



ELSEVIER

## Provenance study of Ligurian pottery by PIXE analysis

S. Pio<sup>a</sup>, P. Prati<sup>a</sup>, A. Zucchiatti<sup>a,\*</sup>, F. Lucarelli<sup>b</sup>, P.A. Mandò<sup>b</sup>, C. Varaldo<sup>c</sup><sup>a</sup> *Dipartimento di Fisica dell'Università and Sezione INFN, Genova, Italy*<sup>b</sup> *Dipartimento di Fisica dell'Università and Sezione INFN, Firenze, Italy*<sup>c</sup> *Istituto di Storia del Medioevo, Università di Genova, Genova, Italy*

Received 8 March 1996; revised form received 9 April 1996

### Abstract

PIXE analysis has been performed on a set of furnace rejects from archaeological excavations in the Ligurian towns of Savona and Albissola and on some finished objects from the Mediterranean area. The results show statistically significant differences between the various pottery productions examined, that can be used for the investigation of provenance. A specific case is debated in connection with historical documents and previous controversial provenance studies.

### 1. Introduction

The importance of archeometry in the classification of pottery, in the understanding of fabrication techniques and also in the identification of provenance has been widely demonstrated [1–3]. Pottery, being the most abundant tracer in all archaeological excavations, the classification at any level of such manufactures has a key role in historical studies [4,5]. The analysis of pottery can indeed supplement the information gathered from written documents to produce a better knowledge of trade routes linking populations of different areas, which is one of the essential ingredients for the comprehension of their history. Particle Induced X-ray Emission (PIXE) has been used successfully in the analysis of pottery [6–9], being capable of identifying major, minor and trace elements from sodium to lead in a non-destructive way.

In a previous paper [10] we have discussed the first results of a PIXE analysis focused on the pottery produced in Savona and Albissola (two neighbour towns along the coast of Liguria in Italy) with the aim of finding possible criteria of identification. Both towns have been important centres for pottery production while the Savona harbour has been for long time the starting point for the trade of manufactures from the whole surrounding area. The industry of quality pottery has been active in Savona from the XII century to the XIX century. In Albissola it started later, at the beginning of the XV century, but still stands as one of the major industrial activities of the town. The extraction of clay took place in two different basins distant about 5

km: from the banks of the river Letimbro in Savona and those of river Sansobbia in Albissola. The extraction activity is sufficiently documented only for Savona [11]. We have demonstrated in our previous work how the PIXE measurements of furnace rejects from the two towns can allow, to some extent, a separation of the two productions, overcoming the limits of a traditional analysis of style, shape, colour and also the limits of a mineralogical analysis of the manufactures. However it appeared necessary to extend both the set of samples and the statistical analysis, for more significant provenance studies. The need of specific measurements on a manufact being the object of a long-debated classification, was also evident. We have therefore increased the set of furnace rejects of Savona and Albissola as well as the set of potsherds from other areas including now Pisa, Montelupo, Spain and Northern Africa. We have also been able to perform new measurements on a tile from Palazzo Cerisola-Vacciolli in Savona, for which our previous analysis was not conclusive. We have finally performed a statistical analysis of all data to highlight differences and similarities between the examined samples.

### 2. Experimental procedure

#### 2.1. The choice of samples

Fifty samples, coming from archaeological excavations in the two towns of Savona and Albissola, as well as from other sites listed in Table 1, have been selected for irradiation at the INFN (Istituto Nazionale di Fisica Nucleare) facility at the University of Florence. The selection includes mostly furnace rejects. The hypothesis that rejects should have a composition more strongly related to the production site than the composition of finished manufactures

\* Corresponding author. Istituto Nazionale di Fisica Nucleare, via Dodecaneso 33, 16146 Genova, Italy. Fax: +39-10-313358, E-mail: zucc@genova.infn.it.

is generally accepted. In our specific case, this hypothesis is strengthened by the fact that only in recent times (after the XVII century) and only for the needs of particular productions (e.g. imitation of patterns of other regions) the importation of clays has been recorded. It has been already emphasised [3] that elemental analysis can, in some instances, make it possible to differentiate geographically quite close clay sources. The geo-chemical formation of clay is inherently an homogenizing process and produces clay deposits whose composition reflects closely that of the original rocks, therefore carrying the information on the geological variability of an area. Possible discrimination criteria must consider the fact that pottery has a variable composition depending on the manufacturing technique. The majority of our samples are previous to the XVIII century and belong to the peculiar production of the *graffita*'s from Albissola: therefore their selection should guarantee the local origin of the clay. However it proved difficult to select large numbers of furnace rejects of homogeneous nature. Indeed our samples belong to two broad groups: those with a red clay body (*argille*) and those with a clay marl body (*marne*), the former including mostly samples from earlier centuries. As a consequence the influence of manufacturing has to be taken carefully into consideration while assessing discriminant or similarity criteria.

## 2.2. The PIXE set-up

The PIXE facility at the University of Florence is specifically designed for the irradiation of large objects in air, and has a long record of examination of antique damageable manufactures [12–15]. PIXE, as a non-destructive analytical tool, with essentially a free geometry, is ideal for objects such as potsherds although it is limited to the analysis of a few tens of microns at most. The facility [16] includes two different Si(Li) detectors for the simultaneous acquisition of the X-ray spectra. One of them (active area 13 mm<sup>2</sup>, target to detector distance 40 mm, angle to the beam 146°) looks at the sample through a cone flushed with helium and is optimised for the detection of low *Z* elements (Na to Fe). The other one (active area 80 mm<sup>2</sup>, target to detector distance 20 mm, angle to the beam 138°) is seen through a 550 μm mylar filter and is therefore optimised for the detection of medium-high *Z* elements (Ca to Pb). In such a way it is possible to obtain significant yields for any element between *Z* = 11 and *Z* = 82 without introducing unwanted pile-up effects.

## 3. Data handling

### 3.1. Data normalisation

The measurement of absolute concentrations in thick samples is possible but would involve the correct scaling

of the data series provided by the two detectors and would be based on iterative calculations for the normalisation of concentrations. The self-consistent iterative approach, which is described in detail elsewhere [17], is in principle absolute, but it might suffer from uncertainties in the cross sections, attenuation coefficients and stopping powers. Furthermore only element oxides are taken into account.

We have chosen a simple approach to the analysis of data. The standard procedure adopted was to use iron (which is abundant in all samples and well seen by both Si(Li) detectors) as an internal reference element and normalise the yields of every element in both detectors to the yield of the respective, high statistics, iron peak. The sequence of element/Fe ratios is taken as a fingerprint of each sample and used for similarity measurements. The characterisation of the different samples retains fully its validity. Besides requiring a simpler data manipulation and preventing systematic errors, such a procedure allowed us to operate under geometric conditions not necessarily strict, since the element/Fe ratio does not depend on geometry for the same sample and the same detector. Our procedure does not cancel other effects which have been taken thoroughly into account.

### 3.2. Matrix homogeneity

For the evaluation of the matrix composition of a few samples listed in Table 2 we have applied the self consistent iterative method, limited to the major elements only. Since the samples of Table 2 come from different Mediterranean regions this evaluation should give a reasonable account of the differences in the clay composition for our samples, without requiring the analysis of the whole set. We have applied these results to the evaluation of matrix effects.

When a proton beam of energy  $E_p$  impinges at an angle  $\theta_i$  on a sample, the yield produced by an element of atomic number *Z*, mass number *A*, present with concentration *C* in a matrix whose stopping power is  $S(E)$  and seen through a solid angle  $\Delta\Omega$  by a detector of efficiency  $\epsilon$  located at an angle  $\theta_o$  is given by:

$$\begin{aligned}
 Y(Z) &= \frac{CN_0\Delta\Omega Q\epsilon}{A4\pi e} \int_{E_p}^0 \sigma_p(E) \frac{dE}{S(E)} \\
 &\quad \times \exp\left(-\mu \frac{\cos\theta_i}{\cos\theta_o} \int_{E_p}^E \frac{dE'}{S(E')}\right) \\
 &= \frac{CN_0\Delta\Omega Q\epsilon}{A4\pi e} \int_{E_p}^0 \sigma_p(E) \frac{dE}{S(E)} T(E) \\
 &= \frac{CN_0\Delta\Omega Q\epsilon}{A4\pi e} I(Z),
 \end{aligned} \tag{1}$$

where  $Q$  is the collected charge,  $e$  is the electron charge,  $N_0$  is the Avogadro's number and  $T(E)$  is the transmission

Table 1  
List of irradiated samples

Area	Type	Label	Century	Site	Procedure	Body
Savona	M	A-SFF-S	XVII	Sc.FerroFranc.	I	**
"	M	B-SFF-S	XVII	"	I	**
"	M	C-SFF-S	XVII	"	I	**
"	M	D-SFF-S	XVII	"	I	**
"	IM	E-SDO-S	XIV/V	S.Domenico	I	*
"	M	F-SDO-S	XVII/VIII	"	II	**
"	GAT	G-SDO-S	XIII	"	II	*
"	GAT	H-SDO-S	XIII	"	II	*
"	GAT	I-SDO-S	XIII	"	II	*
"	GAT	7-SDO-S	XIII	"	IV	*
"	GAT	8-SDO-S	XIII	"	IV	*
"	GAT	9-SDO-S	XIII	"	IV	*
"	IM	4-SDO-S	XII/III	"	IV	*
"	IM	L-LOP-S	XV/VI	Loggia Priamar	II	*
"	M	M-XXX-S	XVI	Not logged	III	**
"	M	N-XXX-S	XVI	"	II	**
"	TN	O-LOP-S	XVIII	Loggia Priamar	III	*
"	M	P-XXX-S	XVI	Not logged	II	**
"	M	Q-XXX-S	XVII/VIII	"	II	**
"	M	R-SIB-S	XVII	Sibilla Priamar	II	**
"	MSB	S-SPA-S	XVI	S.Paolo	II	**
Albiss.	MA	T-CCO-A	XVI	Concordia	I	**
"	M	U-CCO-A	XVII	"	I	**
"	BAC	F1-SG-A	XVII	via S.Grosso	I	**
"	MSB	M-GMB-A	XVI	rec. Gambetta	I	**
"	MSB	F2-SG-A	XVI	via S.Grosso	I	**
"	CNP	I1-IS-A	XVII	Isola	I	**
"		I4-IS-A	XVIII	"	I	*
"	IGP	I6-IS-A	XVII	"	III	*
"	GM	I3-IS-A	XVII	"	I	*
"	PT	I2-IS-A	XVI/VIII	"	I	**
"	GM	I5-IS-A	XVII	"	II	*
"	MBB	F6SG-A	XVII	via S.Grosso	I	**
"	M	F3-SG-A	XVII/VIII	"	I	* (?)
"	M	F5-SG-A	XVII/VIII	"	I	* (?)
"	PT	F4-SG-A	XVI/VIII	"	I	**
Albiss. (?)	MP	3-SDO-A	XVII-VIII	S.Domenico	IV	**
" (?)	MBB	0-SDO-A	XVII-VIII	"	IV	**
Montel.		W-M	XVI	Not logged	III	**
"	MP	1990-M	XVI (?)	S.Domenico	IV	**
"	MBG	2104-M	XVI	"	IV	**
"	MBG	2107-M	XVI	"	IV	**
Hisp.Mor.		Z-H	XV	"	II	**
"	M	1895-H	XV	"	IV	**
"	M	1896-H	XV	"	IV	**
"	M	1900-H	XV	"	IV	**
Pisa	GPS	625-PI	XVI	"	IV	*
"	GPS	647-PI	XVI	"	IV	*
N.Africa	GSV	204-NA	XIV/V	"	IV	*
Pal.C.Vac.	Tile	SPN1-CV	XVI	Broken edge	II	**
"		BKN1-CV	"	Back intact	III	
"		BKAR-CV	"	Back chipped	IV	
"		SPAR-CV	"	Edge chipped	IV	
"		SPN2-CV	"	Broken edge	IV	
"		BKN2-CV	"	Back intact	IV	

M: Maiolica; PT: Potter Tool; IM: Monochrome Ingobbiate; IGP: Polychrome Ingobbiate and Graffita; GAT: Archaic Tirrenic Graffita; GM: Monochrome Graffita; TN: Taches Noires; MBB: White Blue Maiolica; MSB: Maiolica Berettino Enameled; MP: Polychrome Maiolica; MA: Light Blue Maiolica; MBG: Maiolica Blue and Graffita; BAC: Biscotto; GPS: Point and Stick Graffita; CNP: Polychrome Naturalistic Calligraphy; GSV: Green Enameled Jar; \*: Red Clay; \*\* Clay Marl.

Table 2

Composition of the clay (weight fraction) for some samples as deduced from an iterative procedure [17]

Sample	Area	O	Mg	Al	Si	K	Ca	Fe
P-XX-S	Savona	0.454	0.014	0.074	0.266	0.020	0.087	0.085
T-CCO-A	Albissola	0.439	0.024	0.068	0.240	0.021	0.153	0.055
625-PI	Pisa	0.402	0.037	0.061	0.170	0.022	0.226	0.082
2104-M	Montelupo	0.390	0.046	0.042	0.154	0.013	0.281	0.074
1896-H	Hisp. Mor.	0.440	0.018	0.064	0.247	0.024	0.133	0.074
204-NA	N.Africa	0.418	0.022	0.055	0.213	0.035	0.188	0.069
U-CCO-A	Albissola	0.414	0.013	0.061	0.201	0.022	0.207	0.082

coefficient of the X-rays of element  $Z$  through the matrix of absorption coefficient  $\mu$ . From Eq. (1) we can write:

$$\frac{Y(Z)}{Y(\text{Fe})} = \frac{C(Z)\epsilon(Z)56}{C(\text{Fe})\epsilon(\text{Fe})A} \frac{I(Z)}{I(\text{Fe})} = \frac{C(Z)\epsilon(Z)56}{C(\text{Fe})\epsilon(\text{Fe})A} R_m. \quad (2)$$

The yield ratios  $Y(Z)/Y(\text{Fe})$  have substantially the same statistical variability of the concentration ratios  $C(Z)/C(\text{Fe})$  and can well be taken as the fingerprints of our samples. However we could have two samples where the respective  $C(Z)$  and  $C(\text{Fe})$  values are equal but the yield ratio is different because of  $R_m = I(Z)/I(\text{Fe})$ , which carries the effect of a different matrix composition. We have evaluated  $R_m$  for all elements seen in our analysis and for the matrices of Table 2. We have found a dispersion of values  $\sigma(R_m)/\langle R_m \rangle$  which is at most 14% (as reported in Table 3) with the majority of cases limited to a few percent. All values are well below the natural dispersion of our set of samples (also reported in Table 3).

### 3.3. Secondary fluorescence

The formalism for the evaluation of secondary and tertiary fluorescence of an element of mass number  $A$  induced by an element of mass number  $B$  present at concentration  $C_B$  in a sample  $S$  is well developed [18,19] and does not need to be recalled. In our samples the conditions for a simplified approach [20] are met and the ratio  $R_f$  of secondary to primary fluorescence is given by:

$$R_f = \frac{Y_{\text{sec}}}{Y_{\text{pri}}} = \frac{1}{2} \frac{r_A - 1}{r_A} \frac{B}{A} \omega_{K,B} \frac{(\mu_p)_{BA} \sigma_{K,B}(E_p)}{(\mu_p)_{BS} \sigma_{K,A}(E_p)} C_B, \quad (3)$$

where  $E_p$  is the beam energy,  $\sigma_{K,A}$ ,  $\sigma_{K,B}$  are the ionisation cross sections of the  $K$ -shell in  $A$  and  $B$  respectively,  $(\mu_p)_{BA}$ ,  $(\mu_p)_{BS}$ , are the mass attenuation coefficients of  $B$  X-rays by element  $A$  and by the sample,  $\omega_{K,B}$  is the fluorescence yield of the  $K$ -shell in element  $B$  and  $r_A$  is the ratio of the mass attenuation coefficient of element  $A$  taken just before and after the  $K$  absorption edge. We have computed, for the elements detected in our PIXE analysis, only the values of  $R_f$  induced by the nearest element (if

seen in the spectra). As  $C_B$  we have taken the values of Table 2 (sample U-CCO-A) for major elements of the average matrix and assumed 0.01 for all other elements. The results are listed in Table 3: the largest value of 4% is achieved for potassium due to the high concentration of calcium in the matrix and is negligible compared to the natural dispersion of potassium in the set of samples.

### 3.4. Preparation of samples

As it is normal with classified findings of historical and archaeological value, most of the sherds could not be manipulated at all and had to be analysed as they are. Only for the biggest pieces, provided their archaeological value

Table 3

Distribution of element/iron ratios as deduced from PIXE analysis of the set of samples compared to matrix and secondary fluorescence effects

Element	$\langle Y_Z / Y_{\text{Fe}} \rangle$	$\sigma(Y_Z / Y_{\text{Fe}})$	$\frac{\sigma(Y_Z / Y_{\text{Fe}})}{\langle Y_Z / Y_{\text{Fe}} \rangle}$	$\frac{\sigma(R_m)}{\langle R_m \rangle}$	$R_f$
Na	0.06	0.04	0.67	0.04	0.0003
Mg	0.6	0.3	0.50	0.04	0.002
Al	2.5	0.6	0.24	0.03	0.01
Si	10	2	0.20	0.05	0.0004
P	0.09	0.09	1	0.14	0.0007
S	0.1	0.2	2	0.14	0.0009
Cl	0.08	0.15	1.87	0.14	0.002
K	1.0	0.5	0.5	0.13	0.04
Ca	6	3	0.5	0.13	0.001
Ti	0.13	0.02	0.15	0.04	0.0003
Cr	0.008	0.004	0.5	0.02	0.0005
Mn	0.02	0.02	1	0.01	0.005
Co	0.004	0.002	0.5	0.01	0.0007
Ni	0.004	0.002	0.5	0.03	0.0008
Cu	0.002	0.001	0.5	0.04	0.001
Zn	0.006	0.019	3.2	0.04	0.001
Ga	0.0005	0.0003	0.6	0.04	0.001
Rb	0.0006	0.0003	0.5	0.06	0.003
Sr	0.0019	0.0008	0.4	0.06	
Zr	0.0003	0.0003	1	0.06	
Ba	0.007	0.004	0.57	0.04	
Pb	0.03	0.04	1.3	0.05	

was limited and when the operation did not alter significantly their shape and integrity, we were allowed to cut off a small specimen. We did that by using a saw to initiate a cut and then by breaking the piece along this incomplete cut, so to have always available a clean surface free of spurious elements due to machining. A tile from Palazzo Cerisola-Vacchioli in Savona was firstly exposed on two corners, that were already chipped, and on the back surface. Unfortunately, as stressed in our previous paper [10], we suspected contamination of glaze for the tile back surface, which prevented a firm characterisation of this particular sample. Due to the importance of a correct classification of this manufact, for the analyses reported in the present paper we were allowed to chip with a chisel a small area of the back surface and of a corner, to obtain two clean spots not contaminated by glaze or cutting tool and proceed to a second run of measurements. All the samples have then been exposed along their naturally broken surfaces and this imposed attention to assuring, as much as possible, planarity of the exposed surface normal to the beam axis.

### 3.5. Surface planarity

The effect on the X-ray yield of grooves and ridges present on the surface of thick samples, is well known and has been extensively debated [21,22]. The surface inspection of a few samples with a computer controlled mechanical probe has revealed departures from planarity up to  $\pm 500 \mu\text{m}$ . A calculation of the surface effect, in a complex case like ours, would be difficult and probably highly approximated. We have therefore irradiated several points on the same sample and averaged the results. This procedure should reduce drastically surface and homogeneity effects. The samples were made available for analysis in different batches and we could not use the same procedure for all samples. Therefore we have collected a spectrum over 6 different points for 18 samples (procedure I); we have taken the average of spectra collected in two different points for 12 samples (procedure II); we have collected on a single point for 4 samples (procedure III) and we have collected spectra over a few mm for 15 samples by an automatic scanning (procedure IV). The technique adopted for measuring the tile is reported in Table 1 as well. For the case where two spectra were collected, we have evaluated in each sample  $i$  the mean  $M(Z, i)$  of the two values  $V_1(Z, i)$ ,  $V_2(Z, i)$  for element  $Z$ . The distribution of the quantity

$$D(Z, i, j) = \frac{V_j - M(Z, i)}{M(Z, i)} \quad j = 1, 2 \quad (4)$$

is given in Fig. 1a. The observed variations of  $D$  (obviously symmetric) may be due both to surface roughness and to a non-homogeneous sample. The two effects cannot be separated at this stage. If we compare the

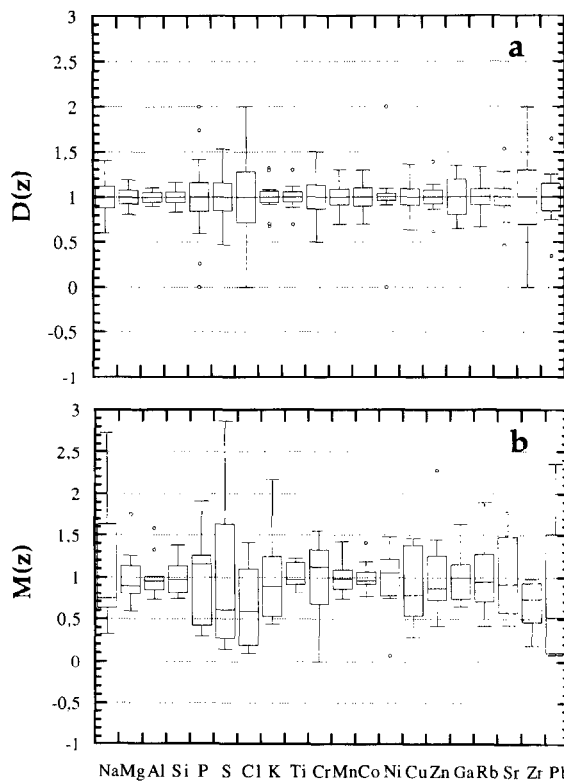


Fig. 1. (a) The box and whisker representation of the  $D(Z)$  values given by Eq. (4) for the detected elements in a subset of 12 samples; (b) The box and whisker representation of the element/iron ratios  $M(Z)$  for a subset of 12 samples.

dispersion of  $D$  with the dispersion of the elemental values, measured with the procedures indicated above over the entire set of samples and reported in Fig. 1b, we can however conclude that the dispersion introduced in the data by considering only one point as representative of the composition of the clay is for most of the elements lower than the natural distribution of the element in the set of 12 samples. The averaging procedure adopted for the most part of the samples, including the cases of a two points average, should reduce to minimum surface and homogeneity effects.

## 4. Results and discussion

For each element we took the element-iron ratio from the detector that gave the highest element yield. In almost all samples we could measure, through spectra deconvolution by the code PIXAN [23], the yields for Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Zr, Ba, Pb. The elements V, Br, Y, Ge were just above the detection limit only in a few cases and were therefore not considered in the analysis. We have first

computed average values and standard deviations for each element over the whole set of samples. The results are given in Table 4. We have already observed [10] that the pair of elements Al–Ni can discriminate the production of the two towns. The ratio  $R = (\text{Al}/\text{Fe})_{\text{small}}/(\text{Ni}/\text{Fe})_{\text{big}}$  showed a clean separation between the two sets at  $R = 2.0 \times 10^{-3}$ . Of the Albissola group 89% was above this value; of the Savona group 86% was below it. The addition of more samples has left the situation practically unchanged as seen in Fig. 2a where the 38 samples (21 from Savona, 17 from Albissola) are divided according to their provenance. In Fig. 2b the samples are instead divided according to the clay type: red clay or clay marl. It is seen that the distribution of type is homogeneous in the Ni–Al plane and therefore does not induce the provenance separation clearly seen in Fig. 2a. In Fig. 2c we have divided the samples according to their provenance using a different data normalisation. Silicon has been chosen as the internal reference element. There is again a neat separation between the data from Savona and Albissola, which therefore does not depend on the reference element. As seen in Fig. 3 we now have the separation at  $R = 2.1 \times 10^{-3}$ . Above this value lies 83% of the Albissola group below lies 86% of the Savona group. The entire set of 50 samples analysed is represented in the Al–Ni plane in Fig. 4. The 12 samples from other regions do not mix with the 38 samples from Savona and Albissola strengthening the validity of the separation criterion envisaged. The only ex-

Table 4

Distribution of element/iron ratios as deduced from PIXE analysis

Element	Average total	S.Dev. total	Average Savona	S.Dev. Savona	Average Albissola	S.Dev. Albissola
Na	0.06	0.04	0.06	0.04	0.05	0.02
Mg	0.6	0.3	0.5	0.1	0.6	0.2
Al	2.5	0.6	2.5	0.3	2.1	0.3
Si	10	2	10	1	9	1
P	0.09	0.09	0.07	0.05	0.10	0.07
S	0.1	0.2	0.07	0.09	0.12	0.09
Cl	0.08	0.15	0.04	0.07	0.03	0.03
K	1.0	0.5	0.8	0.3	0.8	0.2
Ca	6	3	4	3	5	1
Ti	0.13	0.02	0.12	0.01	0.12	0.01
Cr	0.008	0.004	0.01	0.003	0.011	0.002
Mn	0.02	0.02	0.017	0.007	0.02	0.01
Co	0.004	0.002	0.004	0.002	0.004	0.004
Ni	0.004	0.002	0.004	0.001	0.005	0.001
Cu	0.002	0.001	0.001	0.001	0.001	0.001
Zn	0.006	0.019	0.003	0.003	0.004	0.003
Ga	0.0005	0.0003	0.0004	0.0001	0.0004	0.0002
Rb	0.0006	0.0003	0.0005	0.0002	0.0005	0.0002
Sr	0.0019	0.0008	0.0016	0.0009	0.0021	0.0005
Zr	0.0003	0.0003	0.0003	0.0003	0.0003	0.0002
Ba	0.007	0.004	0.006	0.003	0.006	0.002
Pb	0.03	0.04	0.01	0.01	0.02	0.02

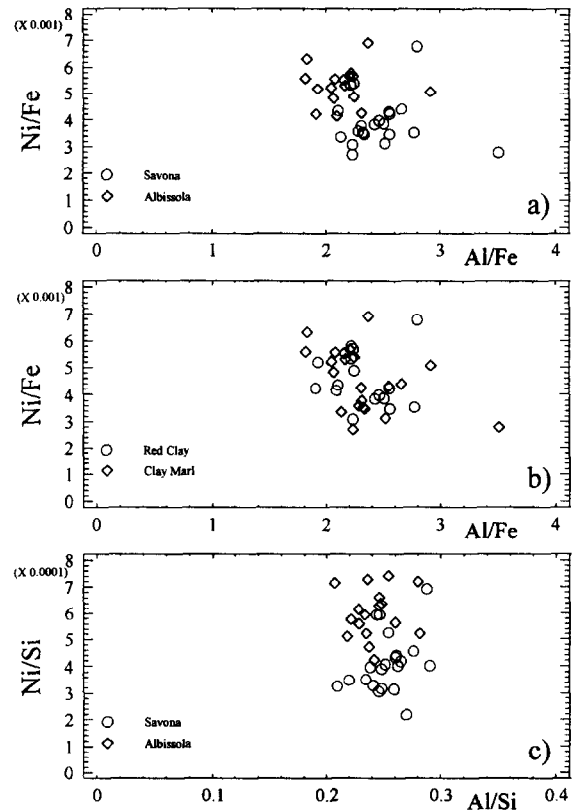


Fig. 2. (a) The distribution of the 38 samples from Savona and Albissola in the (Ni/Fe)–(Al/Fe) plane; (b) The distribution of the 38 samples from Savona and Albissola in the (Ni/Fe)–(Al/Fe) plane. The samples are identified according to their clay type: marl (open diamonds) or red clay (open circles); (c) The distribution of the 38 samples from Savona and Albissola in the (Ni/Si)–(Al/Si) plane.

ception is for two of the data coming from the tile (samples BKN1-CV and BKN2-CV) corresponding to points in the untouched back of the tile. All other tile points are clearly distinct from the Savona–Albissola cluster. They refer to two proton irradiations in broken corners (labels SPN1-CV and SPN2-CV) or to an edge (SPAR-CV) and a point in the back (BKAR-CV), cleaned for the purpose of these irradiations as explained above. It is highly probable that the result for points BKN1-CV and BKN2-CV is due to the contamination of the tile glaze that has spread, during manufacturing, from the front painted surface.

Since we have now a more complete set of data we can interpret it statistically. In particular, we can shed new light on the origin of the enamelled tiles belonging to a large wall decoration of *Palazzo Cerisola-Vaccioni* in Savona and dating from the beginning of the XVI century. We have extended the analysis to all other detected elements making use of a cluster analysis performed with the Statgraphics software package [24]. We have treated each sample as a point in a 22-dimensional space and clustered

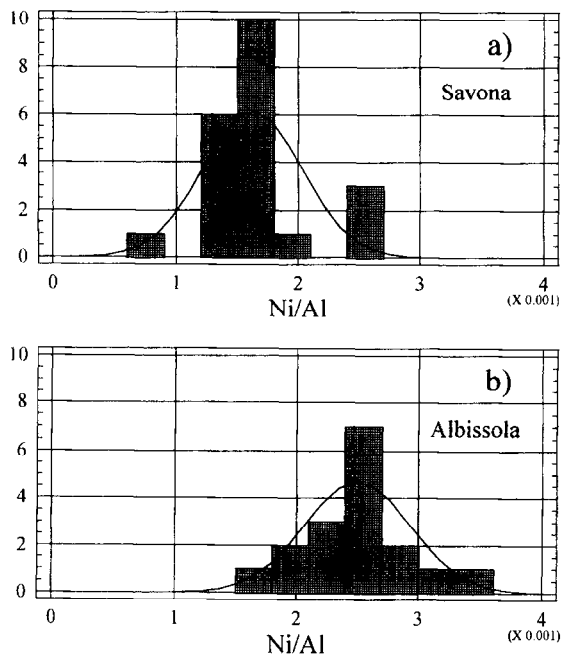


Fig. 3. (a) The histogram of the Ni/Al ratio for the Savona subset; (b) The histogram of the Ni/Al ratio for the Albissola subset.

the samples. We have employed a hierarchical strategy and used the Ward method as a grouping rule, according to the Euclidean distance computed on standardised co-ordinates. We have produced the dendrogram of Fig. 5. The dendrogram shows a few remarkable features. The Savona and Albissola samples tend to cluster in a group (A in Fig. 5) counting 35 members well separated from the samples of different origin. There is only one intruder from Pisa (647-PI) in this large subgroup. In addition it is remarkable that the findings coming from the archaeological site of San Domenico in Savona are very close to each other forming a subgroup (C) of 13 members. Samples from San Domenico are the oldest of the set and their body is made from red clay. It appears that, although the separation in the Ni–Al plane is not affected by the clay type, the inclusion of all elements in the analysis and the hierarchical grouping picks-up manufacturing correlations amongst samples. The remaining 22 members (D) are mixed with prevalence of Albissola samples. The second largest subgroup (B) has 20 members of which only 4 are from Savona and Albissola. It is remarkable that the points relative to the tile are very close to the Hispano-Moresque sherds and to the North-African sample (group E). Furthermore the two points suspected to be polluted by the glaze are close to each other and group (F) at a very late stage

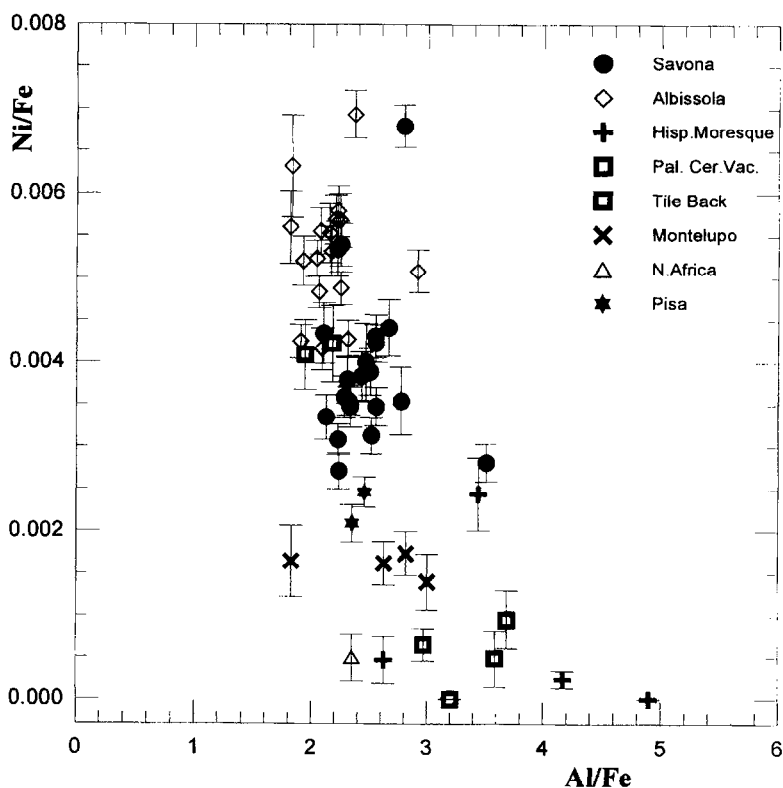


Fig. 4. The representation of all measured points in the (Ni/Fe)–(Al/Fe) plane.

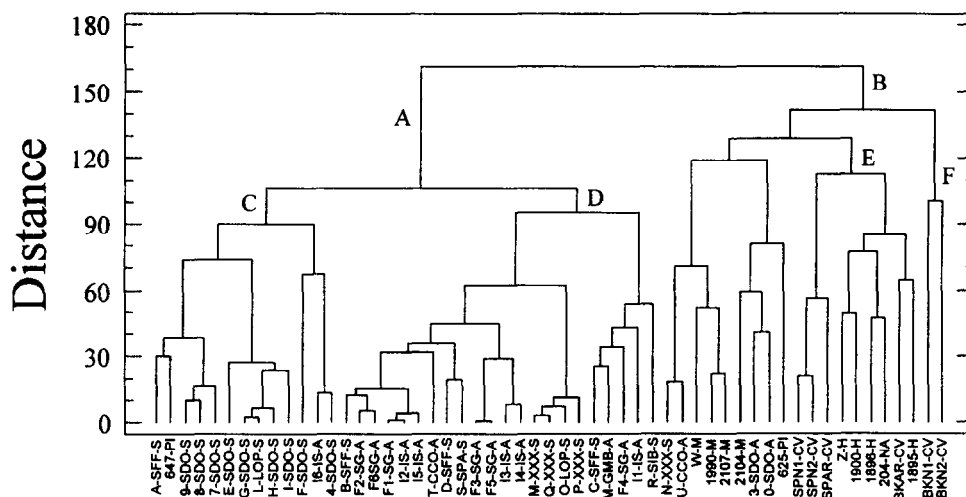


Fig. 5. The dendrogram representation of the cluster analysis of the entire set of samples. Different groups are indicated by letters at their root. See text for explanation.

with the rest of the samples. Different clustering criteria have given similar results.

On the grounds of these results and of other documents and evidences we have a more complete understanding of the Palazzo Cerisola-Vaccioni tile. Its decoration pattern is well known in the Hispano-Moresque production [25] and is very similar to another one found in the excavations of the *Hôtel de Brion* in Avignon, France [26]. The tiles of palazzo Cerisola-Vaccioni have been attributed [27], simply on historical arguments, to the Savona production which was indeed very abundant at the time, and showing similar design patterns, although most of the production was concentrated on different designs and shapes. The chemical-physical analysis of the *Hôtel de Brion* tiles has attributed their production, firstly to Savona [26], therefore giving strength to the initial attribution [27]. But at the conclusion of a long analysis work [28] the *Hôtel de Brion* tiles appeared to come from some furnace of the Provence region, where evidently the Hispano-Moresque style was imitated. Doubts about the origin of tiles from Palazzo Cerisola-Vaccioni are firstly linked to their aspect and shape. Typical enamelled tiles from the Savona area had a few crossing grooves on their back surface to facilitate the adhesion of plaster. Furthermore they were slightly thicker and wider. The typical size was  $14 \times 14 \text{ cm}^2$ . The tile from Palazzo Cerisola-Vaccioni has instead a flat back surface, as in the Spanish production. It is thinner than the typical tiles from Savona and measures only  $12.5 \times 12.5 \text{ cm}^2$ . The hypothesis that the Palazzo Cerisola-Vaccioni tiles could have been produced somewhere in Spain and brought to Savona is absolutely reasonable seen the existence of several documents recording the business relations that Antonio Cerisola, the owner of the building and a wealthy merchant, had in the Spanish area. The PIXE analysis points out remarkable differences with the produc-

tion of Savona and Albissola and shows parentage with the samples of Hispano-Moresque origin.

## 5. Conclusions

The PIXE analysis of potsherds has provided a mean of distinguishing, on the basis of major and minor elements, the pottery production of the two towns of Savona and Albissola, despite the proximity of the two centres. This is certainly a great improvement over the mineralogical essays (like thin sections, polarised light microscopy) that have so far given only generic indications for the Ligurian area. The statistical analysis of major and minor elements gives evidence of significant correlations amongst the subset of the *S. Domenico* findings and amongst the Hispano-Moresque samples and the tile from palazzo Cerisola Vaccioni in Savona, indicating also rather clearly that the Savona–Albissola production is all together well distinguished from the rest of the samples. PIXE has demonstrated its high potential in the study of the abundant pottery production of this area. The extension of the PIXE investigations to larger sets of samples from the whole northern and north-western Mediterranean coast, could add valuable information to the rich and fundamental history of this area.

## References

- [1] H. Mommsen, A. Kreuser and J. Weber, *Archeometry* 30 (1988) 47.
- [2] M. Maggetti, in: *Scienze in Archeologia*, eds. T. Mannoni and A. Molinari (Edizioni all'Insegna del Giglio, Florence, 1990) pp. 65–88.



- [3] Ch. Lanier, F.D. Preuser and L. Van Zelst, Nucl. Instr. and Meth. B 14 (1986) 1.
- [4] G. Demians d'Archinbaud and M. Picon, Coll. Intern. C.R.N.S. no. 584 (Editions du C.N.R.S., Paris, 1980) pp. 16–40.
- [5] M. Picon and G. Demians d'Archinbaud, Coll. Intern. C.R.N.S. no. 584 (Editions du C.N.R.S., Paris, 1980) pp. 125–135.
- [6] M. Peisach, Nucl. Instr. and Meth. B 14 (1986) 99.
- [7] M. Peisach, C.A. Pineda and L. Jacobson, Nucl. Instr. and Meth. B 49 (1990) 309.
- [8] A. Zucchiatti, H.J. Annegarn, M.A. Kneen and C. Varaldo, Nucl. Instr. and Meth. B 75 (1993) 463.
- [9] E.T. Evans, G. Cadet, N.A. Guardala, E. Huang and F. Winter, Nucl. Instr. and Meth. B 22 (1987) 430.
- [10] S. Pio, P. Prati, A. Zucchiatti, F. Lucarelli, P.A. Mandò and C. Varaldo, Nucl. Instr. and Meth. B 109/110 (1996) 681.
- [11] A. Cameirana, Contributo per una Topografia delle Antiche Fornaci Ceramiche Savonesi, extract from: Atti della Soc. Ligure di Storia Patria N.S., IX (LXXXIII), Vol. II (Genova, 1969).
- [12] P.A. Mandò and J.D. McArthur, Il Nuovo Saggiat. 4 (1988) 62.
- [13] J.D. McArthur, P. Del Carmine, F. Lucarelli and P.A. Mandò, Nucl. Instr. and Meth. B 45 (1990) 315.
- [14] P. Canart, P. Del Carmine, C. Federici, F. Lucarelli, J.D. McArthur, P.A. Mandò, M. Maniaci and M. Palma, Scriptorium, Vol. XLV (1991) pp. 205–225.
- [15] P. Del Carmine, M. Grange, F. Lucarelli, P.A. Mandò, in: Ancient and Medieval Book Materials and Techniques, eds. M. Maniaci and P.F. Munafò, Studi e Testi 358 (Biblioteca Apostolica Vaticana, Vatican, 1993) pp. 7–27.
- [16] P.A. Mandò, Nucl. Instr. and Meth. B 85 (1994) 815.
- [17] A.P. Santo, A. Peccerillo, P. Del Carmine, F. Lucarelli, J.D. Mac Arthur and P.A. Mandò, Nucl. Instr. and Meth. B 64 (1992) 517.
- [18] W. Reuter, A. Lurio, F. Cardone and J.F. Ziegler, J. Appl. Phys. 46 (1975) 3194.
- [19] J.L. Campbell, J.X. Wang, J.A. Maxwell and W.J. Teesdale, Nucl. Instr. and Meth. B 43 (1989) 539.
- [20] S.E. Johansson and J.L. Campbell, Pixe: A Novel Technique for Elemental Analysis (Wiley, New York, 1988).
- [21] J.A. Cookson and J.L. Campbell, Nucl. Instr. and Meth. 216 (1983) 489.
- [22] J.L. Campbell, R.D. Lamb, R.G. Leigh, G.B. Nickel and J.A. Cookson, Nucl. Instr. and Meth. B 12 (1985) 402.
- [23] E. Clayton, Pixan, AAEC/M113 (1986).
- [24] Statgraphycs plus, Manugistics Inc., Rockville, Maryland, USA.
- [25] M. Gonzalez-Marti, Ceramica del Levante espanol, Madrid-Barcelona (1944–1952).
- [26] G. Démians d'Archinbaud, L. Vallauri and J. Thiriot, Céramiques d'Avignon, les Fouilles de l'Hotel de Brion et Leur Matériel (Petit Palais Diffusion, Avignon, 1990).
- [27] C. Barile, Antiche Ceramiche Liguri (Cassa di Risparmio di Savona, Savona, 1975) p.348.
- [28] H. Amouric, Un goût d'Italie. Céramique et Céramistes Italiens en Provence du Moyen Âge au XX Siècle (Aubagne, 1993) pp. 53–55.