictile statue. Heating rate 10°C min^{-1}; in an air stream of 100 cm^3 min^{-1}.

divinities). The terracotta material comprising some of the Ariccia 'fictile finds' is characterized by significant differences between the upper and the lower parts (i.e. the base of several of the better preserved statues), particularly as far as the calcite content is concerned, which is substantially different in the upper and lower parts of several of these statues (Fig. 4) [3], while in others the difference is much slighter [1]. The foregoing observations indicate a substantial lack of homogeneity in these artifacts. The equivalent firing temperature [1,3] is, consequently, different, which would seem to indicate that the kiln operators experienced some difficulty in maintaining an even temperature throughout the kiln.

The two pediment terracottas of Civitella in Chieti, although roughly the same size as those of Ariccia, instead display a much more homogeneous paste [9]: see, for instance, the very similar calcite content (Fig. 5) and equivalent firing temperatures [9]. Overall, their technological characteristics are more reproducible, which points to the attainment of a higher degree of specialization in pottery-making in this area. Therefore, not only were definite signs of a progression in manufacturing technology found on-going from the prehistoric Libyan Tadrart Acacus terracottas, through the Roman period finds of Ariccia and Civitella in Chieti, down to the Renaissance material, but significant differences were also found in the processing technology used for the Ariccia fictile finds of terracottas and those of the pediments of Civitella in Chieti. Above all, it is interesting to observe that, although they are only a few decades apart, in the latter two cases there seems to be a considerable difference in the technological capability of the ceramists and kiln operators of the two areas. For instance, it was possible [10] to take a simple indicator, such as the quotient value of the percentage of Al_2O_3 and that of SiO_2 content obtained by plasma emission analysis (ICP) [11], or also the graphical correlation [12] of these values belonging to the Libyan samples, to those from Ariccia and from Civitella in Chieti, in order to 'separate' the pottery roughly into different sample groups [10]. It was also possible to attribute to one or other of two Civitella in Chieti pediments a number of previously dubious artifacts [13].

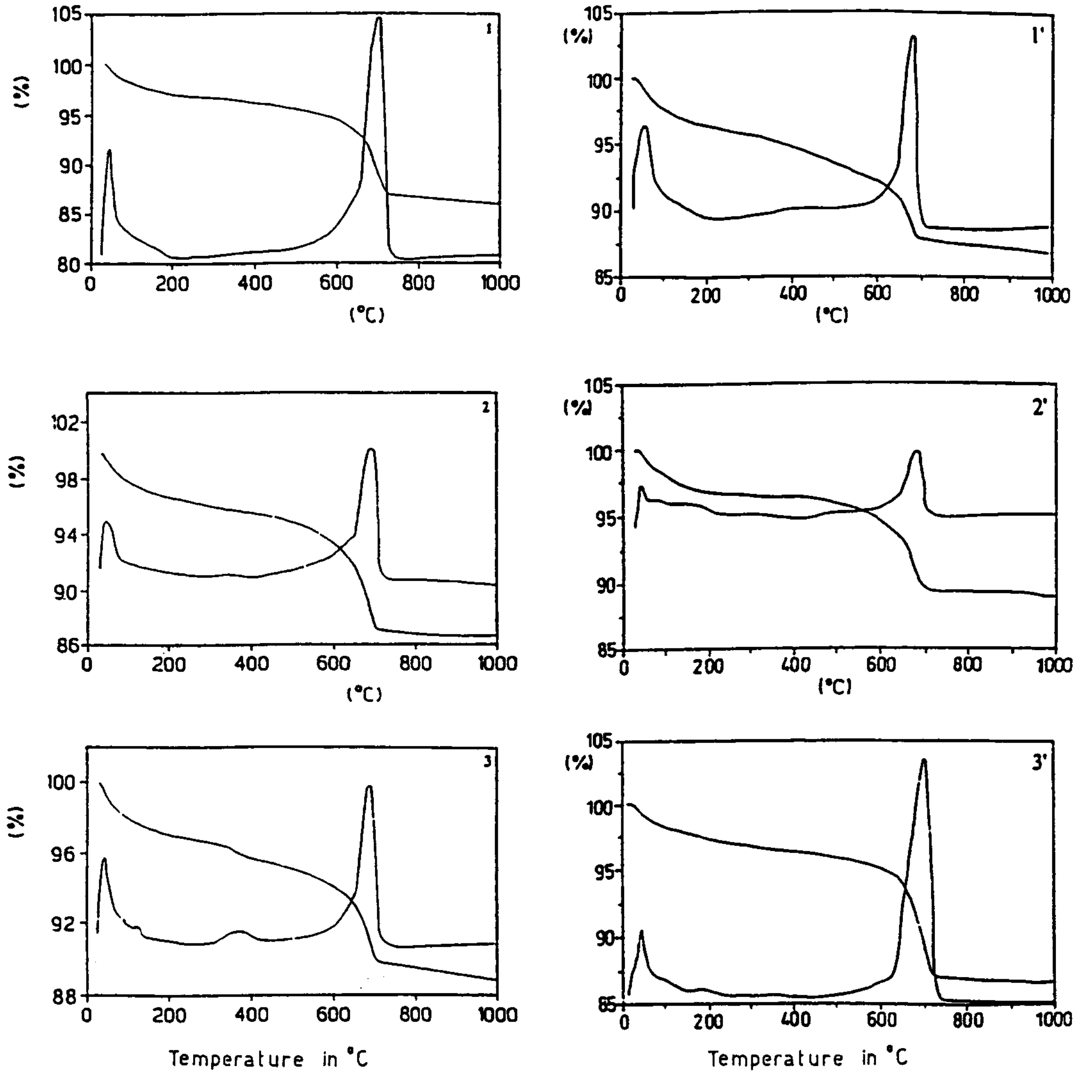

Fig. 5. Typical TG and DTG curves for the characterization of several terracotta samples of fictile gables from Civitella in Chieti (I-II century B.C.). Samples 1, 2, 3 belonging to gable type ‘A’, samples 1′, 2′, 3′, to gable type ‘B’. Heating rate 10°C min^{-1}; in an air stream of 100 $\mathrm{cm}^3\,\mathrm{min}^{-1}$.

5. Conclusions

With the aim of studying both the composition of terracotta materials and to obtain any information concerning the level of technical ability needed to build the artifacts, we analyzed some terracotta finds from different periods (prehistoric, Roman, Renaissance), using general instrumental chemical techniques. Several experimental results related to finds from the various sites have already been described in previous communications [1,3,9,13,14]. Although the samples considered were highly heterogeneous and the equivalent firing temperatures, as well as the mechanical properties and porosity, also depend on the composition of the clays employed, the type of kiln, and the purpose for which the artifacts were used [15,16], the equivalent firing temperature, the porosity of the artifacts and, to a certain extent, the percentage contents of several chemical elements appear as the most suitable parameters for checking the information

Table 2
Type of contribution made by the complex of analytical techniques used to investigate the various terracotta samples examined

	Characterization of material	Solution of specific problems	Verification of stylistic-typological assumption	Identification of historical evolution in the ceramic production technology
TL [a]	x	x	x	x
AR [b]	x	x	x	x
CH [c]	x	x	x	x
CR [d]	x	x	x	x

[a] Libyan Tadrart.
[b] Civitella in Chieti.
[c] Renaissance ceramics.
[d] Ariccia.

Table 3
Contribution made by individual analytical techniques to the solution of the different issues raised when the complete characterization of the different terracotta samples was performed

	Characterization of material [a]	Solution of specific problems [a]	Verification of stylistic-typological assumption [a]	Identification of historical evolution in the ceramic production technology [a]
TL	XR, TG, DTA, IR	XR, DTA, TG	TMA, POR, ICP	TMA, POR
AR	XR, TG, DTA, IR	XR, TG, DTA, IR	TG, DTA, XR	TMA, POR
CH	XR, TG, DTA, IR	ICP	ICP	TMA, POR
CR	XR, TG, DTA, IR	—	XR, ICP	TMA, POR

[a] XR, X-ray diffractometry; TG, thermogravimetry; DTA, differential thermal analysis; IR, infrared; TMA, thermomechanical analysis; POR, porosimetry; and ICP, inductively coupled plasma emission.

regarding the second point of our investigation, namely the different technical level of the craftsmen.

From the methodological point of view, it was possible to select the instrumental methods better suited to the research performed and from which more significant information concerning terracottas could be extracted (Tables 2 and 3). It was found that the more specifically chemical investigations in this sector, such as the ICP tests, were frequently preferable to those using X-ray diffractometry, despite the fact that the two techniques obviously gave different information. Although allowing the material to be characterized mineralogically and occasionally yielding significant results (e.g. the case of the prehistoric terracottas) [14], X-ray diffractometry did not facilitate the distinction between terracotta samples of different provenance as the mineralogical composition was often very similar on account of the fact that the main components of the clays used to make the artifacts are extremely widespread. Conversely, plasma emission spectroscopy (ICP) allows very small variations in the chemical composition of the samples to be detected and the various samples to be classified into homogeneous groups on the basis of their chemical composition. Also, thermomechanical and porosimetric analyses proved very useful as they led to the identification of a number of closely related parameters that could be used as indicators of the historical evolution of terracotta production technology. On the other hand, DTA proved effective, above all, in confirming the assignments made for the various TG steps, while the IR spectra, although also having confirmed several data previously acquired by X ray diffractometry, did not reveal any substantial novelties.

In conclusion, the instrumental analyses performed on terracotta material from different periods yielded information not only about their composition but, at least in the first instance, also concerning the different levels of technical ability attained by the craftsmen.

Acknowledgements

We wish to thank Dr. M.R. Sanzi di Mino, Archaeological Superintendent of Chieti, Dr. G. Bandini, Chief Restorer at the Museo Nazionale Romano, Ms. C. del Gallo di Roccagiovine, Restorer, and R. Ponti for making the finds available and for their invaluable collaboration.Research carried out with the financial support of C.N.R. of Italy.

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