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(https://doi.org/10.1016/j.jasrep.2021.103306)

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Journal of Archaeological Science: Reports, Volume 41, February 2022, 103306

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ABSTRACT

This paper presents a chemical characterization by means of WDXRF and mineralogical characterization by means of XRD of 21 individuals of black gloss pottery from the excavations on the acropolis of Populonia. The results shed new light on the circulation of pottery to this major urban centre in North Etruria during the Roman Republican period, while they also suggest the likelihood of local manufacture. In particular, we identify at Populonia four different black gloss productions that can be archaeometrically defined as Campanian A, Volterra, Etrusco-Latial 1 and a possible local production of ceramics belonging to the Petites Estampilles Group, active in the late fourth and third centuries BCE. Once thought to be a workshop located at Rome itself, this class is now understood as a diffuse network of workshops located in South Etruria and Latium producing pottery of similar technology and style. The present study potentially extends the map of its production to North Etruria in a region at that time newly incorporated into the expanding Roman Republican empire.

KEYWORDS: provenance analysis, black gloss ware, Petites Estampilles Group, *Populonia,* wavelength dispersive X-ray fluorescence, X-ray diffraction

1. INTRODUCTION AND OBJECTIVES

The ancient site of Populonia occupies the northern tip of a promontory along the Tyrrhenian coastline across from the island of Elba (Fig. 1). The settlement consists of two main areas: the acropolis site on a hilltop (164-86 masl) and an industrial *vicus* and burial areas arrayed along the beach below. Populonia's coastal location seems to relate to the site's early prominence in metal production and seaborne trade exploiting iron sources on Elba and the mainland. This metallurgical activity supported the settlement's early urbanization process starting in the Early Iron Age and its emergence as the key Etruscan city in the region. In the early third century BCE, the site fell under expanding Roman rule but continued to function as an important center for iron production until the Early Empire.

There has been steady interest in the considerable quantities of black gloss ceramics found in excavations at the site (Romualdi 1992; Capecchi and Romualdi, 1994-95: 343-85; Moriello 2002; Rizzitelli 2003; Pagliantini 2008, 2014). Along with the present study, this research engages with two wider debates. The first one bears on the nature of Populonia's productive economy. Populonia was famous in antiquity for its industrial processing of iron ore from mines on Elba. At issue is the extent to which this industrial character extended to other activities. In contrast to the metallurgical workshops excavated along the beach (Acconcia and Cambi, 2009), no potters' quarter has been identified at the site, and only a few kilns are known from the wider territory (Fedeli and Romualdi, 1997; Giorgi et al. 2009: 213-4; Fusi 2020: 2). Nonetheless, Minto (1934: 416) already suspected Populonia's involvement in ceramic manufacture during the Hellenistic period, while Romualdi (1992: 129) suggested that the quantity of examples from the Petites Estampilles Group (PEG) found at Populonia indicated local manufacture. A first archaeometric attempt to confirm these suspicions proved inconclusive (Gliozzo and Memmi Turbanti, 2004: 214). The topic of local production gains new energy thanks to kiln spacers and misfired pottery, including fragments of black gloss ware, recovered by recent excavation along the beach at the necropolis of Casone and the site of the *Casa dei Semi* in contexts dating to the late fourth and third century BCE (Fusi 2020). If this material confirms the presence of potters at Populonia in the period before and after Roman conquest, questions remain over the nature and scale of their production.

Fig. 1 Map of North Etruria (Italy) showing reconstruction of ancient coastline and location of Populonia and other sites mentioned in text. (Drawn by Seth Bernard)

A second debate concerns the cultural implications of the consumption of black gloss wares in Roman Italy. Black gloss ceramics traditionally form a critical index in debates over the acculturation of Italy and the Western Mediterranean following Roman conquest, a process conventionally referred to as Romanization (Keay and Terrenato, eds. 2001). While earlier work emphasizes Rome's role as driver of production and consumption patterns across Italy, recent scholarship allows for greater local agency (Roth 2007; Morel 2009). A number of local studies has especially supported this shift, and this paper falls within this ambit. The earliest widely distributed black gloss pottery produced in Italy from the Petites Estampilles Group (late fourth to third century BCE) reflects this debate. Initial study placed production at Rome itself (Lamboglia 1952; Morel 1969); however, we follow recent scholarship in treating the PEG not as a single workshop or *atelier*, but as a diffuse network of producers creating pottery with shared characteristics in South Etruria, Latium, and some Roman colonies, with Rome still playing an important role (Ferrandes 2007; Stanco 2009; Olcese 2016: 45-6).

Because of the material's relationship to questions of Romanization, Populonia's black gloss ware has potential to shed light on the city's complex history during the early stages of Roman imperialism in the region beginning after 300 BCE. No source directly records Rome's capture of the Etruscan city, and Populonia never receives a Roman colony. Populonia's iron industry flourishes during the third and second centuries (Camilli 2016, 2018), and there are signs of cultural continuity. Epigraphic material from the acropolis demonstrates the continued use of the Etruscan language for religious dedications and public inscriptions into the mid-second century BCE (Maggiani 1992; Benelli 2015). It is possible we find a situation of negotiated Roman expansion (Terrenato 2019), as Populonia's old elite turned to the productive economy as a means of maintaining regional prominence within a shifting political landscape. Populonia's use of ceramic styles often understood as Roman or Romanizing should be viewed in this context.

To reach a better understanding of the origins of black gloss pottery recovered at Populonia and to explore the hypothesis of local production of the PEG, a sample of 21 individuals has been selected for its archaeometric characterization. Chemical characterization by means of WDXRF has been performed for provenance studies and mineralogical characterization by means of XRD were performed to obtain information on some technical aspects such as the nature of the pastes prepared for the elaboration of these wares, and the estimated equivalent firing temperatures (EFT) at which the pottery was fired in the past.

2. ARCHAEOLOGICAL CONTEXT AND SAMPLING STRATEGY

In the period following the Roman conquest, a well-articulated urban site develops along the two peaks of the acropolis, Poggio del Telegrafo and Poggio del Castello (Fig. 2). Within this area, excavations conducted between 1998 and 2011 by the Universities of Pisa, Roma Tre, and Siena in collaboration with the Soprintendenza Archeologica per la Toscana (now the Soprintendenza Archeologia, Belle Arti e Paesaggio per le Province di Pisa e Livorno), and the Comune di Piombino have revealed a sacred precinct flanked by three temples built between the late third and early second century BCE in the saddle between the peaks (Romualdi 2002; Mascione 2007, 2008), two broad paved roads climbing Poggio del Telegrafo, and a series of monumental terraces supporting residences, including a large aristocratic *domus* (Coccoluto and Gasperi, 2007). Uphill behind the *domus*, the site's largest terrace structure defines the façade of a grand monumental complex known by its modern name as *Le Logge* after six blind arches along the northern wall of its substructure, which supported a platform ca. 8 m tall (Fig. 3). This structure's construction is assigned to the late-second/early-first century BCE based on stylistic analysis of wall-paintings and pavements from rooms along its front side (Cavari 2007, 2020; Cavari and Donati 2014, forthcoming). During the first century BC the acropolis was gradually abandoned, and there are only sporadic signs of occupation across the entire acropolis in the Imperial period. Excavation reports appear in eleven published volumes of the series *Materiali per Populonia*.

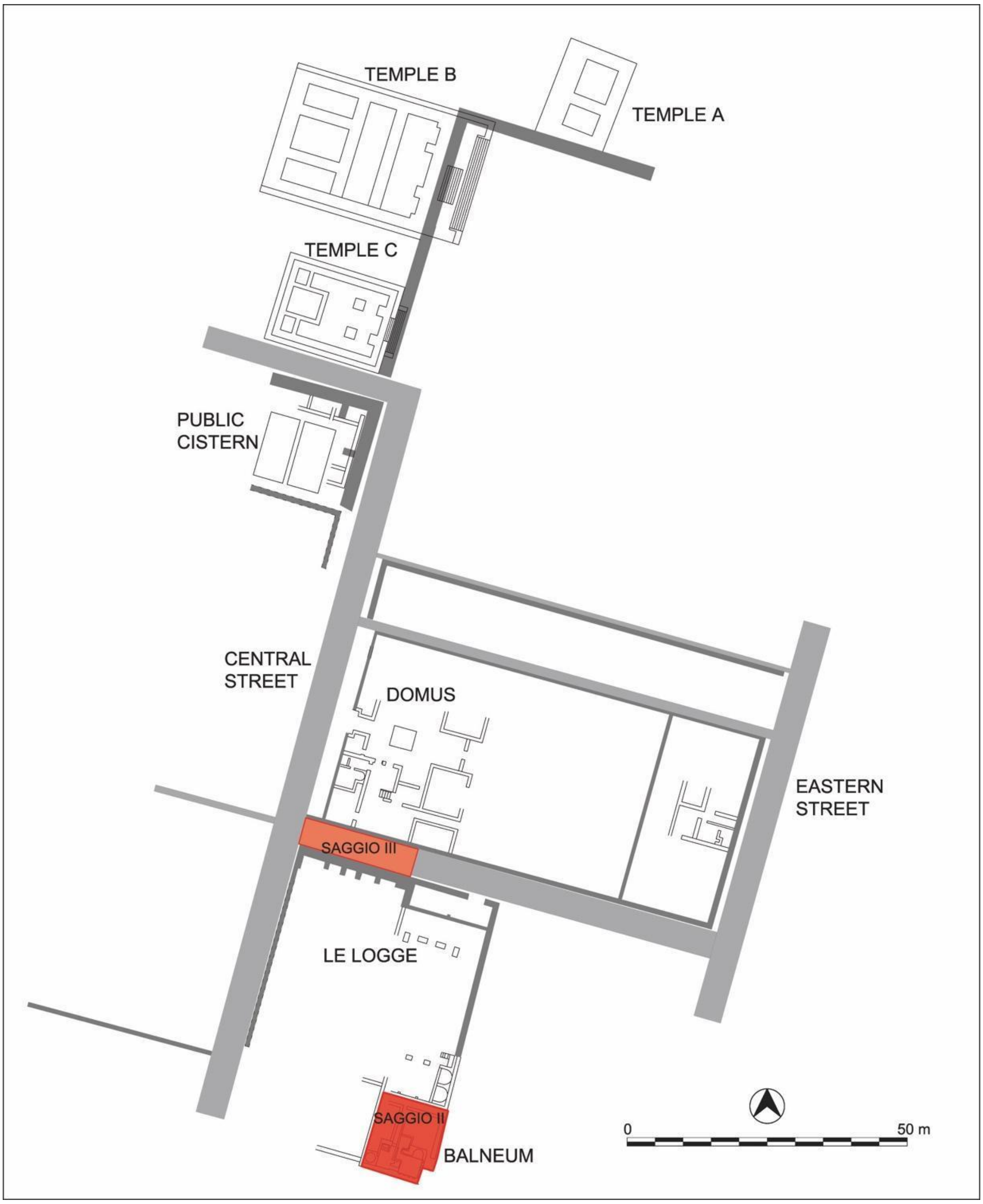

Fig. 2 Reconstructive plan of the archaeological area of Populonia’s acropolis. The ancient terraces are outlined in dark grey and roads in light grey. The two excavation areas (Saggio II and III) from which the black gloss ware comes are indicated in red. (Elaboration by Cynthia Mascione)

Fig. 3 Populonia's acropolis, view of *Le Logge* looking south from the *domus*. (Photo by Seth Bernard)

The architectural dominance of *Le Logge* within the acropolis site confirms its importance to the overall urban design. Starting in 2018, excavations intending to shed light on the complex's phasing and function concentrated on two areas related to the structure[1]: at the base of the arcuated terrace wall (Saggio III) and on the upper terrace (Saggio II) at the site of a *balneum* identified in 2000 and partially excavated in 2001 and 2005 (Zanini et al. 2002: 93-96; Mascione et al. 2003: 35-51; Santoni, Casola 2007). Excavations remain in progress with preliminary results in Bernard et al. 2019.

Black gloss ware from these two areas should be considered to derive from contexts of secondary deposition. In Saggio III, stratigraphy is composed of two sections of redeposited fill, interrupted by the surface of the construction site for building the arcuated substructure of *Le Logge*. The lower section of fill was formed by throwing earth full of material probably taken from surrounding structures or rubbish heaps to raise the ground level of the area between the aristocratic *domus* and the planned course of *Le Logge*'s foundations. Excavation of this section revealed a dense sequence of thin, fairly homogeneous layers compacted for the imposition of the construction site. From this first sequence dating to the later second century BCE derive samples numbered PPL004-6 and PPL009-10 (cf. table 1). After the conclusion of the construction of *Le Logge*, the area

[1] In 2015-2017, a project of restoration and cultural development of the archaeological area was carried out, financed by the Ministero per i Beni Culturali and coordinated by the Comune di Piombino and the Società Parchi val di Cornia, which has since 2007 managed the archaeological park in which the area of the acropolis is located. The coordination of archaeological work has been entrusted to the Università di Siena: Mascione 2021; Mascione forthcoming. In 2018, new research and excavations began thanks to an agreement between the Soprintendenza and the universities of Siena and Toronto.

was probably paved and linked into the network of streets. This paving no longer preserves, presumably removed during one of many activities of spoliation on the acropolis site after its abandonment, probably commencing already in the first century CE.

The second section of redeposited earth directly covers the surface used as the floor level of the construction site. Fill was used to create a new path of beaten earth to replace the earlier paved street. The ceramics are still under study but include fragments of lamps and *terra sigillata italica* datable between the second half of the first century BCE and the first century CE. From these layers of redeposited fill derive samples PPL001-3, PPL007-8, and PPL011-13; PPL021 comes from abandonment layers in the same area (cf. table 1).

The second context taken into consideration is a small thermal structure or *balneum* (Saggio II) build in the southeast sector of the terrace of *Le Logge* against the hillside's naturally sloping bedrock. The structure consists of three rooms destined for bathing functions, a *tepidarium*, *laconicum* or *sudatorium*, and *caldarium*, as well as a large service room with *praefurnium* and vaulted cistern (Bernard et al. 2019). In the southern part of the structure, the elevation stands up to the spring of the vaulted roof. Pavements in mosaic and *opus spicatum* remain *in situ*, except the floor of the *calidarium* which was destroyed in antiquity as part of the site's spoliation. While final publication will refine the *balneum*'s dating, a tentative chronology between the late second and early first century BC is suggested by previous, limited stratigraphic excavation (Mascione et al. 2003: 46) and stylistic analysis of the mosaic decorating the exedra of the *caldarium* (Gualandi 2002; 2003).

Black gloss ware sampled in this study derives from destruction layers of the *balneum*'s elevation and roof (PPL014, 15, 17, 19-20), from the final abandonment layers (PPL016), and from a later robber trench (PPL018) (cf. table 1). Ceramics, therefore, do not pertain to the use phase of the complex. Considering the structure's location, some material was possibly carried here by erosion from structures on the hill's summit (Acconcia et al. 2006). Samples PPL014-15 and PPL017-18 identified archaeologically with the PEG, datable to the first half of the third century BCE, seem decisively earlier than the *balneum*'s construction but find punctual comparison with material recovered from structures higher up on the hill (Acconcia et al. 2006: 58).

Comprehensively, excavations of 2019-20 in Saggio II and III produced 1,023 fragments of black gloss ware pertaining to those different productions into which scholarship articulates the broader ceramic class. The most frequently attested production in stratigraphic excavations of Saggio III and II pertain to Campanian A, represented by 702 fragments. Also well attested are examples of Campanian B and the so-called "B-oid" class, together accounting for 194 fragments. The PEG and imitative workshops constitute 72 fragments. Only a single fragment of Genucilia plate and four undiagnostic fragments of *sovradipinta* ware belong to earlier Etruscan production. Table 1 describes the 21 samples subjected to analysis, thirteen from Saggio III (*Le Logge*) and eight from Saggio II (*balneum*). The sampling intends to form a representative selection of different productions identified on the basis of macroscopic observations of fabric and gloss, as well as previously published typological classifications.

Table 1 and illustrations in figure 4 (cf. Fig. 12) provide typological correspondence between sampled material and standard references. No sample identified with PEG exhibits stamps or decoration otherwise associated with this production, but identification is based on typological and macroscopic qualities. PO14, PO15, and PO18 are PEG bowls with incurving rims from the series Morel 2783-2784, whose frequent appearance at Populonia was emphasized by Romualdi (1992: 123). PO17 is a widely attested bowl with almond shaped rim of type Morel 2538a from the last phases of production. Bowl fragments PO16 and PO21 are not typologically associable with known forms but share characteristics of fabric and gloss with PEG products.

Number	**Context**	**Sherd type**	**Vessel class**	**Typology**	**Macroscopic identification**
PPL001	Saggio III-Logge	rim	bowl	Morel 2941a1 (1st half of 1st century BC)	Campanian A
PPL002	Saggio III-Logge	body	bowl	Morel 2258a1 (mid to 2nd half of 2nd century BC).	Circle of Campanian B
PPL003	Saggio III-Logge	rim	bowl	Unidentifiable (2nd-mid 1st century BC)	Campanian A
PPL004	Saggio III-Logge	body	kylix	Morel 3121 (2nd century BC)	Volterra
PPL005	Saggio III-Logge	rim	dish	Morel 2287a1 (first half of 1st century BC)	Circle of Campanian B
PPL006	Saggio III-Logge	handle	*krater* or *oinochoe*	Unidentifiable (2nd century BC)	Volterra
PPL007	Saggio III-Logge	base	dish?	Morel 221b1 (2nd half of 2nd century BC)	Campanian A
PPL008	Saggio III-Logge	body and rim (2)	dish	Morel 2257b1 (late 2nd century BC)	Circle of Campanian B
PPL009	Saggio III-Logge	base	bowl?	Morel 212e3 (2nd quarter of 2nd century BC)	Campanian A
PPL010	Saggio III-Logge	base	bowl	Morel 212c2 (half of the second century BC)	Campanian A
PPL011	Saggio III-Logge	body (4)	dish	Unidentifiable (2nd century BC)	Campanian A
PPL012	Saggio II-Logge	body and rim (2)	dish	Morel 2257a1 (2nd half of 2nd century BC)	Circle of Campanian B
PPL013	Saggio II-Logge	body	dish	Unidentifiable (mid 2nd to mid 1st century BC)	Circle of Campanian B
PPL014	Saggio II-Balneum	rim	bowl	Morel 2784 (1st half of 3rd century BC)	PEG
PPL015	Saggio II-Balneum	body (2)	bowl	Morel 2783-2784 (1st half of 3rd century BC)	PEG
PPL016	Saggio II-Balneum	body (4)	bowl	Unidentifiable (1st half of 3rd century BC)	PEG
PPL017	Saggio II-Balneum	rim (2)	bowl	Morel 2538a (3rd quarter of 3rd century BC)	Production of southern Etruria - imitation PEG

PPL018	Saggio II-Balneum	rim	bowl	Morel 2784 (1st half of 3rd century BC)	PEG
PPL019	Saggio II-Balneum	base (4)	bowl	Morel 2323a1 (1st half of 1st century BC)	Circle of Campanian B
PPL020	Saggio III-Balneum	rim	dish	Morel 1441h (2nd half of 2nd century BC)	Campanian A
PPL021	Saggio III-Logge	body	dish?	Unidentifiable (third century BC)	South Etruria imitation of PEG

Table 1. Archaeological classification of analyzed samples of black gloss ware from the acropolis of Populonia. (Laura Pagliantini)

3. MATERIALS AND METHODS

To carry out the statistical treatment of the chemical data, the results of Populonia were studied jointly with the individuals of the MedConTaCCt database analysed during the first phase of the project coming from the three Spanish sites of *Ilduro*, *Iluro* and *Emporion* where the chemical groups of Cales 1, Cales 2, Cales 3 on the one hand, and Etrusco/Latial 1 (from now on, EL 1) and Etrusco/Latial 2 (from now on, EL 2), and Volterra on the other hand, were firstly defined (Madrid i Fernández and Sinner, 2019, 2021). This makes up a set of 105 individuals. Sinner (2015) provides archaeological introduction to Roman presence at *Ilduro*, *Iluro*.

Chemical characterization was conducted by means of wavelength Dispersive X-ray fluorescence (WDXRF) analysis. The concentrations were quantified using an AxiosmAX-Advanced PANalytical spectrometer with a Rh excitation source calibrated by a suite of 56 international Geological Standards. Interferences were taken into account and the correction of matrix effects was done using PANanalytical Pro-Trace software for trace elements. The determined elements were: Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, V, Cr, MnO, Fe_2O_3 (as total Fe), Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Sn, Ba, Ce, W, Pb and Th. Minor and major elements are expressed as concentrations of oxides in percentage by mass (wt %). Trace elements are conveyed as concentrations of elements in µg g-1 (or ppm). The determination of Loss on ignition (LOI) took place by firing 0.3 g of dried specimen at 950 °C during 3 hours. The summation of trace, minor and major element concentrations and LOI, is positioned within a range of 98—102 % (Table 2). Because of analytical imprecisions, the concentrations of Sn and Mo were discarded, as were those of W and Co due to possible contamination from the tungsten carbide cell mill employed during the preparation process. Similarly, concentrations of Pb and P_2O_5 were not used because the values were considered erratic, perhaps due to contamination during burial, for example, in the case of P_2O_5 from organic matter (Buxeda i Garrigós, 1999) or in the case of Pb from metallic objects. Mineralogical characterization of all samples was performed by means of X-ray diffraction (XRD). Our measurements were obtained by means of a Bragg-Brentano geometry diffractometer PANalytical X'Pert PRO MPD Alpha-1 (radius = 240 mm) using the Ni-filtered Cu Kα radiation (λ = 1.5418 Å) at a working power of 45 kV and 40 mA, equipped with an X'Celerator detector (active length = 2.122°). Measurements were taken from (5 to 80)°2θ with a 0.026° step size and an acquisition time of 50 s, spinning the sample at 1 Hz. Valuations of crystalline phases present in every specimen were conducted by using the software package PANalytical X´Pert HighScore Plus which includes the database of the International Centre for Diffraction Data–Joint Committee of Powder Diffraction

Standards, 2006 (ICDD–JCPDS). A complete description of method together with the accuracy and precision can be found in Madrid i Fernández and Sinner (2019, 2021).

4. RESULTS

4.1 *Chemical results*

XRF chemical analysis results correspond to a special case, the d+1-dimensional vector space arising from the *d*-dimensional projective space, the simplex ~~S^d~~$\mathbb{S}^d$, in which the projective points are represented by homogeneous coordinates with a constant sum *k* ($k \in R^+$) (R+: the set of positive real numbers):

$$\mathbf{x} = [x_1,..., x_{d+1}] \mid x_i \geq 0 \ (i = 1,..., d + 1), x_1 + ... + x_{d+1} = k$$

(in this case $k = 100$), and its vector space is the positive orthant, which follows a multiplicative model with a logarithmic intervals metric (Barceló-Vidal et al., 2001; Aitchison, 2005; Buxeda i Garrigós, 2008). The original chemical data **x** have been transformed using the centred logratio transformation (CLR) (Aitchison, 1986; Buxeda i Garrigós, 1999):

$$\mathbf{x} \in \mathbb{S}^d \rightarrow \mathbf{z} = \ln\left(\frac{\mathbf{x}}{\mathrm{g}(\mathbf{x})}\right) \in \mathbb{H} \subset \mathbb{R}^{d+1}$$

where the $\mathbb{S}^d$ is the *d*-dimensional simplex g(**x**) is the geometric mean of all the d+1 components of **x**; or the additive logratio transformation (alr):

$$\mathbf{x} \in \mathbb{S}^d \rightarrow \mathbf{y} = \ln\left(\frac{\mathbf{x}_d}{x_{d+1}}\right) \in \mathbb{R}^d_+$$

where $\mathbb{S}^d$ is the *d*-dimensional simplex and $\mathbf{x}_d = [x_1,...,x_d]$. Lastly, the isometric logratio transformation (ilr) is an isometry in $\mathbb{R}^d$ using an orthonormal basis. This change allows a Euclidean space to be acquired, eliminating the restriction to the constant sum *k* and avoiding the effects of a possible contamination, in which standard statistical techniques are able to be applied.

To preform the statistical treatment of the chemical on the retained values, the software R(R Core Team 2020) was employed. This process measures variability in the data set as a reflection of differences in chemical composition, and of how regularly chemical differences relate to retained components (Aitchison 1986). Total variation is high in this case (vt = 2.2), indicating a polygenic set (Buxeda i Garrigós and Kilikoglou 2003). Then, the compositional evenness is measured according to information entropy (H2), otherwise known as the Shannon index (Shannon, 1948), on the $\tau_{.i}$ values in decreasing order (Buxeda i Garrigós and Madrid i Fernández, 2016).

POP	Fe_2O_3	Al_2O_3	MnO	P_2O_5	TiO_2	MgO	CaO	Na_2O	K_2O	SiO_2	Ba	Rb	Mo	Th	Nb	Pb	Zr	Y	Sr	Sn	Ce	Co	Ga	V	Zn	W	Cu	Ni	Cr	PAF
PPL001	4.96	19.29	0.14	0.23	0.72	1.49	3.66	3.34	5.29	59.64	275	274	2	34	60	50	388	43	166	4	188	16	23	79	88	146	19	17	42	1.20
PPL002	5.88	15.03	0.09	0.35	0.69	2.71	12.58	0.89	2.68	53.64	336	126	0	15	20	20	151	25	312	2	61	18	17	114	92	39	35	58	130	6.10
PPL003	4.50	18.56	0.13	0.20	0.68	1.45	2.97	3.30	5.62	60.09	280	266	2	31	54	49	362	42	158	5	179	21	21	72	84	188	16	12	28	1.30
PPL004	6.13	15.80	0.10	0.31	0.73	2.92	11.62	0.86	2.75	55.30	357	131	1	15	21	19	156	26	299	3	71	18	19	112	103	40	36	63	140	4.13
PPL005	6.60	16.59	0.15	0.30	0.80	3.23	12.54	0.85	2.41	52.05	424	121	0	16	22	22	138	27	305	2	72	25	21	130	106	75	43	80	163	4.66
PPL006	6.81	17.36	0.14	0.32	0.84	3.27	12.02	0.84	2.45	53.22	423	126	0	16	22	20	140	28	305	2	77	26	22	140	121	37	50	85	170	2.57
PPL007	4.81	18.82	0.13	0.21	0.68	1.48	3.59	3.46	5.03	60.58	298	240	2	32	55	46	366	42	180	5	179	16	20	80	83	137	21	16	30	1.30
PPL008	6.04	15.60	0.09	0.30	0.72	2.86	11.85	0.86	2.75	53.87	358	129	0	14	21	22	153	25	305	2	68	17	18	108	97	32	40	62	133	5.64
PPL009	4.89	19.08	0.14	0.21	0.71	1.46	2.84	3.45	5.79	60.57	276	278	2	32	57	125	379	43	157	6	184	10	21	77	88	57	20	12	22	1.10
PPL010	4.95	18.96	0.14	0.24	0.70	1.54	3.70	3.50	4.96	60.20	294	233	2	31	53	49	353	40	178	3	171	11	21	79	85	45	20	18	38	1.10
PPL011	4.78	18.87	0.13	0.20	0.70	1.46	3.24	3.38	5.30	60.66	301	260	2	31	55	48	370	42	174	5	175	14	21	74	83	110	22	16	30	1.07
PPL012	5.96	15.56	0.12	0.44	0.72	2.74	11.53	0.88	2.80	54.91	399	126	0	15	21	21	154	26	311	1	70	18	19	116	100	36	32	58	131	4.60
PPL013	6.12	15.73	0.10	0.35	0.72	2.62	11.09	0.90	2.83	56.09	374	144	0	16	21	18	160	27	298	1	78	17	19	102	99	41	44	62	130	4.11
PPL014	7.28	18.48	0.14	0.27	0.84	2.75	11.25	0.94	2.57	54.75	630	182	0	30	25	47	216	33	396	3	142	27	22	141	115	74	52	79	136	0.63
PPL015	6.29	17.62	0.14	0.39	0.76	2.56	10.31	1.56	3.30	55.26	454	179	0	25	31	37	234	33	319	4	124	18	20	107	104	39	45	60	108	1.60
PPL016	6.45	16.16	0.13	0.25	0.80	2.71	10.20	0.85	2.59	56.45	342	133	0	15	21	24	149	28	260	2	71	26	20	120	112	70	43	73	144	3.77
PPL017	5.66	14.81	0.14	0.37	0.68	2.30	11.90	1.27	2.32	55.48	607	146	0	25	22	37	215	30	381	2	118	21	17	98	90	61	38	62	109	5.16
PPL018	6.54	16.43	0.14	0.50	0.76	2.66	12.45	0.98	2.49	53.16	587	156	0	23	23	35	187	31	372	2	104	24	20	118	107	32	43	81	134	3.90
PPL019	6.08	15.68	0.10	0.33	0.72	2.96	11.45	0.94	2.69	55.03	351	132	0	15	21	20	161	27	332	4	79	18	19	114	98	31	36	61	135	4.23
PPL020	6.58	17.06	0.14	0.27	0.81	3.37	11.68	0.96	2.50	53.30	430	130	0	15	22	20	145	28	320	3	85	26	21	120	112	47	47	87	161	2.67
PPL021	6.01	15.75	0.09	0.31	0.74	2.80	12.50	0.92	2.71	54.47	360	125	0	14	21	18	154	25	325	2	73	17	17	103	96	34	35	58	132	4.27

Table 2. Elemental concentrations determined for the 21 individuals from Populonia. Major and minor elements and LOI (loss on ignition) expressed in mass %. Trace elements expressed in $\mu g\ g^{-1}$ (Marisol Madrid i Fernández).

Looking at the compositional evenness plot (Fig. 5), it is clear that most of the variability is connected to relative concentrations of the elements Cr, Na_2O, Ni, and CaO. As observed elsewhere, these components are among the essential chemical elements for the discrimination of pottery made in Italy during the Roman Republican period and are especially helpful for differentiating between Campanian A and other black gloss productions (Madrid i Fernández and Sinner, 2019, 2021). Focusing on the scatterplot matrix using those four components (Fig. 6) the most evident compositional differences between samples are as follows. First, the distribution of samples into two groups is clear for four cases, as is also evident from the density plots of the four components located in the diagonal. This division corresponds to the significant difference between Campanian A, in orange, and the other samples that retain greater similarities of composition, suggesting common characteristics. However, some samples classified as imitations of Campanian A, in pink, seem to be distinguished in some plots, especially in $\ln(Na_2O/g(x))$ — $\ln(Cr/g(x))$ and $\ln(Na_2O/g(x))$ — $\ln(Ni/g(x))$. Moreover, these plots show clear negative correlation between relative concentrations of Na and Ni and Cr, while positive correlation between Ni and Cr appears in scatterplot $\ln(Ni/g(x))$ — $\ln(Cr/g(x))$.

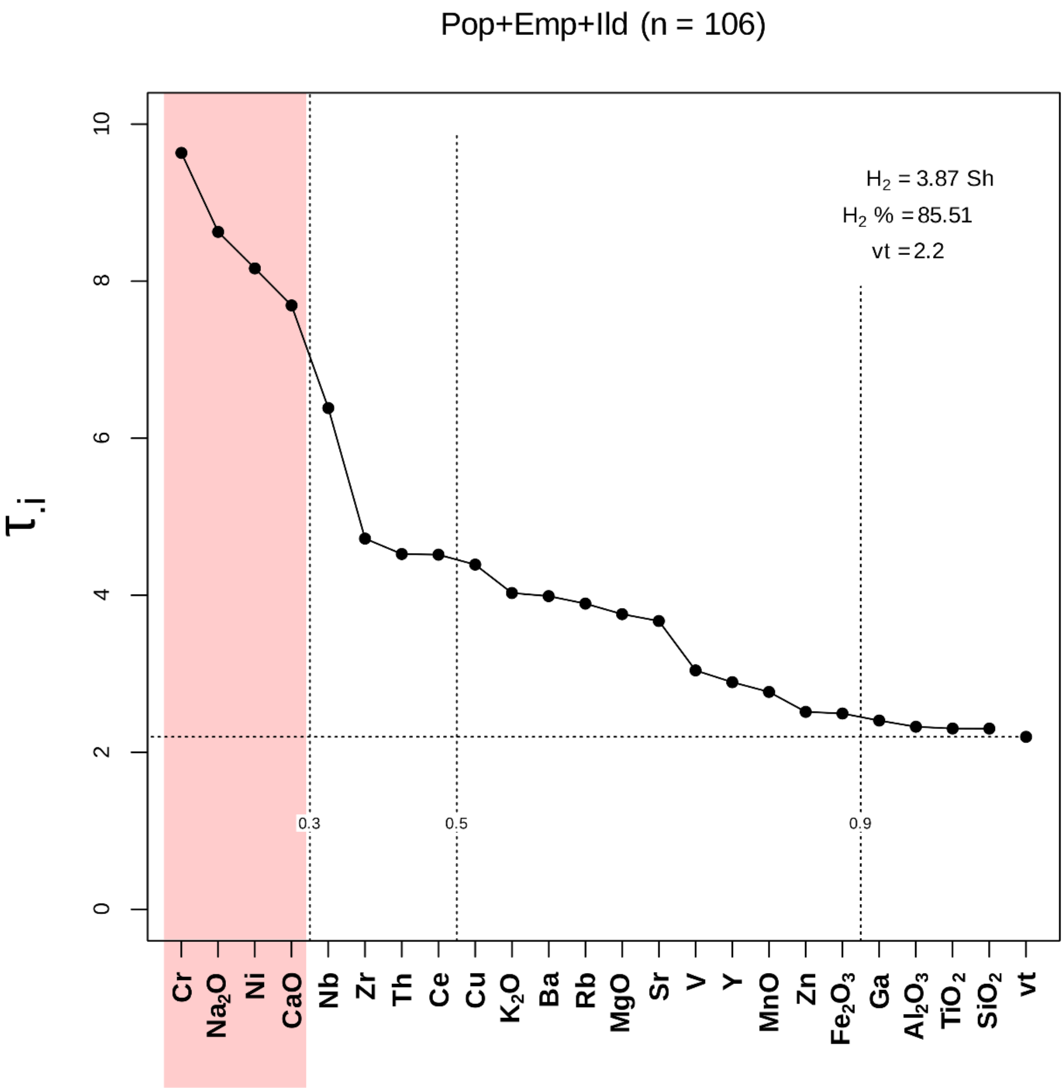

Fig. 5 Compositional evenness plot of the 106 individuals in the defined groups. H_2 = information entropy (in shannons, symbol Sh –i.e., bits). H_2 % = percentage of information entropy relative to the possible maximum attainable. vt = total variation. τ.i

sum of variances of alr transformed concentrations using element i as denominator (Marisol Madrid i Fernández).

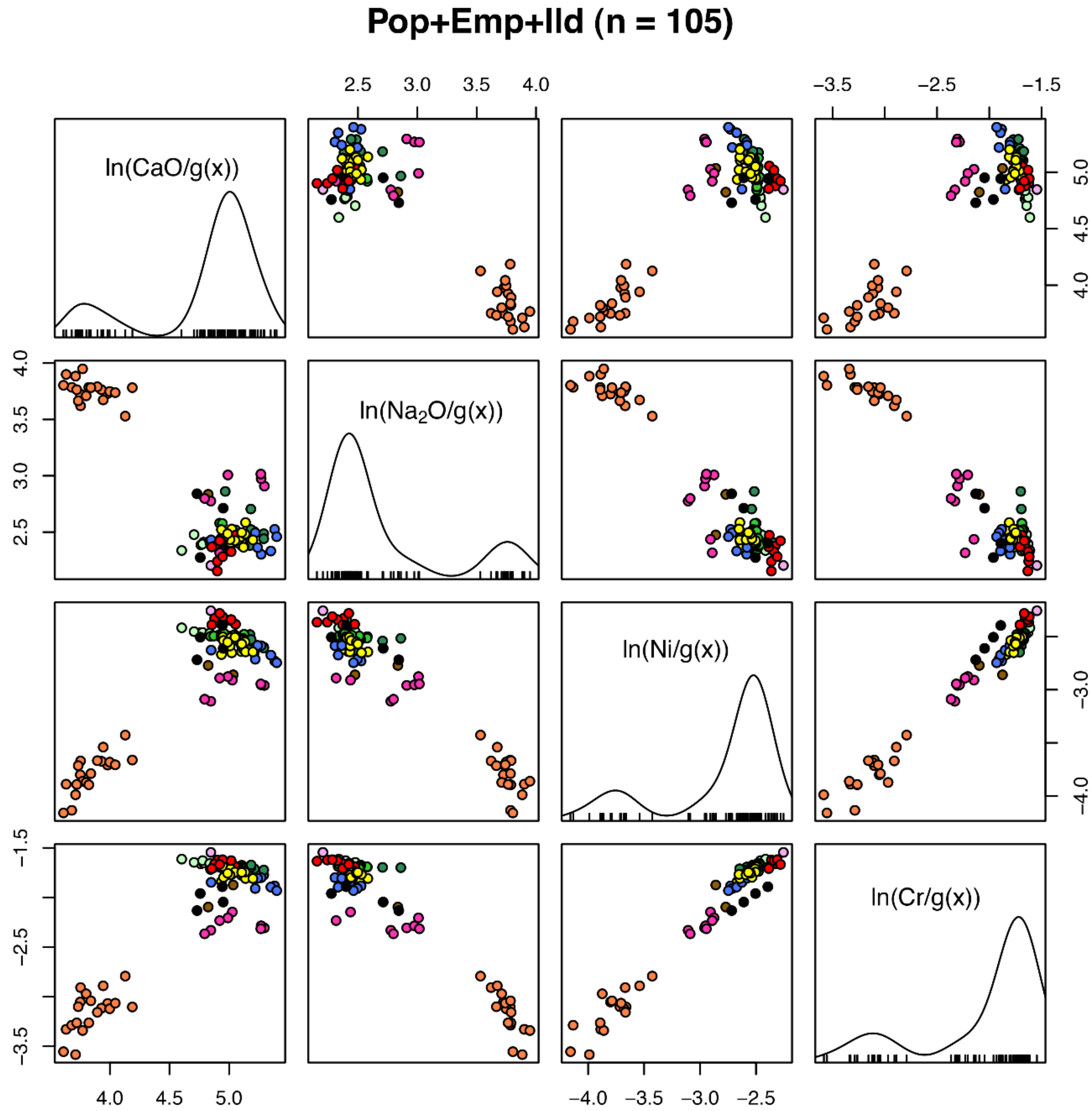

Fig. 6 Scatterplot matrix using the clr transformed components CaO, Na_2O, Ni and Pb. In the diagonal are located the KDE density plots of the four components (Orange: CAMP A, dark green: CALES 3, green: CALES 2, light green: CALES 1, lilac: ETR, pink: Camp A local/reg 1, yellow: EL 1, blue: EL 2, red: VOLT, black: POP, salmon: ungrouped) (Marisol Madrid i Fernández).

The structure of the dendrogram of figure 7 clearly divides into two parts: low calcareous ceramics on the left side of the plot and calcareous ones on the right. Low calcareous pottery corresponds to Campanian A, and all samples from Populonia macroscopically classified as such are included in this group with only one exception. Inversely, calcareous individuals show a structure divided into eight groups along with three isolated samples, two of which are ungrouped. As with Campanian A, most of these groups have been defined and associated with specific workshops or regions according to chemical characteristics by previous studies (Madrid i Fernández and Sinner, 2019, 2021). Regarding the analyzed material from Populonia, seven samples for which an origin in Etruria has been proposed join established group EL 1 of Erusco/Latial provenance.

Another four samples have been archaeometrically classified as Volterran products. In this case, the macroscopic classification (table 1) correctly identified two of these samples as Volterra, while two were misidentified as Campanian A and PEG. Finally, the remaining four samples cluster together without joining any of the groups previously defined by archaeometric characterization. These sherds were classified as coming from the *Atelier des petites estampilles* except one presumed imitation of this classification made in the Etrusco/Latial area (table 1).

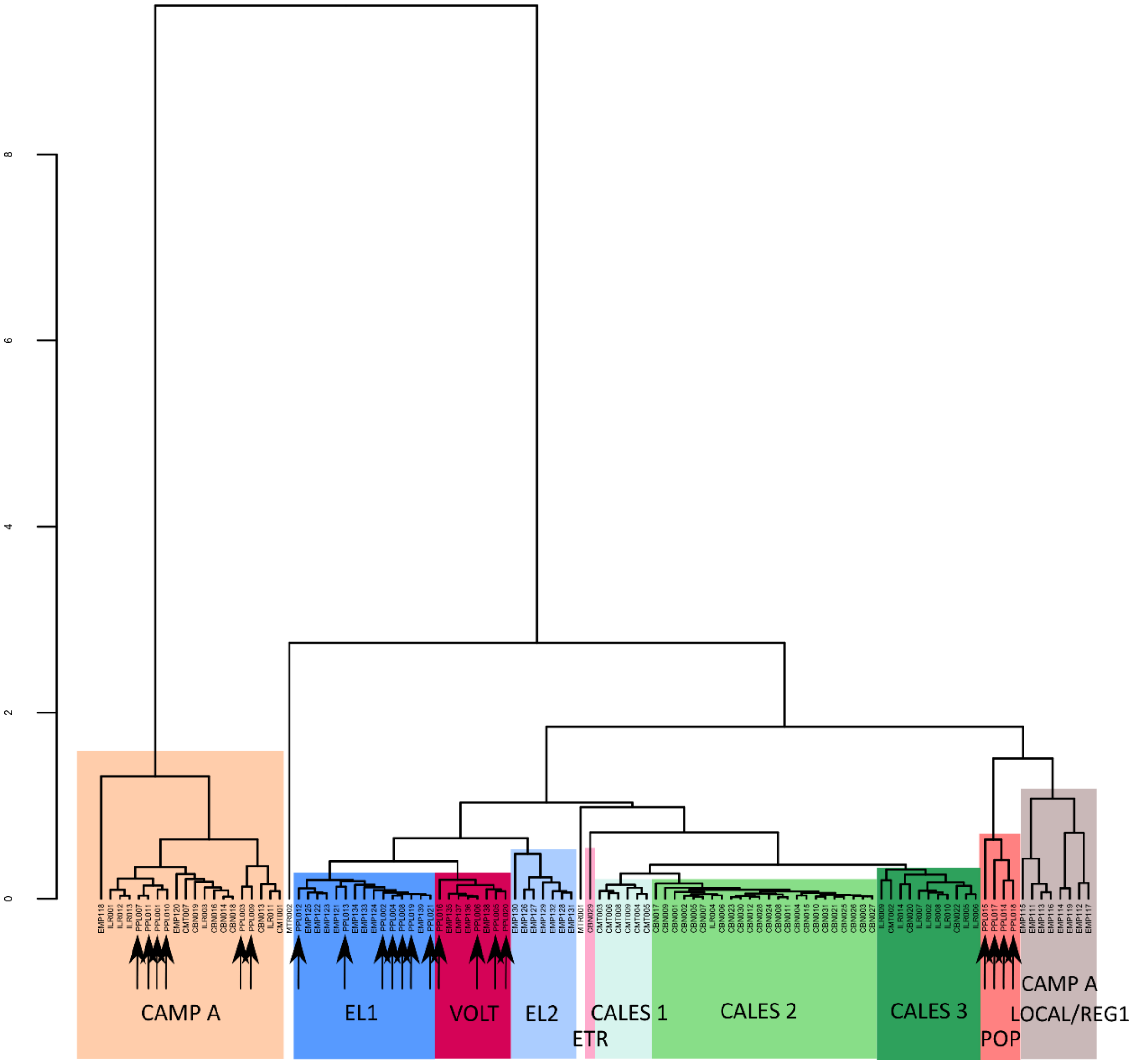

Fig. 7 Dendrogram performed by using the squared Euclidian distance and the McQuitty's linkage method on the clr transformed subcomposition Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2, V, Cr, MnO, Fe_2O_3 (as total Fe), Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, Ce and Th. Black arrows: individuals from Populonia (Marisol Madrid i Fernández).

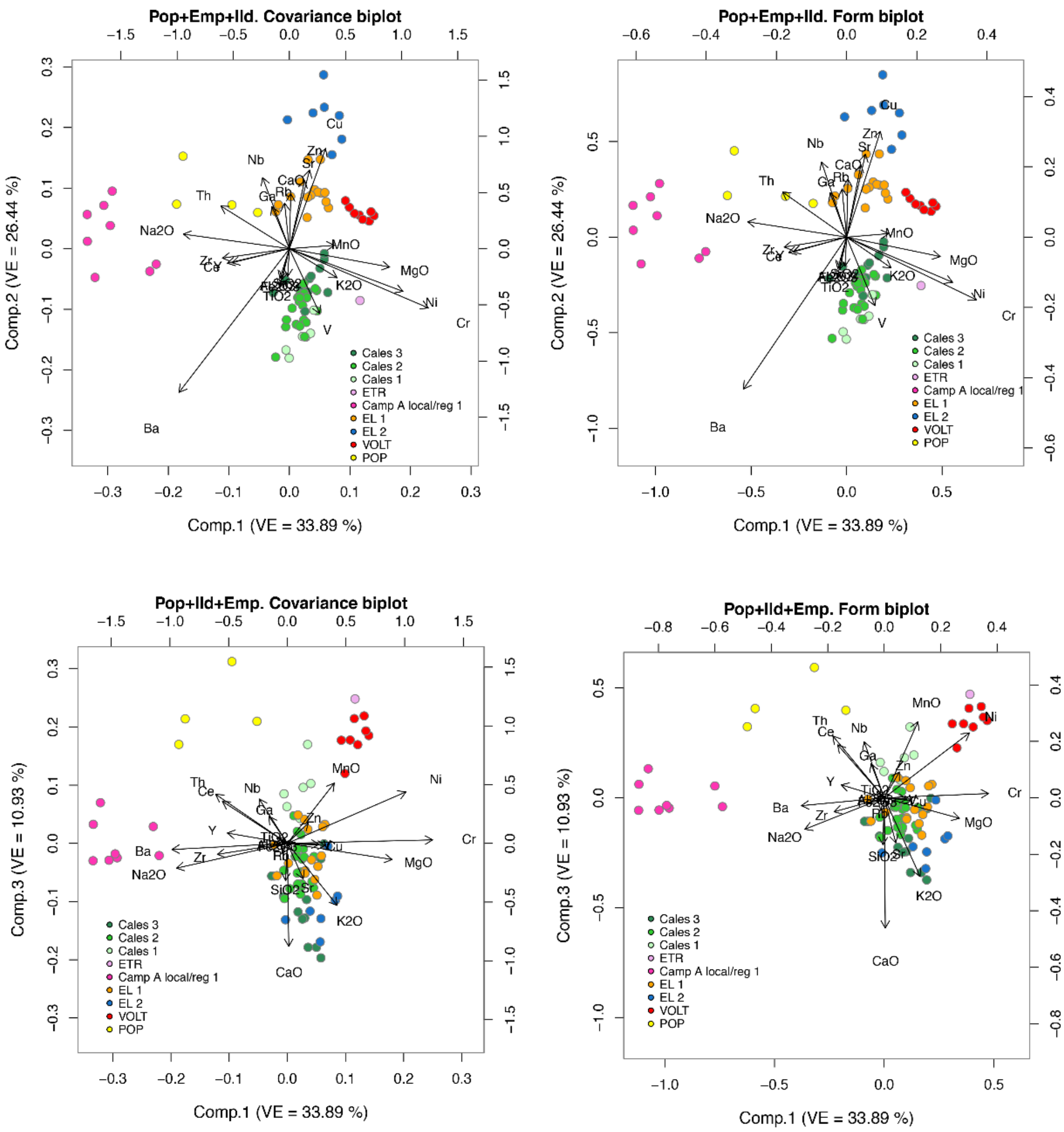

Fig. 8 Biplots of the singular value decomposition on the double centred clr transformed mentioned subcomposition; top: plots of the Comp. 1 and Comp. 2; bottom: plots of the Comp. 1 and Comp. 3. VE: variance explained (Marisol Madrid i Fernández).

With the aim of investigating the consistency of the structure suggested by the previous dendrogram, these results are compared with the form and covariance biplots (Fig. 8) resulting from the singular value decomposition of the clr transformed data (Aitchison and Greenacre, 2002; Greenacre, 2010; van de Boogaart and Tolosana-Delgado, 2013). The relationships between the samples and transformed retained components are reflected clearly in those biplots. For this analysis we do not consider either Campanian A or the ungrouped samples in an effort to avoid sharp contrasts in the plot created by strong differences between Campanian A, the ungrouped samples, and the rest of the material. The resulting form biplots and covariance of the first three principal components explain more than 70% of the variance (VE = 71.26 %). As visible in the form and covariance plots of the first two components, the three groups related to Cales workshop in green cluster together at the lower right side of both graphs, indicating major compositional similarities. At the top of the plot and clearly discriminated from Cales, we find groups associated with EL 1, EL 2, and Volterra. Visibly different at the left of the graph are plotted those samples classified as imitations of Campanian A, confirming results of the previous analytical treatment. The most significant components in this discrimination are revealed by the compositional evenness plot of figure 4: The first component exhibits the opposition of Cr, Ni and MgO in the positive values, and Na_2O and Ba in the negative ones. The second component, Cu and Zn in the positive values, and Ba in the negative ones. It is important to note that the samples classified as coming from the PEG (labelled as yellow dots -POP) do not join any of the existing clusters. Although they do not join together in a compact group, their proximity to the Etrusco/Latial and Etruscan products indicates compositional similarities. The same can be said of the covariance and form plots of the first and third components, especially regarding Volterran pottery, imitations of Campanian A and samples related to PEG. All of them remain clearly apart from the other groups. In this case, however, the influence of the third component, especially the MnO, Th, Ce, Nb and Ni in the positive values, while CaO and K_2O are attracted to the negative ones very similar in the Etrusco/Latial and Calenan productions.

Lastly, results were compared with the ARQUB database including black gloss from Italy and Northeast Hispania. The database contains analytical results of samples of black gloss found at the Roman Republican colony of Cosa, where black gloss wares were widely consumed between the third and the first centuries BCE (Scott 2008; Madrid i Fernández and Buxeda i Garrigós, 2013). Cosa is relatively close to Populonia and makes for an important point of comparison for thinking about regional production and consumption in coastal North Etruria. The database also records data on terra sigillata from Arezzo, Pisa, Latium and Campania. While terra sigillata is a later product than the black gloss pottery considered in this article, raw materials used for both classes of fine ware ceramics are the same, and certain workshops even fabricated both products, making comparison relevant to a provenance study.

As shown in the new dendrogram (Fig. 9), Campanian A from Populonia joins a large group on the left of the graph together with individuals from Cosa and different Catalan sites, pointing out that this tableware was widely distributed to the Italian peninsula as well as to the northeast of Hispania. The structure of this group with several subgroups suggests that probably more than one workshop should be involved in the production and distribution of this pottery. In fact, individuals from Populonia join different subgroups, possibly reflecting different recipes or perhaps production periods. Continuing to the right, group EL 1 includes the same seven individuals from Populonia and those from Catalan sites that we could observe in the previous dendrogram plus two individuals from Cosa. That means that products from EL 1 were spread out in both Italian cities and north-eastern Hispania. The group of Volterra includes the same individuals from Populonia and Emporion as in the previous dendrogram, plus three from another Catalan site. Finally, the group made up of the four individuals of Populonia join now six individuals from Cosa plus one individual from another northeastern Hispanian site.

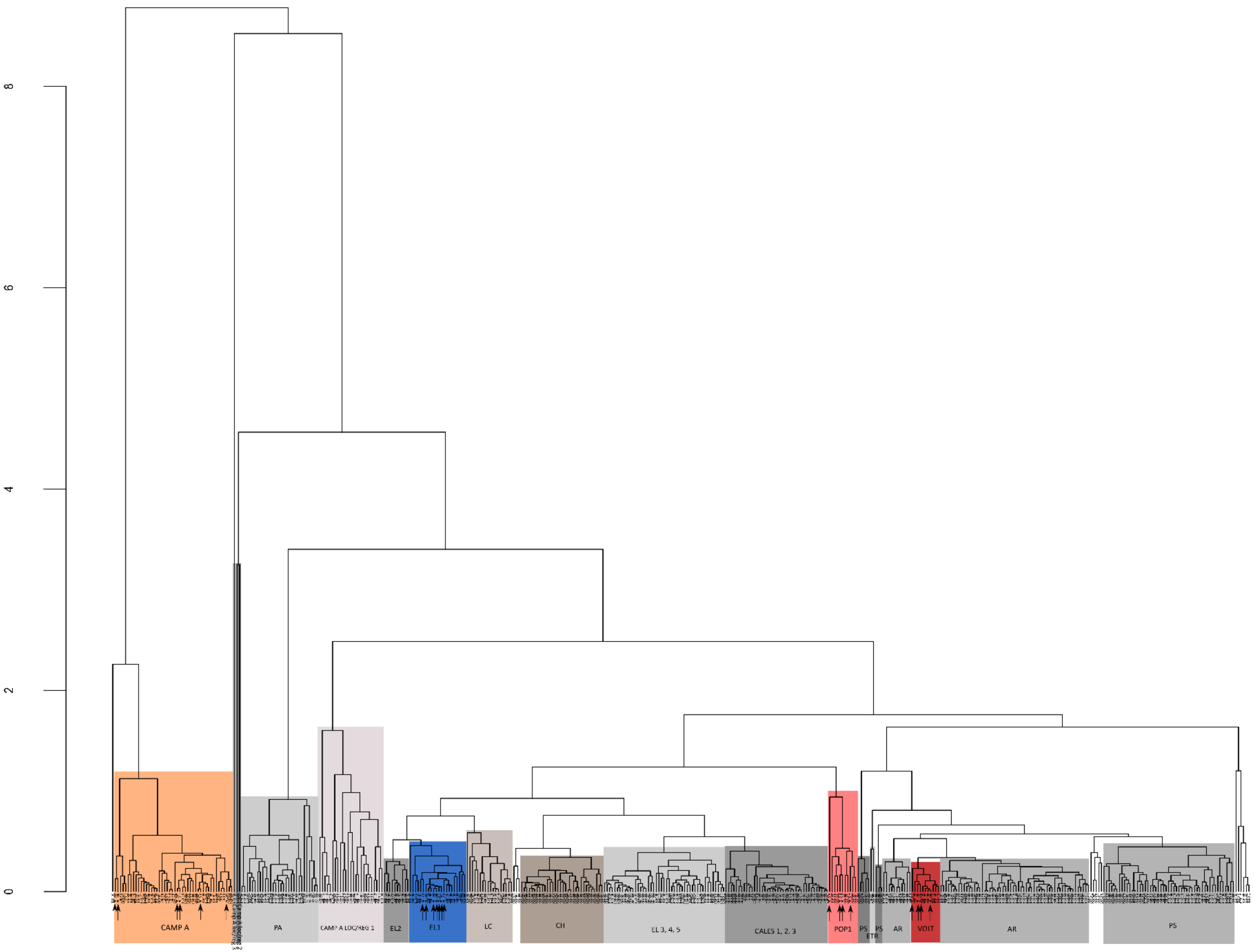

Fig. 9 Dendrogram performed using the squared Euclidian distance and the centroid agglomerative algorithm on the clr transformed subcomposition Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2, V, Cr, MnO, Fe_2O_3 (as total Fe), Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, Ce and Th. Grey groups: defined groups of the ARQUB database; colored groups: defined groups including Populonia individuals, marked by the arrow (Marisol Madrid i Fernández).

At this stage, we think that the results obtained are consistent, improve the classification of Black Gloss pottery recovered at Populonia, and, thanks to the comparison with similar materials from our database, enable us to suggest a circuit of production and distribution of this kind of ceramics through the Italian territory. Thus, individuals from Populonia can be associated to four different chemicals groups, Campanian A, related with the Campanian area, most probably with the city of Naples; EL 1, a group that can be associated with the Etrusco/Latial area; Volterra, corresponding to products from Etruria probably fabricated in the city of Volterra; and, finally, one group that cannot be assigned to any archaeometrically known workshop, city, or specific area. For this reason, the hypothesis of local production in Populonia can be supported for the three individuals archaeologically classified as coming from the PEG and one as an imitation in the Etrusco/Latial area of the products of this workshop (Table 3).

	CAMP A (n=46)		**EL 1 (n=22)**		**POP (n=11)**		**VOLT (n=11)**	
	m	**sd**	***m***	**sd**	***m***	**sd**	***m***	**sd**
Na_2O	3.21	0.34	0.94	0.1	1.1	0.21	0.87	0.09
MgO	1.62	0.14	2.89	0.21	2.6	0.17	3.37	0.2
Al_2O_3	19.17	0.31	16.24	0.32	17.1	0.78	17.83	0.57
SiO_2	60.45	0.66	57.14	1.01	56.46	1.63	54.96	1.16
P_2O_5	0.22	0.03	0.36	0.09	0.39	0.12	0.31	0.03
K_2O	5.03	0.38	2.92	0.14	2.69	0.26	2.52	0.07
CaO	4.09	0.79	12.21	1.18	11.78	1.38	12.02	0.79
TiO_2	0.71	0.02	0.74	0.02	0.78	0.03	0.86	0.02
V	81	6	113	6	115	12	138	9
Cr	36	7	136	6	122	15	167	8
MnO	0.14	0.01	0.1	0.01	0.14	0.01	0.14	0.01
Fe_2O_3	5.18	0.28	6.3	0.15	6.75	0.4	6.94	0.15
Ni	18	3	60	4	74	9	84	4
Cu	21	3	42	8	44	6	50	6
Zn	89	8	102	6	111	7	122	6
Ga	19	2	19	2	21	2	22	2
Rb	226	24	135	7	167	11	126	6
Sr	178	17	322	28	377	32	324	24
Y	40	2	27	1	32	2	28	1
Zr	348	27	160	5	214	20	144	5
Nb	51	5	20	2	21	4	22	1
Ba	312	36	385	33	664	98	425	27
Ce	167	11	75	4	109	17	80	5
Pb	58	27	26	13	78	116	47	44
Th	31	3	15	1	25	4	16	1

Table 3. Mean (m) and standard deviation (sd) for the four defined groups on normalized data (Campanian A, EL 1, Populonia and Volterra). Major and minor elements are expressed in mass %. Trace elements are expressed in $\mu g\ g^{-1}$ (Marisol Madrid i Fernández).

4.2 Mineralogical Results

In addition to chemical analysis, samples were analysed according to mineralogical character to reveal further technical aspects of production. Chemical results show that the individuals analysed in this study are ceramics considered as low calcareous (CaO < 5–6%) and calcareous (5–6%< CaO < 20-25 %) from a technical point of view. Looking at phase transformations, low calcareous ceramics are characterized by developing few high-temperature phases together with a denser microstructure and quick formation of a vitreous phase. On the other hand, calcareous ceramics commonly develop more high-temperature phases and a lighter microstructure with a progressive formation of a vitreous phase (Maggetti et al., 1981; Maniatis and Tite, 1981; Maniatis et al. 1981; Tite et al. 1982; Heimann and Maggetti, 2014). The triangle ceramic phase diagram CaO(+ Fe_2O_3 + MgO)–SiO_2 + Al_2O_3 (Fig. 10) shows how the Campanian A group is positioned in the limit of the quartz–anorthite–wollastonite and anorthite–mullite–quartz thermodynamic equilibrium triangles owing to its low calcareous nature. All the other individuals analysed in this study are positioned in the quartz–anorthite–wollastonite triangle, which is characteristic of calcareous ceramics.

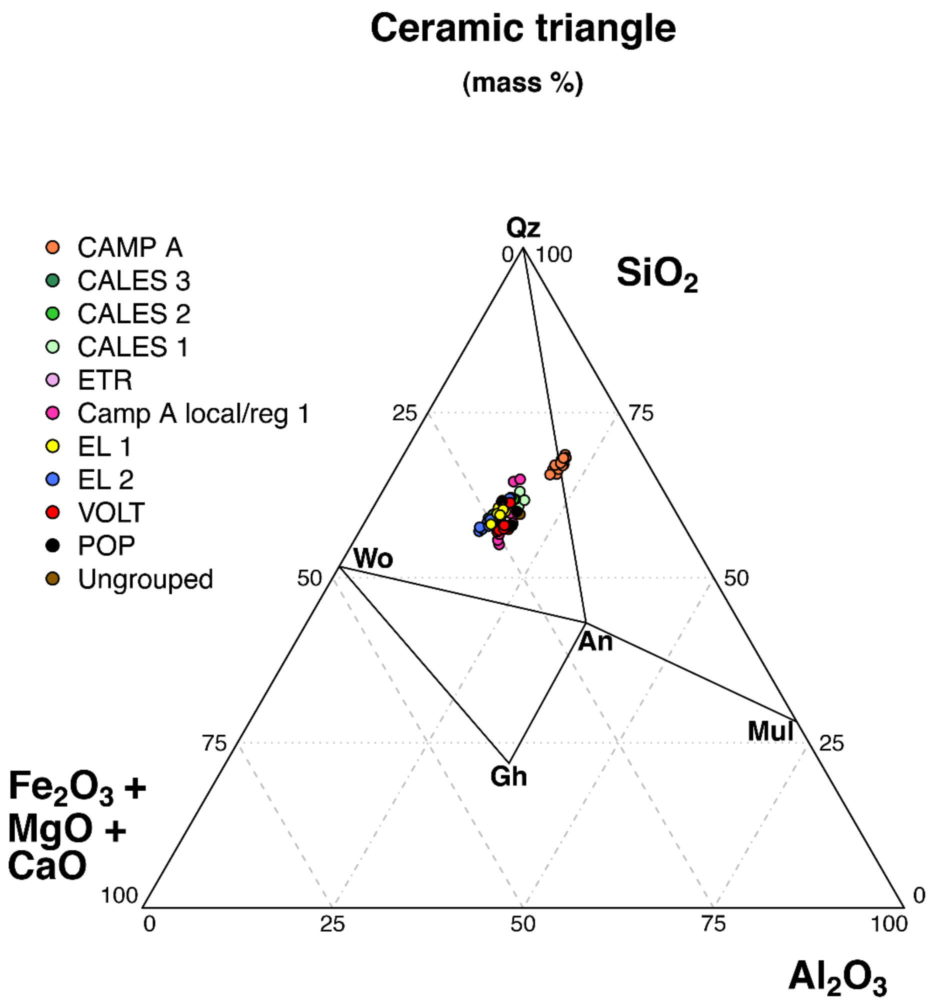

Fig. 10 Phase diagram of the ceramic triangle CaO(+Fe_2O_3+MgO)-SiO_2+Al_2O_3 showing the situation of the individuals analyzed. An: anorthite (Ca[$Al_2Si_2O_8$]), Gh: gehlenite ($Ca_2Al(Si,Al)_2O_7$); Mul: mullite (Al_6[Si_2O_{13}]); Qz: quartz (SiO_2); Wo: wollastonite ($CaSiO_3$) (Abbreviations according to Whitney and Evans 2010) (Marisol Madrid i Fernández).

Examination of the XRD diffractograms allows identifying the fabrics[2], i.e. different categories of association of crystalline phases for each chemical group, to estimate the equivalent firing temperature (EFT) of the pottery and compare the technical process. In the following lines, we will discuss exclusively the fabrics identified in this study.

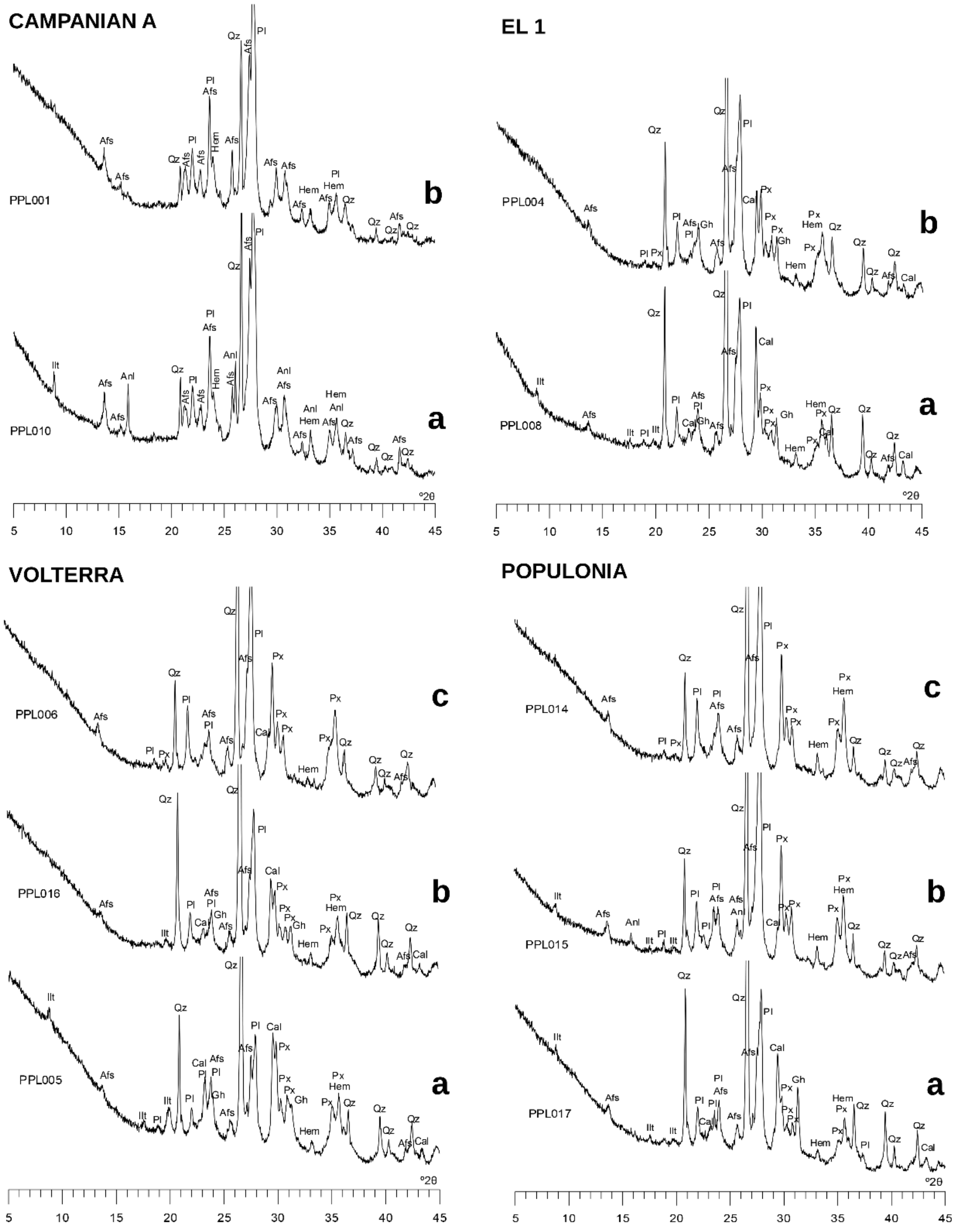

Fig. 11 XRD patterns for categories of association of crystalline phases, as detected by XRD. Afs: potassium-feldspars, Anl: analcime, Cal: calcite, Gh: gehlenite, Hem:

[2] Fabric is the final product of a paste after firing. A paste can result in one or more different fabrics (Buxeda i Garrigós and Madrid i Fernández 2016: 36)

hematite, Ilt: illite-muscovite, Pl: plagioclase, Px: pyroxene, Qz: quartz (Abbreviations according Whitney and Evans 2010) (Marisol Madrid i Fernández).

4.2.1 Campanian A

The study of the XRD diffractograms (Fig. 11, CAMPANIAN A) of the 6 individuals of Campanian A identified in Populonia (PPL001, 3, 7, 9, 10 and 11) are similar to fabrics 2 and 4 of Campanian A known in *Ilduro/Iluro* (Madrid i Fernández and Sinner, 2019, fig.12, b and d). In fact, all Populonian samples correspond to fabric 2 for which an EFT below 800 °C was estimated (Fig. 10, a), except PPL001, which resembles fabric 4 for which an EFT exceeding 950 °C /1000 °C is suggested (Fig. 10, b). The fact that only one sample shows a different EFT suggests that most Campanian A ceramics distributed to Populonia were made following the same technical process in which the intended EFT was below or about 800 °C.

4.2.2 EL 1

As discussed above, in the definition of this group through a study of black gloss pottery from the town of Emporion in *Hispania*, four different fabrics were recognised in nine samples, showing a wide range of EFT, from 800-850 °C to over 950/1000 °C. In the Populonian material, the number of individuals is similar (n=7). Their diffractograms permit the identification of two fabrics (Fig. 11, EL1), but most samples (PPL002, 8, 12, 13, and 19) fall into the first group defined in the material from Emporion. This fabric (F1) has an estimated EFT in the range of 800-850 °C (Fig. 10, a). Only two samples from Populonia were fired at a higher temperature above 950/1000 °C (PPL004 and PPL021) (Fig. 10, b). Therefore, the best documented EL 1 pottery from Populonia is the low fired one. It is worth noting that the ideal EFT for this kind of black gloss ceramics is the higher range of 900-950 °C, perhaps reflecting the lower quality of this material reaching Populonia, although the difference was imperceptible to the naked eye.

4.2.3 Volterra

The four samples that belong to this group allow the identification of three different fabrics (Fig. 11, VOLTERRA). The first is a low fired fabric F1 (PPL005) for which the EFT is estimated in the range of 800-850 °C, since the three characteristic peaks of illite at lower angles are still present together with calcite, pyroxene, and an initial gehlenite. The fabric F2 (PPL016) still shows one peak of illite, calcite and a development of pyroxene and gehlenite compared to F1 (Fig. 10, b). The third fabric (PPL006 and PPL020) corresponds to that identified in the material from Emporion as Volterran (Madrid i Fernández and Sinner, 2021, fig. 15, C) (Fig. 10, c). For these two latter fabrics, the EFT is estimated in the range of 900-950 °C. In this case, where the majority of material has a higher EFT, it may be that the higher quality pottery was selected for trade, as seems to be the case at Emporion. There the four individuals belonging to this group were fired at the exact same temperature showing an excellent control of the firing process by the potters.

4.2.4 Populonia

Finally, the difractograms of the four samples with a probable origin in Populonia reveal three fabrics for which two different EFT are proposed (Fig. 11, POPULONIA). On the one hand, fabric F1 (PPL017) (Figure 10, a) and fabric F2 (PPL015) (Figure 10, b) show similar mineral phases, with the three characteristic peaks of illite at lower angles, calcite, pyroxene and gehlenite for the first, and just pyroxene and an important reduction of the peak of calcite for the second. Despite this difference, the EFT for fabrics F1 and F2 is estimated in the range of 800-850 °C. Fabric F3 (PPL014 and PPL018) does not show peaks of illite or calcite, indicating the decomposition of both mineral phases and the increasing intensity of the peaks of pyroxene (Fig. 10, c). The EFT is thus estimated in the range of 900-950 °C for this third fabric, as a result of reducing conditions, which is an appropriate temperature for this type of pottery.

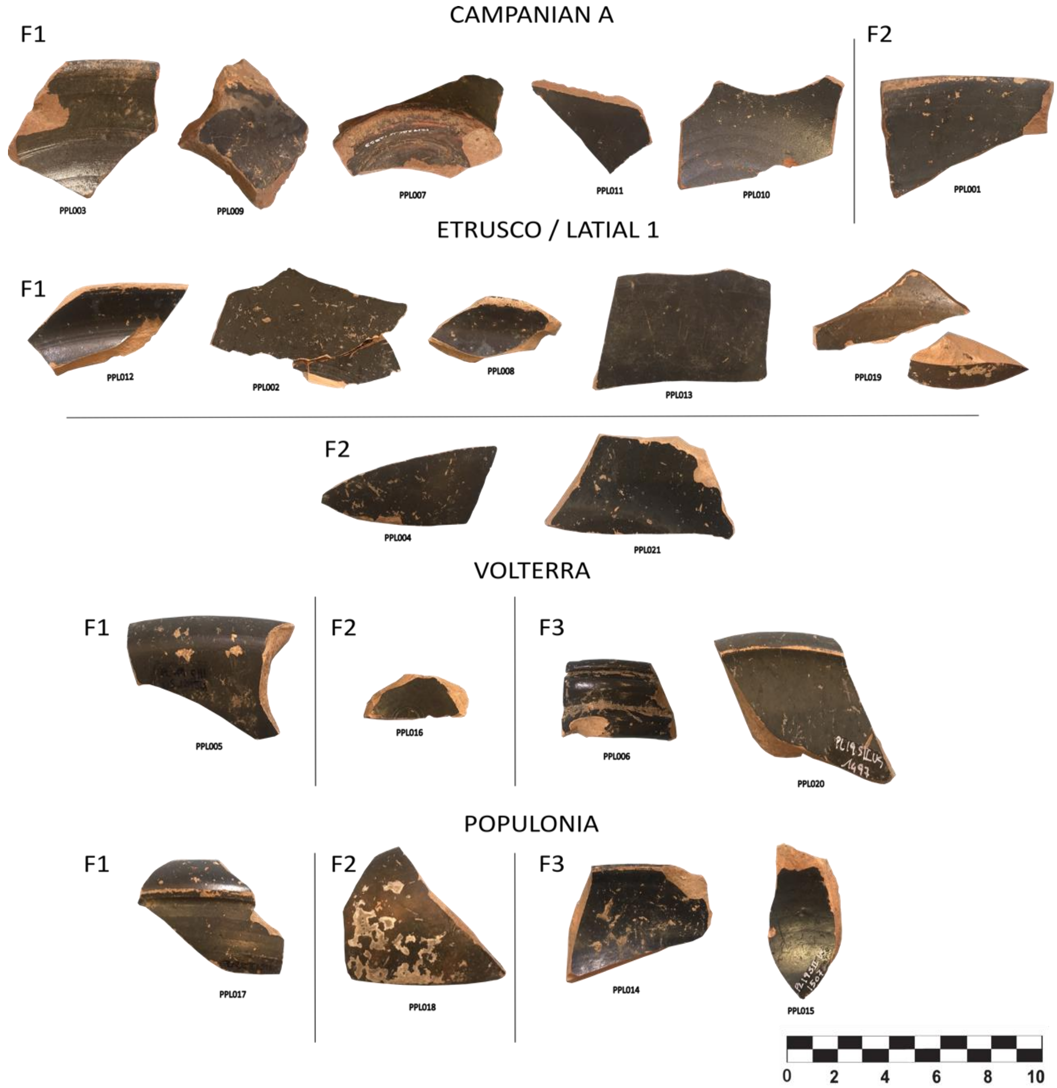

Fig. 12 Individuals from Populonia organized according to the chemical groups defined in this study (Marisol Madrid i Fernández).

In sum, from a technical point of view, the four categories of black gloss pottery identified at Populonia would be good quality tableware even if some within-groups differences can be observed. With respect to Campanian A, it is the only low calcareous pottery of the sample analysed in this study. Technically, potters must have had great control of the firing process since, as noted above, this pottery develops a more dense microstructure with a quick formation of a vitreous phase. If this process takes too long, there is the risk that the pottery collapses. In this sense, it is interesting to observe that most of Campanian A individuals from Populonia are low fired. This study enables us to observe the presence of analcime, a primary phase related to the Vesuvius area, reinforcing their origin in Naples (Madrid i Fernández and Sinner, 2019, 3186). The rest of the categories, EL 1, Volterra, and those probably made in Populonia, are calcareous products. The main advantage during the firing process is that calcareous ceramics develop a lighter microstructure with a gradual formation of a vitreous phase. That means that continuous monitoring of the firing process is unnecessary for a wide range of temperatures, and post-kiln rejections during manufacturing are also reduced. Thus, all these products can be thought of as an improvement in the process of making pottery from the first products of Campanian A, promoting the establishment of several workshops all over Italian territory (Madrid i Fernández and Sinner, 2021). As noted above, the proper EFT for firing this pottery has been shown to be in the range 900-950 °C, and this EFT has been estimated for some individuals of Volterra and Populonia, but all but two of the individuals of EL 1 are low fired. However, the reducing conditions accelerate the decomposition process of the primary phases as well as the development of new firing phases and the sintering stage (Maniatis et al. 1983). For this reason, most individuals exhibited a good quality appearance in terms of preservation of the ceramic and gloss resulting from optimal temperature for this production (Lühl et al., 2014; Chavaria and Aloupi, 2016, 510-511) (Fig. 12).

5. CONCLUSIONS

The results of this characterization study of black gloss ware recovered in excavations on Populonia's acropolis offer new insights into both the city's own history of ceramic production and those networks of exchange in which it was involved, strengthening our understanding of the primary class of fine ware ceramics at this site from the third to first centuries BCE.

Our study shows that four categories of black gloss, archaeometrically classified as Campanian A, Volterra, EL1 and Populonia were used at Populonia's acropolis site. The Campanian A products, the only low calcareous one documented, shows that potters had great control of the technological process and allows us to trace the origin of these ceramics to the Bay of Naples. Very different is the origin of the other three groups, all calcareous, documented in this study. At this point, it is not feasible to connect the EL1 production with a specific city or workshop. All we can say is that the EL 1 group can be linked to the Etrusco/Latial area. Its chemical characteristics does not correspond to the Campania area nor to that of Etruria. Picon pointed out that workshops corresponding to Etruscan/Latial area should show intermediate characteristics of both regions (Cuomo di Caprio and Picon, 1994: 181). In collaboration with Olcese (Olcese and Picon, 1998), Picon also underlined the difficulty of distinguishing between regional productions, unless working directly with reference groups of certainly identified production centres. However, our EL 1 group fits within the reference group for South Etruria and Latial black gloss provided by Morel and Picon (1994: 26, Table 1) and displays characteristic similarities with the area's production established by other studies (cf. Olcese and Picon, 2003). Geochemical similarities of the area comprised from southern Etruria practically to northern Campania make it difficult to locate workshops more precisely but group EL 1 can be associated with this general area.

Notably, none of the Populonian samples archaeologically classified as Campanian B and PEG analyzed in this study comes from Campania. Therefore, in addition to the existing long distance trade networks that supplied the city with Campanian A and EL1, the picture also suggests the existence of local/regional commercial circuits providing black gloss to Populonia (e.g. from Volterra).

The comparison of results with those already published in the framework of the MedConTaCCt project, including the characterization of black gloss ware from the cities of Cosa, *Ilduro, Iluro* and *Emporion*, are also interesting. The four black gloss groups documented at Populonia also reached the nearby Roman colony of Cosa and the northeastern territories of Hispania, suggesting that these territories shared, at least in part, common supply networks. However, in Hispania, while Campanian A reached all the sites discussed here in significant numbers, EL1, Volterran and possible Populonian products are only documented in the harbour of *Emporion* but are so far absent from *Ilduro* and represented by a single individual of EL1 at *Iluro*. Campanian A, Volterra, EL1 and possible Populonian products are also present in *Tarraco* (paper in preparation).

Particularly interesting is the definition here of the group named Populonia, consisting of samples macroscopically identified with the PEG (3) and a local imitation of this workshop (1). These individuals form a group that cannot be currently assigned to any archaeometrically known workshop, city, or specific area, making feasible their identification as local products from Populonia. This association should be refined by further sampling but holds significant potential importance, as it would significantly extend the map of known production sites of the PEG. As noted, scholarship has expanded from considering this a Roman production to associating it with workshops in South Etruria and Latium, while still retaining its Roman cultural character. The Roman character is further reinforced by evidence for the production of the PEG away from Rome but in Roman colonies, especially at *Ariminum* on the Adriatic coast, where it is often held that ceramicists from Latium moved with the colony's establishment in 268 BCE (Brecciaroli Taborelli 2000, 15-16; Van Kerckhove 2004, 62-63). Populonia would represent the first production site associated with the class in North Etruria, while its significance to our overall picture comes not only from its great distance from Rome but also from the fact that it was not a Roman colony. As the earliest major black gloss production in Italy, the PEG forms an innovative product in the wider history of Italian ceramic production. Ferrandes (2018) attributes the elaboration of this and other Mid-Republican ceramic classes to Greek ceramicists arriving along with technological knowledge to Central Italy and Rome. The potential involvement of Populonia would complement the picture, especially given its non-colonial status and signs of cultural continuity. Chemical characterization of material assigned to this workshop from other regional centers in North Etruria such as Pisa, where pottery of this class is known (e.g. Taccola, 2019), would be instructive.

This hypothesis of local ceramic production at Populonia in the late fourth and third century supports the impression made by Romualdi (1992), who suspected locally manufactured products of the PEG. It is further suggestive in light of kiln spacers and waste material from the same period published by Fusi (2020). The present paper has offered an intriguing possible response to questions of the nature of local potters' productive activities in the period just after Rome's entrance into the region. We close by encouraging further investigation of Populonian ceramic production at an early date in Italian black gloss ware through scientific analysis. We especially encourage sampling of black gloss ceramics found at the site in well dated archaeological contexts, as well as those kiln spacers and wasters to detect any similarities in the recipes.

ACKNOWLEDGEMENTS

Permission to study the material was kindly granted by Dr. Andrea Camilli for the Soprintendenza Archeologia, Belle Arti e Paesaggio per le Province di Pisa e Livorno. Excavation of the *balneum* resumed in 2019 thanks to the awarding of a new project for the development of the archaeological park financed by the Regione Toscana from funds from the Comunità Europea (PorCreo 2014-2020). Archaeometrical work was supported by the Social Sciences and Humanities Research Council of Canada (SSHRC) funding the projects *Mediterranean Connectivity: Economy, Trade and Commercial Circuits in the Roman West (2nd c. BCE –1*st *c. BCE)* (890-2019-0037, A.G. Sinner) and *The Formation of the Economy of Roman Italy: Latium, Etruria, and Samnium, 500 - 200 BCE* (430-2018-00546, S. Bernard). Analyses by X-ray fluorescence (XRF) and X-ray diffraction (XRD) were performed at the Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB).

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