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THE PUNIC-HELLENISTIC CERAMIC OF PAULI STINCUS (SARDINIA, ITALY) AND IBIZA (BALEARIC ISLANDS, SPAIN): NON-DESTRUCTIVE PXRF ANALYSIS OF CERAMIC BODY AND SLIP

Abstract - C. Interdonato, M. Ramacciotti, G. Gallello, M. Lezzerini, J. Pérez Ballester, Á. Morales Rubio, *The Punic-Hellenistic ceramic of Pauli Stincus (Sardinia, Italy) and Ibiza (Balearic Islands, Spain): non-destructive pXRF analysis of ceramic body and slip.*

The present work shows the preliminary archaeometric study of the Punic-Hellenistic pottery from the archaeological sites of Pauli Stincus (Sardinia, Italy), and Avenida de España and Can Vicent d'en Jaume (Balearic Islands, Spain). An analytical non-destructive approach was employed. The sherds were analysed by a portable X-ray fluorescence spectrometer in order to characterise the ceramic body and the slip coating from the chemical point of view. Data analysis evidenced that most samples from Balearic Islands sites have similar compositions and pointed out the difference between them and those from Sardinia, suggesting the presence of different productive centres.

Key words - pXRF, archaeological pottery, PCA, non-destructive analysis, multielement analysis, Italy, Spain

Riassunto - C. Interdonato, M. Ramacciotti, G. Gallello, M. Lezzerini, J. Pérez Ballester, Á. Morales Rubio, *La ceramica punico-ellenistica di Pauli Stincus (Sardegna, Italia) e Ibiza (Isole Baleari, Spagna): analisi pXRF non distruttiva del corpo ceramico e del rivestimento.*

Questo lavoro mostra lo studio archeometrico preliminare della ceramica Punico-Ellenistica rinvenuta nei siti archeologici di Pauli Stincus (Sardegna, Italia), e Avenida de España e Can Vicent d'en Jaume (Isole Baleari, Spagna). Le analisi sono state effettuate usando un approccio non distruttivo e i lacerti sono stati analizzati con uno spettrometro di fluorescenza di raggi X portatile in modo da caratterizzare chimicamente il corpo ceramico e l'ingobbio. L'analisi dei dati ottenuti ha evidenziato che la maggior parte dei campioni provenienti dai siti delle Isole Baleari ha una composizione simile, mettendo in risalto la differenza tra questi ultimi e quelli sardi, suggerendo la presenza di centri di produzione diversi.

Parole chiave - pXRF, ceramica archeologica, PCA, analisi non distruttive, analisi multielementale, Italia, Spagna

Introduction

Ceramic sherds, found during an archaeological excavation, are valuable source of information about several aspects of the past. However, in many cases the typological studies cannot answer to all the questions asked by the archaeologists. Archaeometric analyses are often useful for determining provenance issues, reconstruction of commercials routes, and to answer questions related to the manufacturing technology (Orton & Hughes 2013; Raneri *et al.*, 2019; Vega Maeso *et al.*, 2021). In the last decades, the development of analytical approaches to integrate the results from traditional archaeological methods permitted to validate or to reject previous conjectures, leading to more robust hypothesis on provenance and technology (Whitbread, 2001; Ceccarelli *et al.*, 2018; Ramacciotti *et al.*, 2020). In particular, portable energy dispersive X-ray fluorescence spectrometers (pXRF) have become very popular to carry out multielement analysis in archaeological samples since they are easy to use, fast and require no sample treatment or minimal one, allowing the development of non-destructive approaches (Frahm & Doonan, 2013; Simsek *et al.*, 2015; Wilke *et al.*, 2016; Colomban *et al.*, 2020; Belfiore *et al.*, 2022). Anyway, these devices have weaknesses like those related to light major elements determination, especially for Na and Mg, as well as to the higher limits of detection than those of standard laboratory XRF (Hall *et al.*, 2014; Lezzerini *et al.* 2014; Hunt & Speakman, 2015). Nevertheless, though the factory calibration of different spectrometers makes it difficult to compare the concentrations obtained by the use of different devices (Brand & Brand, 2014), the results of the same model can be considered internally consistent and sufficiently accurate (Frahm, 2013; Piercey & Devine, 2014), providing for information similar to those obtained from other well-established techniques (Tanasi *et al.*, 2017; Lemoine & Halperin, 2021). This preliminary work shows the results of the archaeometric study of Punic-Hellenistic slipware (3rd-2nd BC) from the site of Pauli Stincus (Terralba) in Sardinia (Italy) and from two archaeological sites at Ibiza Island (Spain): Avenida de España (Ibiza) and Can Vicent d'en Jaume (Santa Eulària des Riu; Fig. 1). The functional study of this ceramic typology was recently carried out by Pérez

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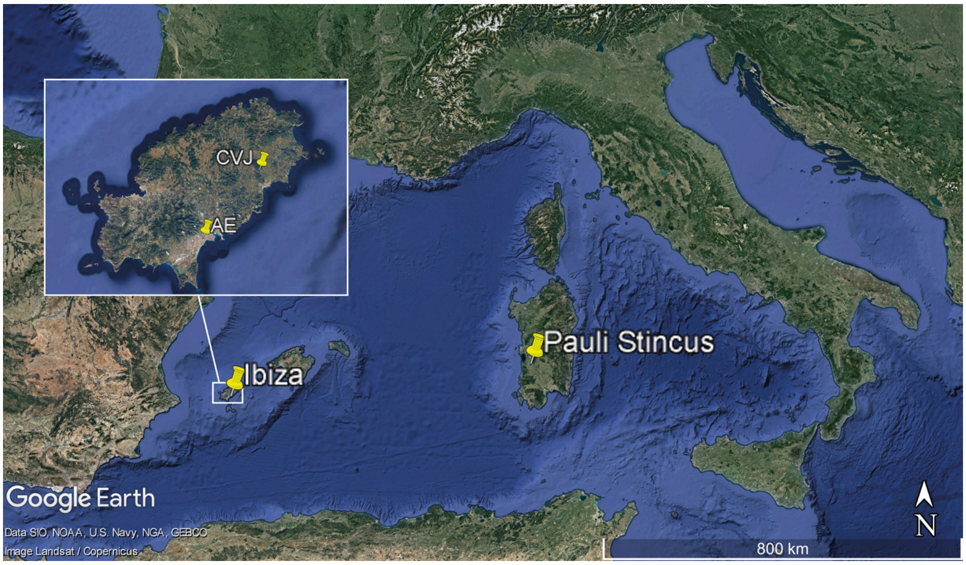

Figure 1. Localisation of Pauli Stincus (Terralba) archaeological site in Sardinia and Ibiza Island, where Avenida de España (AE; Ibiza) and Can Vicent d'en Jaume (CVJ; Santa Eulària des Riu) sites were found.

Ballester (2018), taking into account the state of the art and the main Mediterranean sites, and aligning with specifical typologies the different studied classes known by several researchers such as Morel (1980; 1986) and Pérez Ballester (2018). The diffusion of Punic black-gloss ware of Hellenistic Age interested the whole Punic and punicised world (northern Africa, Sardinia, Sicily, Balearic Islands, south-eastern Iberian coast) between the end of the 4th and the middle of the 2nd century BC, in order to cope with the reduction of pottery caused by the end of Attic importations. This definition is referred to all the local productions characterised by the technological and morphological features coming from both the Punic substratum and the Greek, and later Italic, culture (Zamparo, 2021). The present study is focused on the characterisation of the ceramic bodies and on their slips, taking advantage to a non-destructive archaeometric approach, whose limitations and potentials were evaluated as a preliminary step for further analyses.

Materials and methods

The analysed pottery

The sample list is shown in the Tab. 1. Fifteen pottery samples come from the archaeological site of Pauli Stincus (PS, Terralba; Díes Cusí *et al.*, 2010; Roppa, 2013; Perez Jordà *et al.*, 2019) in Sardinia, while the other thirty-nine samples come from the excavations of Can Vincent d'en Jaume (CVJ, Santa Eulària des Riu, five sherds; Pérez Ballester & Gómez Bellard, 2009) and Avenida España (AE, Ibiza, thirty-four sherds; Duarte, 2016) in the Island of Ibiza (Fig. 2).

The samples are sherds from tableware pottery such as plates and cups characterised by open forms like the Attic ones and with Punic influences, very common in the Mediterranean area and pertaining to the same chronological period between the 3rd and 2nd centuries BC. Some samples have a grey ceramic body and grey to black coatings, others have light brownish or rose body and black or orange slip thin, in some cases different in the outer and in the inner surfaces (Del Vais, 1997). Two black-gloss cups characterised by *petite estampilles* with a small rose on the bases stand out among the samples (Fig. 2, samples M16 and M50). These engraved decorations, as well as that shown by a Sardinian sherd with circles of grey paste (Fig. 2, sample M17), the edge of a red-gloss small cup with diagonal incisions, and the horizontal band decorations with polychrome colorations (Fig. 2, sample M37) form part of a well-known category of slipware and white-washing characterised by a non-homogeneous unique patina.

Sherds, some of which show traces of black gloss on the external surface, were cleaned with ultrapure water to remove earth remains. Sample M27 was used as a test, and it was analysed before and after cleaning (Tab. 2).

Concerning the contaminations, as can be observed in the pictures (Fig. 2, sample M27), ceramic sherds may have been affected by post-depositional processes, which could have influenced the composition of the samples by leaching or by contaminations (Schwedt 2004). The analyses before the cleaning (M27) indicated lower amounts of Al, Si and Ca than after treatment (M27e).

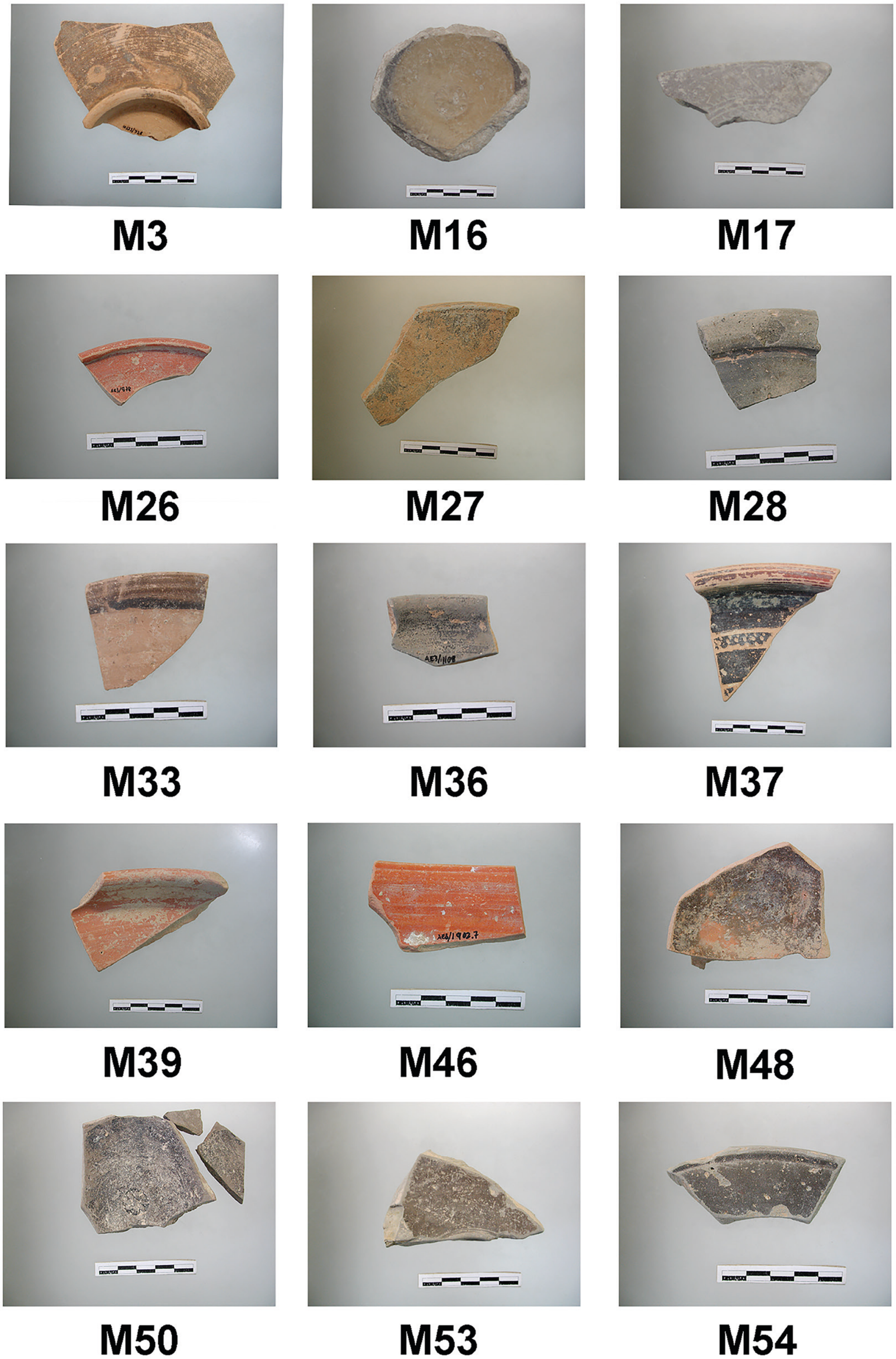

Figure 2. Example of some analysed fragments from the three archaeological sites: M3 = Ibiza, Can Vicent d'en Jaume, M16-M17 = Sardinia, Pauli Stincus and M26-M54 = Ibiza, Aves Cala.

Table 1. Samples list, provenance, and main macroscopic features.

Sample	Provenance	Shape	Type	Colour		
				Paste	Int.	Ext.
M1	IB CVJ	II	1A aprox. L55	G		B
M2	IB CVJ	IV 1 B	1b aprox. L25	G		B
M3	IB CVJ	Base		OR	R	BR
M4	IB CVJ	V-1	aprox. Guerrero 27	R/ OR	R	R
M5	IB CVJ			Y		B
M6	SA PS	I-1a	aprox. L36	Y	R/BR	
M7	SA PS	IV-1a	aprox. L27b	Y		B/BR
M8	SA PS	Base		P		OR
M9	SA PS	IV-1a	aprox. L27b	P/AN		R/OR
M10	SA PS	II-2		R		R
M11	SA PS	I-2	aprox. L23	Y		B
M12	SA PS	Shape II-1b		Y		B/BR
M13	SA PS			P		BR
M14	SA PS	Shape V-22	aprox. L22	R/OR		OR
M15	SA PS			OR		BR/R
M16	SA PS	Base ros cent		G		B
M17	SA PS	Base circ inc		G		G
M18	SA PS	Base		G	B	
M19	SA PS	Base		G		G
M20	SA PS	V-1b	aprox. Guerrero 27	G		B
M21	IB AE1 Lev 3	I-2	aprox. L23	Y		BR
M22	IB AE 1 Lev 3	IV-1a	aprox. L27b	P		BR
M23	IB AE1 Lev 3	I-4		P		BR/OR
M24	IB AE 1 Lev 3	IV-1a	aprox L27b	P		OR
M25	IB AE 1 Lev 3	V-1b	aprox. Guerrero 27	OR		R
M26	IB AE 1 Lev 3	II-1a	aprox. L55	P/OR		R
M27	IB AE 1 Lev 3	I-2	aprox. L23	G		B
M28	IB AE 1 Lev 3	II-1b		G		G
M29	IB AE 1 Lev 3	I-2	aprox. L23	G		B
M30	IB AE 1 Lev 3	IV-1a	aprox. L27b	P		R/BR
M31	IB AE 1 Lev 2	IV-1a	aprox. L27b	P		BR
M32	IB AE 1 Lev 2	V-1b	aprox. Guerrero 27	P		R/OR
M33	IB AE 1 Lev 2	III-1	aprox. L31/33	P		B/BR
M34	IB AE 1 Lev 2	III-4		G		B
M35	IB AE 1 Lev 2	Base		G		N
M36	IB AE 1 Lev 2	IV-1a	aprox. L27b	G		B
M37	IB AE1 Lev 2	V-3		P	BR	BR
M38	IB AE1 Lev 2	V-1	aprox Guerrero 27	P/OR		BR/OR
M39	IB AE 1 Lev 2	V-1	aprox Guerrero 27	P/BR		B/BR
M40	IB AE 1 Lev 2	V-1	aprox Guerrero 27	P		B/BR
M41	IB AE 1 Lev 2	V-1	aprox Guerrero 27	P		R
M42	IB AE1 Lev 2	V-1	aprox Guerrero 27	P		BR/OR
M43	IB AE 1 Lev 2	III-1	aprox L31/33	P		BR
M44	IB AE2 Lev 4			G		G?
M45	IB AE2 Lev 4		studied	R		R/BR
M46	IB AE 2 Lev 4	V-1	aprox Guerrero 27	OR	R	BR
M47	IB AE 2 Lev 4			P		R/OR
M48	IB AE 2 Lev 4	Base		P	B/BR	
M49	IB AE 2 Lev 4	Base		Y		B
M50	IB AE 2 Lev 4	Base ros centr		G		G/BR
M51	IB AE 2 Lev 4	I-3	aprox L6	G		G?
M52	IB AE 2 Lev 4	Base		G/BR		B
M53	IB AE 2 Lev 4	I-2	aprox. L23	G		B
M54	IB AE 2 Lev 4	I-2	aprox. L23	G		G?

Int.: internal surface, Ext.: external surface; B: black; G: Grey; BR: brown; Y: yellow; P: pink; OR: orange; IB AE: Ibiza Aves Cala; IB CVJ: Ibiza Can Vicent d'en Jaume; SA PS: Sardinia Pauli Stincus.

Table 2. Chemical composition of sample M27 before and after cleaning (M27e).

Sample	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Zn	Rb	Sr	Zr	Ba
M27	22.92	53.34	2.26	14.83	0.71	0.05	5.74	0.01	0.01	0.04	0.02	0.07
M27e	27.39	50.49	1.90	14.66	0.58	0.05	4.77	0.01	0.01	0.04	0.02	0.08

Concentrations are expressed as mass percentage; Na_2O, MgO and P_2O_5 are below detection limits.

Table 3. Results of the analysis of the ceramic body of samples from CVJ.

Sample	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Zn	Rb	Sr	Zr	Ba
M1m	24.07	55.00	4.61	9.20	0.89	0.07	6.03	0.01	0.02	0.03	0.02	0.05
M2m	22.79	56.36	3.50	10.54	0.88	0.02	5.79	0.01	0.02	0.03	0.02	0.04
M3m	20.04	54.45	3.06	15.68	0.90	0.04	5.72	0.01	0.01	0.03	0.02	0.04
M4m	19.52	55.17	3.21	16.10	0.80	0.02	5.03	0.01	0.02	0.03	0.02	0.07
M5m	16.76	61.03	2.01	13.98	0.92	0.02	5.16	0.01	0.01	0.02	0.03	0.05
Mean	*20.64*	*56.40*	*3.28*	*13.10*	*0.88*	*0.03*	*5.55*	*0.01*	*0.02*	*0.03*	*0.02*	*0.05*

Concentrations are expressed as mass percentage; Na_2O, MgO and P_2O_5 are below detection limits.

Table 4. Results of the analysis of the slip for samples from CVJ.

Sample	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Zn	Rb	Sr	Zr	Ba
M1e	27.57	53.71	4.35	8.55	0.82	0.05	4.84	0.01	0.02	0.02	0.02	0.04
M2e	24.50	56.51	5.57	6.18	0.99	0.04	6.08	0.01	0.02	0.02	0.02	0.06
M3e	23.48	54.96	5.76	8.59	0.99	0.05	6.05	0.02	0.01	0.03	0.02	0.04
M4e	24.45	55.32	5.14	7.54	1.35	0.04	6.02	0.01	0.02	0.03	0.02	0.06
M5e	22.74	58.79	2.19	9.52	1.05	0.02	5.58	0.01	0.01	0.02	0.03	0.04
Mean	*24.55*	*55.86*	*4.60*	*8.08*	*1.04*	*0.04*	*5.71*	*0.01*	*0.02*	*0.02*	*0.02*	*0.05*

Concentrations are expressed as mass percentage; Na_2O, MgO and P_2O_5 are below detection limits.

Energy dispersive X-ray fluorescence spectroscopy (pXRF)

Non-destructive analyses were performed on the samples using a S1 Titan pXRF by Bruker, equipped with a Rhodium X-ray tube (50 keV) and X-Flash®SDD detector (resolution: 147 eV; Full Width at Half Maximum, FWHM: 5.9 keV). Geochem Trace application with factory calibration was used to obtain quantitative data on Al_2O_3, SiO_2, K_2O, CaO, TiO, MnO, Fe_2O_3, Zn, Rb, Sr, Zr and Ba concentrations.
For each sample, three measurements were carried out on different clean areas of both ceramic body and slip coating. Results were then averaged.

Data analysis

Statistical data analysis was carried out by R (version 4.1.2; R Core Team, 2021) using the factoextra R package (version: 1.0.7; Kassambara & Mundt, 2020). Two principal component analysis (PCA) models were built taking into account all the analytes (Al_2O_3, SiO_2, K_2O, CaO, TiO, MnO, Fe_2O_3, Zn, Rb, Zr, Sr and Ba) previously standardised (i.e., Z-scores were employed for each variable). PCA was applied to all the chemical data, including ceramic body and slip coatings.

Results

Ibiza

The results of the analysis of ceramic body and slip thin of the samples from Can Vincent d'en Jaume (CVJ) are shown in Tabs 3 and 4, respectively. The analyses show similar contents of trace elements, although the slip thin has higher or slightly higher concentrations of most of the analysed major elements except for Ca.
Concerning CVJ, the sherds show some differences through which two groups can be distinguished. M1 (patera base) and M2 (small cup edge) are black-glossed ceramic with grey matrix and are characterised by low levels of calcium and potassium compared to the average. M3 and M4 are covered by red and brown gloss and show higher levels of the above-quoted elements. Sherd M5, characterised by yellow matrix and black gloss, has the lowest levels of potassium.

Table 5. Results of pXRF analysis for ceramic body of AE samples.

Sample	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Zn	Rb	Sr	Zr	Ba
M21m	19.03	51.34	2.61	19.83	0.78	0.08	6.20	<0.01	0.01	0.04	0.02	0.06
M22m	14.67	57.40	3.27	18.62	0.75	0.03	5.13	<0.01	0.01	0.05	0.02	0.05
M23m	18.20	55.25	3.06	17.48	0.75	0.02	5.10	0.01	0.02	0.04	0.02	0.05
M24m	18.85	58.03	3.08	13.65	0.82	0.02	5.40	0.01	0.02	0.04	0.02	0.06
M25m	20.38	57.35	3.27	11.12	0.91	0.04	6.78	0.01	0.02	0.03	0.03	0.06
M26m	18.26	56.13	3.31	15.70	0.81	0.02	5.65	0.01	0.01	0.03	0.02	0.05
M27m	19.57	51.44	2.70	19.85	0.64	0.06	5.59	0.01	0.01	0.04	0.02	0.07
M28m	24.96	49.84	1.58	17.38	0.69	0.03	5.37	0.01	0.01	0.04	0.02	0.07
M29m	19.13	55.47	2.91	13.67	0.87	0.04	7.78	0.01	0.02	0.02	0.02	0.06
M30m	13.23	46.49	2.54	32.53	0.63	0.05	4.38	0.01	0.01	0.05	0.02	0.06
M31m	21.33	55.12	3.25	13.51	0.86	0.02	5.78	0.01	0.02	0.04	0.02	0.04
M32m	17.66	63.72	4.93	7.54	0.83	0.03	5.17	0.01	0.01	0.03	0.02	0.05
M33m	20.23	55.40	3.25	14.85	0.85	0.02	5.28	0.01	0.02	0.03	0.02	0.04
M34m	23.23	54.56	3.99	10.30	0.93	0.06	6.79	0.01	0.02	0.03	0.02	0.06
M35m	17.41	55.77	2.84	17.23	0.91	0.04	5.66	0.02	0.01	0.04	0.02	0.05
M36m	20.82	58.00	2.01	10.70	1.02	0.04	7.27	0.01	0.01	0.04	0.02	0.06
M37m	17.90	57.66	2.94	15.06	0.94	0.02	5.37	0.01	0.01	0.03	0.02	0.04
M38m	20.84	58.05	3.57	9.77	0.95	0.04	6.62	0.01	0.02	0.03	0.02	0.08
M39m	19.79	61.91	3.66	7.39	0.94	0.02	6.13	0.02	0.02	0.03	0.03	0.06
M40m	16.38	53.50	3.09	20.22	0.78	0.02	5.89	0.01	0.01	0.03	0.02	0.05
M41m	21.42	57.86	2.72	9.28	0.88	0.04	7.63	0.02	0.01	0.04	0.03	0.07
M42m	20.62	62.17	4.20	5.97	1.09	0.03	5.77	0.02	0.02	0.03	0.02	0.06
M43m	24.44	55.40	3.79	8.81	1.00	0.04	6.37	0.01	0.02	0.03	0.02	0.07
M44m	21.47	57.80	3.75	9.49	0.97	0.04	6.34	0.01	0.02	0.03	0.02	0.06
M45m	17.46	56.26	3.26	15.10	0.94	0.03	6.82	0.01	0.02	0.04	0.02	0.04
M46m	22.70	54.29	3.98	11.53	0.88	0.06	6.40	0.01	0.02	0.04	0.02	0.07
M47m	14.88	53.37	3.01	22.92	0.77	0.02	4.91	0.01	0.01	0.04	0.02	0.04
M48m	19.16	60.75	2.96	10.69	1.07	0.03	5.20	0.01	0.01	0.04	0.02	0.06
M49m	21.38	57.32	1.40	12.28	1.02	0.03	6.44	<0.01	0.01	0.04	0.02	0.06
M50m	14.74	54.10	3.29	22.46	0.76	0.02	4.50	0.01	0.01	0.04	0.02	0.05
M51m	20.32	54.29	3.57	14.60	0.86	0.04	6.15	0.01	0.02	0.05	0.02	0.07
M52m	18.50	56.22	3.29	15.17	0.86	0.02	5.81	0.01	0.02	0.03	0.02	0.05
M53m	21.30	59.70	5.04	6.39	0.90	0.03	6.48	0.01	0.02	0.02	0.02	0.09
M54m	20.59	58.71	4.86	7.53	0.92	0.04	7.21	0.01	0.02	0.02	0.02	0.07
Mean	*19.44*	*56.20*	*3.26*	*14.08*	*0.87*	*0.03*	*5.98*	*0.01*	*0.02*	*0.04*	*0.02*	*0.06*

Concentrations are expressed as mass percentage; Na_2O, MgO and P_2O_5 are below detection limits.

Samples from Avenida de España (AE) have chemical compositions (Tabs 5 and 6) similar to those from CVJ for Al_2O_3, SiO_2, K_2O, CaO and Fe_2O_3. Those samples can be distinguished in two groups on the basis of matrix calcium levels. M50, base of a black-gloss small cup, and M30 can be distinguished due to the lowest levels of aluminium and silicon, and the highest ones of calcium.

Sardinia

The samples from Sardinia are mostly heterogeneous. Results from pXRF of slip coating show higher levels of aluminium and silicon than the ceramic body (Tabs 7 and 8). They show lower concentrations of Al_2O_3 and SiO_2, as well as of CaO and K_2O, as evidenced also by the study of Vendrell *et al.* (2014, no published report).

Table 6. Results of pXRF analysis for slip coating of AE samples.

Sample	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Zn	Rb	Sr	Zr	Ba
M21e	21.63	57.93	1.86	10.78	0.98	0.04	6.66	0.00	0.01	0.04	0.02	0.05
M22e	23.07	53.29	4.59	11.30	0.88	0.03	6.71	0.00	0.01	0.04	0.02	0.06
M23e	22.50	58.83	4.73	7.53	0.83	0.04	5.39	0.01	0.02	0.04	0.02	0.06
M24e	24.34	59.67	4.50	4.70	0.92	0.03	5.70	0.01	0.02	0.03	0.02	0.06
M25e	21.89	54.09	4.83	10.86	0.94	0.04	7.20	0.01	0.02	0.03	0.03	0.06
M26e	23.99	56.99	4.76	6.52	0.87	0.02	6.71	0.01	0.02	0.03	0.02	0.06
M27e	27.39	50.49	1.90	14.66	0.58	0.05	4.77	0.01	0.01	0.04	0.02	0.08
M28e	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M29e	23.48	52.76	4.44	9.74	0.98	0.06	8.41	0.01	0.02	0.02	0.02	0.06
M30e	26.42	52.74	5.03	8.99	0.86	0.05	5.77	0.01	0.01	0.04	0.02	0.06
M31e	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M32e	20.08	60.27	5.58	6.75	1.03	0.05	6.12	0.01	0.01	0.03	0.02	0.05
M33e	27.08	52.79	4.62	8.23	0.87	0.03	6.23	0.01	0.02	0.03	0.02	0.07
M34e	25.04	53.82	3.81	8.91	1.01	0.05	7.21	0.01	0.02	0.03	0.02	0.07
M35e	15.93	66.84	2.52	7.06	1.15	0.04	6.32	0.02	0.01	0.04	0.02	0.05
M36e	21.00	57.72	1.95	10.00	1.06	0.03	8.10	0.02	0.01	0.04	0.02	0.05
M37e	26.65	53.77	7.52	4.53	0.93	0.04	6.44	0.01	0.02	0.03	0.02	0.04
M38e	26.88	55.88	4.60	4.81	1.02	0.03	6.64	0.01	0.02	0.02	0.03	0.06
M39e	21.79	61.87	4.41	4.24	0.99	0.03	6.49	0.04	0.02	0.02	0.03	0.07
M40e	22.85	58.09	4.36	6.39	0.89	0.04	7.25	0.01	0.02	0.03	0.02	0.05
M41e	20.64	60.96	1.96	8.46	1.03	0.03	6.75	0.02	0.01	0.04	0.03	0.07
M42e	24.31	59.97	5.21	2.79	1.06	0.04	6.48	0.02	0.02	0.03	0.02	0.05
M43e	26.14	54.41	4.47	7.51	0.99	0.03	6.31	0.01	0.02	0.03	0.02	0.06
M44e	23.38	59.00	4.73	5.53	1.07	0.02	6.13	0.01	0.02	0.03	0.02	0.06
M45e	24.74	53.43	4.60	9.24	0.90	0.04	6.90	0.02	0.02	0.04	0.02	0.05
M46e	23.66	55.82	5.33	7.20	1.12	0.03	6.69	0.01	0.02	0.04	0.02	0.06
M47e	21.48	51.19	4.07	15.79	0.84	0.08	6.40	0.01	0.01	0.05	0.02	0.06
M48e	27.62	54.76	5.54	5.00	0.90	0.02	6.04	0.01	0.01	0.04	0.02	0.04
M49e	20.03	57.99	1.67	11.84	1.08	0.04	7.21	0.00	0.01	0.05	0.02	0.06
M50e	14.45	55.16	3.70	20.72	0.93	0.03	4.89	0.01	0.01	0.04	0.02	0.04
M51e	22.34	53.47	3.25	13.43	0.80	0.04	6.50	0.01	0.01	0.05	0.02	0.08
M52e	23.71	54.93	5.50	7.83	0.93	0.04	6.94	0.01	0.02	0.03	0.02	0.04
M53e	20.50	61.01	5.38	6.29	0.88	0.04	5.72	0.03	0.02	0.02	0.02	0.09
M54e	22.87	58.64	5.41	4.97	0.97	0.03	6.95	0.01	0.02	0.02	0.03	0.08
Mean	*23.06*	*56.52*	*4.28*	*8.52*	*0.95*	*0.04*	*6.50*	*0.01*	*0.02*	*0.03*	*0.02*	*0.06*

Concentrations are expressed as mass percentage; Na_2O, MgO and P_2O_5 are below detection limits; n.d. = not determined.

However, samples from Pauli Stincus can be distinguished on the basis of Ba and Sr concentrations.
However, some samples show peculiar chemical features:
– M6, sherd of a plate with extroverted edge characterised by light coloured matrix and red on the external surface, and M7, fragment of a small cup with light coloured ceramic body and black external surface, show the highest amounts of Ba and Sr. Slip coating of both samples have higher concentrations of aluminium and silicon.
– M13, characterised by rose matrix and brown slip, is similar to the samples from Ibiza due to high levels of Ca and low ones of Ba.

Table 7. Results of pXRF analysis for ceramic body of PS samples.

Sample	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Zn	Rb	Sr	Zr	Ba
M6m	11.68	57.44	4.05	18.16	0.80	0.09	7.53	0.02	0.02	0.07	0.02	0.12
M7m	13.23	62.02	3.09	14.47	0.73	0.09	6.09	0.02	0.02	0.08	0.02	0.14
M8m	17.40	58.83	3.59	11.61	0.86	0.07	7.41	0.01	0.02	0.05	0.02	0.13
M9m	20.01	58.71	3.54	8.55	0.82	0.16	7.99	0.01	0.02	0.01	0.02	0.16
M10m	15.18	60.80	3.00	14.75	0.67	0.04	5.43	0.01	0.01	0.04	0.02	0.05
M11m	16.27	57.89	2.85	15.35	0.76	0.05	6.63	0.01	0.01	0.06	0.02	0.10
M12m	15.47	57.27	3.11	16.83	0.58	0.07	6.44	0.01	0.01	0.05	0.02	0.14
M13m	21.10	55.26	2.48	14.27	0.89	0.02	5.86	0.01	0.01	0.04	0.02	0.04
M14m	23.11	64.35	3.30	1.29	0.80	0.08	6.89	0.01	0.01	0.01	0.03	0.12
M15m	16.07	57.48	2.94	16.90	0.69	0.07	5.66	0.01	0.02	0.05	0.02	0.09
M16m	23.05	65.26	3.52	0.54	1.01	0.06	6.38	0.03	0.02	0.01	0.02	0.10
M17m	16.17	58.17	3.53	13.09	0.80	0.15	7.88	0.01	0.01	0.01	0.02	0.16
M18m	16.90	62.55	3.26	9.07	0.89	0.08	6.95	0.01	0.01	0.05	0.02	0.21
M19m	14.25	57.07	2.64	19.73	0.63	0.06	5.42	0.01	0.01	0.06	0.02	0.10
M20m	19.01	57.77	2.28	12.25	0.76	0.12	7.61	0.01	0.01	0.02	0.02	0.14
Mean	*17.26*	*59.39*	*3.15*	*12.46*	*0.78*	*0.08*	*6.68*	*0.01*	*0.01*	*0.04*	*0.02*	*0.12*

Concentrations are expressed as mass percentage; Na_2O, MgO and P_2O_5 are below detection limits.

Table 8. Results of pXRF analysis for slip coating of PS samples.

Sample	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Zn	Rb	Sr	Zr	Ba
M6e	26.41	52.61	8.11	5.53	0.61	0.18	6.30	0.02	0.02	0.06	0.02	0.13
M7e	38.91	45.18	5.09	3.22	0.73	0.12	6.46	0.05	0.02	0.06	0.02	0.14
M8e	24.91	53.85	4.72	7.65	0.89	0.10	7.67	0.01	0.01	0.05	0.02	0.12
M9e	21.61	57.65	4.67	6.95	0.90	0.09	7.89	0.02	0.02	0.01	0.02	0.17
M10e	24.17	58.35	3.49	7.32	0.84	0.05	5.63	0.01	0.01	0.03	0.02	0.08
M11e	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M12e	21.46	55.70	7.57	7.46	0.61	0.07	6.90	0.03	0.02	0.05	0.02	0.11
M13e	21.02	54.25	3.22	13.86	0.86	0.06	6.61	0.01	0.01	0.04	0.02	0.04
M14e	31.69	54.89	4.02	1.04	0.77	0.06	7.35	0.02	0.01	0.02	0.03	0.10
M15e	29.17	53.68	4.04	6.90	0.57	0.03	5.43	0.01	0.02	0.05	0.02	0.08
M16e	20.96	61.90	3.62	5.26	1.02	0.09	6.95	0.04	0.02	0.01	0.02	0.11
M17e	17.80	59.09	4.23	10.87	0.80	0.12	6.87	0.01	0.02	0.01	0.02	0.16
M18e	31.70	50.68	4.62	4.55	0.94	0.08	7.15	0.01	0.01	0.05	0.02	0.19
M19e	14.52	53.98	2.74	22.11	0.64	0.07	5.74	0.01	0.01	0.05	0.02	0.11
M20e	24.83	52.54	4.17	9.43	0.79	0.11	7.93	0.01	0.01	0.02	0.02	0.14
Mean	*24.94*	*54.60*	*4.59*	*8.01*	*0.78*	*0.09*	*6.78*	*0.02*	*0.02*	*0.04*	*0.02*	*0.12*

Concentrations are expressed as mass percentage; Na_2O, MgO and P_2O_5 are below detection limits; n.d. = not determined.

– M14, red-glossed small cup has very low concentrations of CaO, which is 1.29% in the ceramic body and 1.04% in the slip thin. It has the highest concentrations of Sr, which is 0.12% in the mass and 0.03% in the slip.
– M16, base of a black-gloss ceramic with a rose stamp, shows high amounts of Al_2O_3 and SiO_2, and low amounts of CaO compared to the other samples, which is just 0.54% in the ceramic body and 5.26% in the slip.
– M19, fragment of a black-glossed plate with extroflected edge with grey ceramic body, have the highest CaO percentages.

PCA study

PCA was carried out on both ceramic body (Fig. 3) and slip coating (Fig. 4).

The first two PCs explain 51.6% of the overall variance in ceramic body PCA, and 46.1% of it in slip coating one. The results from the two PCAs are very similar. Indeed, we can observe in the samples/scores plots (Figs 3a and 4a) that pottery from the two Ibiza sites fall together and can be discriminated from most of those from Sardinia on the PC2-axis for ceramic body and on the PC1-axis for the slip, due to the low scores of the former. However, it must be pointed out that, according to the PCA, samples M10 and M13 from Sardinia have chemical features closer to those from Ibiza both in ceramic body and slip. As can be observed in loadings plots (Figs 3b-c and 4b-c), the variables with the highest influence on the discriminant axes are MnO and Ba, which are negatively correlated with these PC.

Discussion

As can be observed in Tabs 2-8, in most of the cases slip coatings show higher contents of major elements (Al_2O_3, SiO_2, K_2O, TiO, MnO and Fe_2O_3) except for calcium that is higher in ceramic body. As suggested by previous studies on the same typologies (Nicosia *et al.*, 2013; Vendrell *et al.*, 2014; Amadori *et al.*, 2017; Maritan *et al.*, 2019), slip thin is a *barbottina* applied by immersion composed by selected clay, which functions as a flux during the firing, developing vitrification and increasing the hardness and the brightness of the slip. Vendrell *et al.* (2014) carried out petrographic and chemical analyses of the pottery from both Ibiza and Pauli Stincus, some of which were studied in the present work (M2-5, M9, M15, M50). Data indicated that the coating has variable width up to 50 µm. The study suggested that in this case the slip is not present and the alternation of oxidising and reducing phases produced blackish and reddish colours due to the oxidation of iron oxides.

As regards black-glossed pottery from the Hellenistic age, though the scarce variability of the typologies, they have autochthone features with different colourations and firing techniques. Analytical results evidenced in most of the samples features (M8, M9, M11, M12, M17, M18) similar to the ones of the ceramics from the Sardinian sites of Tharros (Amadori *et al.*, 2004; 2006; 2017) and Nora (Maritan, 2019). Major elements and some traces (e.g.: Ba and Sr) evidenced a certain homogeneity in the pottery from Sardinia, except for the above-quoted samples (M10-M13), which were probably imported from Ibiza. These samples can be discriminated from the ceramic of Cartago (Amadori *et al.*, 2017) and from some Italic productions (Bacci Tigano, 2002). It can be hypothesized a local production that imitated some typologies. The ceramic from Ibiza and those from Cartago show also higher levels of CaO, compared to the Sardinian ones, but more research is needed to obtain conclusive results.

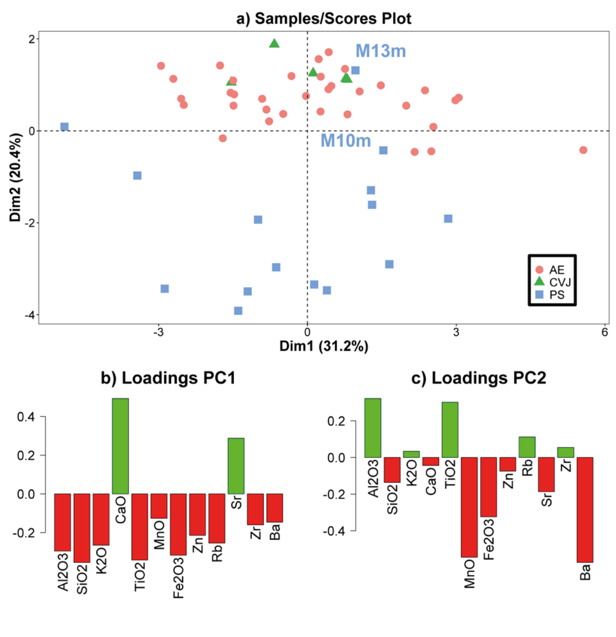

Figure 3. Samples/scores plot (a) and variables/PC correlation plot (b) for ceramic body.

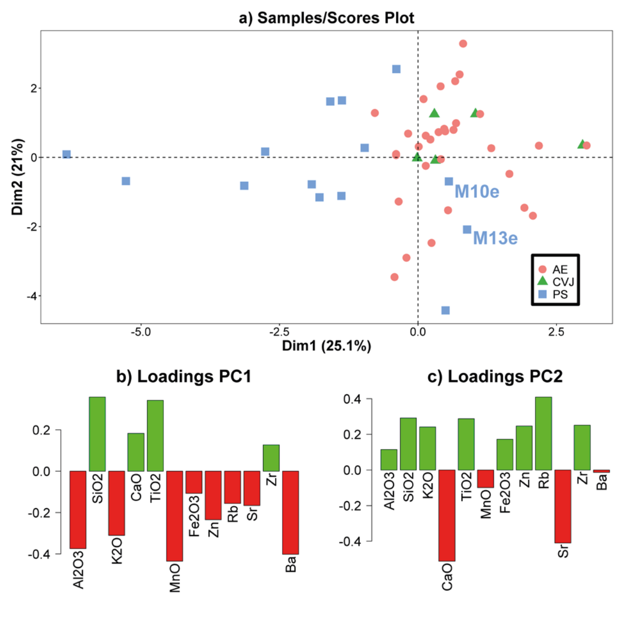

Figure 4. Samples/scores plot (a) and variables/PC correlation plot (b) for slip coating.

Conclusions

The non-destructive chemical analyses of the studied ceramic assemblages evidenced the importance of some trace elements. In the samples of Pauli Stincus, the amounts of Ba and Sr, combined with other major elements (Al_2O_3, SiO_2 and CaO) was crucial in order to individuate an autochthonous production. The results of this preliminary work suggest the need of a following study, possibly including data on rare earth elements, which could be able to improve the conclusions. The study of the slip thin would probably necessitate a different approach. In particular, microscopy and analysis on some painted areas could improve our knowledge of the polishing techniques, which according to our data seem to have been carried out using diluted clays rich in calcium, silicon and potassium.

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