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## Archaeometric study on *terra sigillata* from Cales (Italy)

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### Abstract

Mineralogical and petrographical studies on 23 ancient pottery fragments of *terra sigillata* from ancient Cales (today Calvi Risorta, Caserta) are here discussed. Stamps on pottery surfaces assigned the fragments to Cales and other Italian workshops acting in Arezzo and Northern Italy area between 1<sup>st</sup> century B.C.-1<sup>st</sup> century A.D., other stamped fragments have an uncertain provenance.

The mineralogical and petrographical features of pastes have been detected using optical microscopy, X-ray diffraction, X-ray fluorescence, and DTA-DTG analyses.

The geochemical comparisons among ceramics, production indicators of Calenian pottery (Black Glazed pottery spacers) and local clayey raw materials allowed to distinguish locally produced potsherds from imported ones. Moreover, the whole archaeological and archaeometric data set allowed to draw main technological aspects of a fine ware production much used on rich roman tables.

*Key words:* *terra sigillata*; Calenian stamps; *Satrius* stamp; Cales.

### Introduction and historical background

The “Latin” colony of Cales (modern-day Calvi Vecchia – Caserta; Figure 1) located on the *Via Latina*, 8 km ca. south of *Teanum Sidicinum* (today called Teano) and 20 kms ca. north of *Capua* (modern-day S. Maria Capua Vetere), was the most important Roman outpost in Campania during the Romanization of Southern Italy, from the Samnite to the Hannibalic Wars. The city had

an important strategic function because from its position Romans could control the *Ager Falernus* (colonized by the Romans in the same period), the *Campus Stellatis* and the *Ager Campanus*, the so-called *Capuan* territory at the other side of the river *Volturnum* (Pedroni, 1993).

Exhausted by the Hannibalic War, the city received a new colony in 185 B.C. (Pedroni, 1990); the *Liber Coloniarius* reported land assignments of Gracchan type (from 133 B.C.)

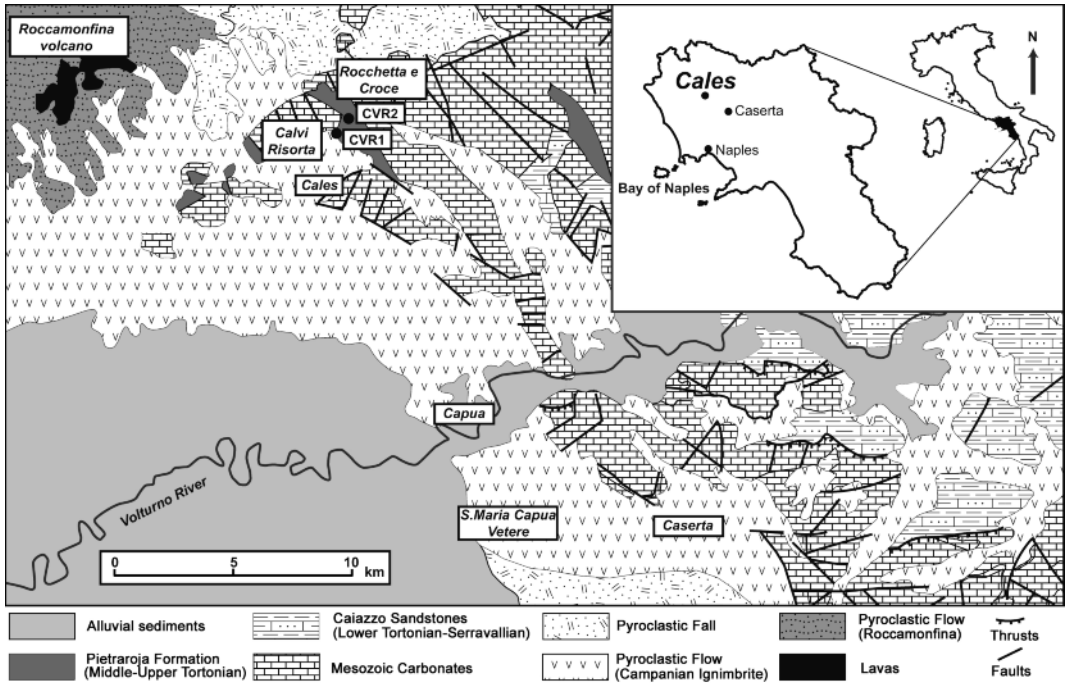


Figure 1. Geological sketch map of Cales area.

in the Calenian territory. Romans used the city as fortress during the Social War (91-87 B.C.) fought against the Italic rebellious, and it was surely involved in the Civil War, entertaining on his territory Silla's troops on the way back from Greece in 83 B.C.

Its territory was redistributed in Augustan age, period in which Cales knew a new prosperity, as testified by urban and architectural interventions sponsored by local elite (Johannowsky, 1961; Pedroni, 1993).

In the Late Antiquity, the perimeter of the city was restricted, the city suffered the invasion of the Vandals, and in medieval time reduced to a suburb around the castle risen on the little *arx* of the Roman colony, dominating the old *Via Latina*.

Cales was known in antiquity for the fine ware productions. One of the most diffused production was the Black-Glazed pottery (hereafter *BG*)

exported from the first half of the third century to the half of the first century B.C. (Pedroni, 1993; 1996) when was gradually replaced by the so called *terra sigillata* (hereafter *TS*). Also the Calenian workshops converted their production following the new style (*Arretino modo*) started from *Arretium* (modern-day Arezzo) and quickly diffused throughout the Empire (Cuomo di Caprio, 2007).

For long time the definition of "Calenian Pottery" has been used as synonym of *BG* pottery decorated with relief, produced in many centres of ancient Italy between the end of the fourth and the beginning of the third century B.C. (Pagenstecher, 1909; Jentel, 1976; Sanesi Mastrocinque, 1982). The plain black coarsed Calenian ceramic timidly appeared in modern studies only in 1960 in which Lamboglia (1960) attributed a production of Campanian pottery of

“type B” to Cales. During the following decades, a precise knowledge of the existence of black-glaze production named “*B-oïde*” manufactured in Cales was given by Arcelin and Morel (Arcelin, 1978; Morel, 1978; 1980; 1981; 1988; 1989; 1990).

The first study on Calenian TS was published by Morel (1989) and following contributions (Pedroni and Soricelli, 1996; Pedroni and Tasser, 2002) pointed out the good quality of Calenian TS, the repertory perfectly comparable to other Italian TS productions such as the *Arretina* with their characteristic relief decorations.

It seems to have been produced from the half of the first century B.C. to the whole Augustan age; the absence of stamps *in planta pedis* (stamps with frame in the shape of a human foot) used from the beginning of the Tiberian age, could be simply imputable to a casual gap in the findings. The Calenian TS seems to have had a diffusion that has overcome the regional boundaries, reaching, although in limited quantity, more distant areas like the Apulian region and some sites of the Spanish coasts (Pedroni and Soricelli, 1996).

The aim of the present paper is a preliminary mineralogical and petrographical characterization of some samples of Calenian TS samples, identified by presumed stamps of Calenian workshops, and a comparison with other Italian TS samples and others with an uncertain provenance. The whole data set allowed a preliminary technological characterization, in terms of component of the paste, firing temperatures and clayey raw materials, of a fine ware ceramic widespread on roman tables during Imperial age.

### Geological setting

The city of Calvi Risorta (ancient Cales) is located in the northern sector of the Campanian Plain, South of *Roccamonfina* volcano and just West from the *Monti Trebulani* a mountain chain

formed by Mesozoic carbonates (Lazio-Campania-Molise carbonate platform; Bonardi et al., 2009), found in the northern area of the Volturno River plain (Figure 1).

Extensive deposits of clays outcrop on the southern side of the *Monte Maggiore* relief, between the towns of Calvi Risorta and Rocchetta e Croce. These deposits, belonging to the foredeep succession of the Pietraraja Formation (Middle-Upper Tortonian), have been exploited up to modern times for pottery and brick productions.

South of Calvi Risorta is located the archaeological area of Cales, which lies on pyroclastic flow deposits from Phlegraean Fields, represented by the Campanian Ignimbrite (39 ka, De Vivo et al., 2001; Fedele et al., 2008) and, subordinately, by the incoherent facies of the Neapolitan Yellow Tuff (15 ka, Deino et al., 2004).

### Materials and methods

The analyzed fragments were found in an area NE of the plateau hosting the Roman city but, unfortunately, the chronology cannot be precisely assigned because of the lack of a stratigraphic context.

The fragments have been divided in six groups according to their area of production, certain or hypothetical, on the base of the stamp or the peculiar decorations (Table 1):

- n. 4 vessels of “*Arretina*” manufactured in the workshops of Arezzo (or Cincelli), signed by: *Umbr(icius)* (sample 18); *Soter A. Sesti* (OCK 1945, sample 21); *C. Gavius* (OCK 868/869, sample 25); sample 30 likely belongs to this group, too;

- n. 2 vessels for which a Padanian origin could be hypothesized. In particular, sample 36 shows the signature of *Agath(us)* (OCK 54); sample 37 is a fragment of an “Aco beaker”, with shape and decoration typical of a North-Italian production;

- n. 2 vessels ascribable to Late-Italian manufacturers (Pisa origin). The sample 38 is

Table 1. Archaeological features of Italian TS samples.

Samples	Stamps	Provenance	Classes	Cronology (centuries)
4	<i>Satri(us)</i>	<i>Cales</i>	<i>TS</i>	I B.C.-I A.D.
5	<i>(T)heophil(a)</i>	<i>Cales?</i>	<i>TS</i>	I B.C.-I A.D.
6	<i>Darn(...) Vecil(ius)</i>	<i>Cales?</i>	<i>TS</i>	I B.C.-I A.D.
9	<i>Cra(...) Meno(laus)</i>	<i>Cales?</i>	<i>TS</i>	I B.C.-I A.D.
10	<i>Satri(us)</i>	<i>Cales</i>	<i>TS</i>	I B.C.-I A.D.
11	<i>Auctus</i>	<i>Cales?</i>	<i>TS</i>	I B.C.-I A.D.
18	<i>Umbr(icius)</i>	<i>Arezzo</i>	<i>TS</i>	I B.C.-I A.D.
21	<i>Soter A. Sesti</i>	<i>Arezzo</i>	<i>TS</i>	I B.C.-I A.D.
25	<i>C. Gavius</i>	<i>Arezzo</i>	<i>TS</i>	I B.C.-I A.D.
30		<i>Arezzo?</i>	<i>TS</i>	I B.C.-I A.D.
32	<i>Cupitus</i>	<i>Cales?</i>	<i>TS</i>	I B.C.-I A.D.
33	<i>Iucu(ndus) Valeri Tyranni</i>	<i>Central Italy</i>	<i>TS</i>	I B.C.-I A.D.
34	<i>Notus</i>	<i>Central Italy</i>	<i>TS</i>	I B.C.-I A.D.
35	<i>Pistus (or Iustus)</i>	<i>Central Italy</i>	<i>TS</i>	I B.C.-I A.D.
36	<i>Agath(us)</i>	<i>Padanian origin</i>	<i>TS</i>	I B.C.-II A.D.
37		<i>Padanian origin</i>	<i>TS</i>	I B.C.-I A.D.
38	<i>L.(ucius) R.(asinius) P.(isanus)</i>	<i>Pisa</i>	<i>TS</i>	I B.C.-I A.D.
39	<i>Cra(...) Meno(laus)</i>	<i>Pisa</i>	<i>TS</i>	I B.C.-I A.D.
40		<i>Cales?</i>	<i>TS</i>	I B.C.-I A.D.
CAL1		<i>Cales</i>	<i>BG spacer</i>	III B.C.-I A.D.
CAL2		<i>Cales</i>	<i>BG spacer</i>	III B.C.-I A.D.
CAL3		<i>Cales</i>	<i>BG spacer</i>	III B.C.-I A.D.
CAL4		<i>Cales</i>	<i>BG spacer</i>	III B.C.-I A.D.

signed by *L.(ucius) R.(asinius) P.(isanus)* in *planta pedis* (OCK 1690), and sample 39 by *L. Rasini(us) Pis(anus)*, in *lunula*;

- n. 6 vessels of possible Calenian origin for the presence of signatures well known in Campania or attested only at Cales. The stamps are: *(T)heophil(a)* (Sample 5); *Darn(...)* *Vecil(ius)* (sample 6); *Auctus* (sample 11); *Cupitus* (sample 32); *Cra(...) Meno(laus)* (sample 9). Sample 40 is a wall fragment with relief decorations for which it was hard to find

any attribution;

- n. 3 vessels of uncertain origin, with signatures diffused in Central Italy and in the region of Rome: *Iucu(ndus) Valeri Tyranni* (OCK 2307, sample 33); *Notus* (sample 34), *Pistus* (sample 35, as *Iustus*).

- n. 2 vessels of Calenian origin. The stamp is *Satri(us)* (OC 1671) for samples 4 and 10.

All these sherds generically are of Augustan age (27 B.C.-14 A.D.), the Padanian TS seems chronologically later and two Late-Italian TS

fragments can be dated between the half of the I century A.D. and the beginning of the II century A.D.

In order to identify the local products all pottery were compared with 4 kiln refuses samples (BG spacers, CAL1, CAL2, CAL3, CAL4), and two clayey sediments coming from the surrounding area of Cales. The sediments are represented by greyish clayey silts belonging to the Pietraraja Formation. The first sample (CVR1) was collected in Rocchetta e Croce area, the second one (CVR2) in a clay quarry next to Calvi Risorta town. The samples were chosen in a minero-petrographic dataset of clayey raw materials collected in Campania region (De Bonis et al., 2010; De Bonis, 2011), based on their sedimentological and compositional homogeneities and the proximity of the outcrops to the archaeological area.

The following investigations were carried out on the above described samples:

- Optical Microscopy (OM, Leitz Laborlux 12 POL) on thin sections;

- X-Ray Fluorescence Spectrometry (XRFS): major and trace elements were analysed with a Philips PW1400 spectrometer. The detection limits and standard calibrations are reported in Melluso et al. (2001).

- X-Ray Diffraction Analysis (XRD): semi-quantitative mineralogical analyses were carried out with a Philips PW1730/3710 diffractometer using the following operative conditions: CuK $\alpha$  radiation, incident and diffracted-beam Soller slits, curved graphite monochromator, 40 kV, 30mA, 3-70° scanning interval, step size = 0.020° 2 $\theta$  and counting time of 5s per step. Powders with grain size < 10  $\mu$ m were obtained using a McCrone microniser mill. Treatments (Air dried, EG solvated, and heated at 375° and 550 °C) on < 2 $\mu$ m fractions, allowed to identify clay minerals (Moore and Reynolds, 1997).

- Thermal Analysis (DTA-DTG): carried out with a Multiple thermoanalyzer Netzsch STA 409 on 100 mg samples.

## Results

### *Optical Microscopy (OM)*

Direct observations of thin sections in optical microscopy gave information on textural features and no-plastic inclusions of the ceramic pastes. Sample 10 was not analysed as the thin section was not available.

All TS samples show an overall homogeneity (Figure 2), and are characterized by a very fine isotropic or anisotropic matrix, ranging in colour from light brown to dark brown, and from reddish brown to brown. No-plastic inclusions are small-size rounded or sub-rounded grains (0.01-0.5 mm) of quartz, white mica, and oxides; brown mica and feldspar along with traces of clinopyroxene, volcanic fragments and scoriae were also observed in few samples (see Table 2). Porosity is generally low. Some samples showed calcite microcrysts, as remains of shells, reacted grains or as post-deposition carbonate. The presence of a red-brown slip, 0.01 to 0.02 mm thick, was also evidenced in TS samples (Table 2).

The 4 kiln refuses (BG spacers, CAL1, CAL2, CAL3, CAL4, also described in detail by Langella and Morra, 2001) are characterized by a coarser fraction composed of no-plastic inclusions consisting of quartz, feldspar, white and brown mica and rare clinopyroxene crystals. Carbonate clasts are visible, and in some cases are very abundant. A slip of about 0.02 mm also occurs in these samples.

### *XRD analyses*

Semi-quantitative results of mineralogical analyses are reported in Table 3.

All the samples (TS and BG spacers) are characterized by prevailing quartz and feldspars and minor goethite. Mica represents the other common phase; in some samples (30, 34, 36, 38, and 39) they are recorded in very low amounts.

In TS samples, clinopyroxene always occurs, except in samples 4 and 10; it should be remarked that this phase was identified in low

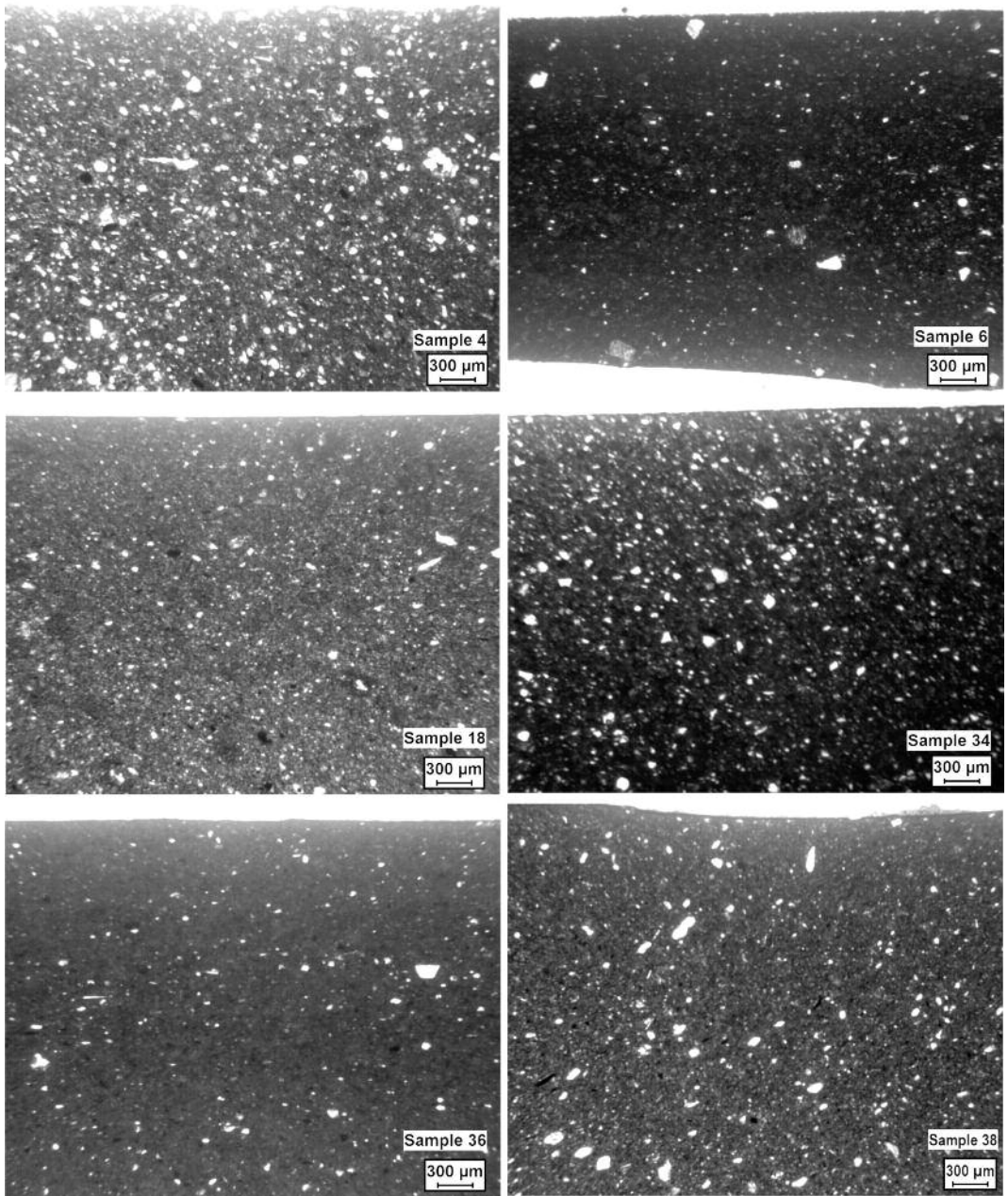


Figure 2. Representative thin sections of TS samples.

Table 2. Representative optical microscopic features of TS samples.

Samples	Matrix	Colour	Texture	Slip	Size (mm)	Porosity	Qz	Feld	w-Mica	b-Mica	Ox	Cpx	Volcanic fragments	Scorias	Secondary calcite	Calcite	Fossil remains
4	weakly anisotrope	light brown	serial	thin layer red-brown (0.02 mm)	0.02-0.3	very low	xxxx	xx	xx	x	xx	tr	//	//	//	x	//
5	isotrope	light brown	serial	thin layer red-brown (0.01 mm)	0.01-0.1	very low	xxxx	xx	xx	//	xx	//	//	//	x	//	//
6	weakly anisotrope	reddish brown	serial	thin layer red-brown (0.01 mm)	0.02-0.2	very low	xxxx	//	xx	//	x	//	//	//	//	//	//
9	weakly anisotrope	reddish brown	serial	thin layer red-brown (0.01 mm)	0.01-0.1	very low	xxxx	//	xx	//	x	//	//	tr	xx	x	//
11	anisotrope	light brown	serial	thin layer red-brown (0.01 mm)	0.01-0.1	very low	xxxx	x	xx	//	x	//	//	tr	//	//	//
12	anisotrope	light brown	serial	thin layer red-brown (0.02 mm)	0.02-0.2	very low	xxxx	x	xx	//	x	//	//	//	//	//	tr
18	weakly anisotrope	brown	serial	thin layer red-brown (0.01 mm)	0.01-0.1	very low	xxxx	//	xx	x	x	//	//	//	x	//	//
21	isotrope	brown	serial	thin layer red-brown (0.02 mm)	0.01-0.2	very low	xxx	//	xx	x	x	//	//	//	//	//	//
25	weakly anisotrope	reddish brown	serial	thin layer red-brown (0.01 mm)	0.01-0.1	very low	xxx	//	xx	//	x	//	//	//	x	//	//
30	isotrope	brown	serial	thin layer red-brown (0.01 mm)	0.01-0.1	very low	xxx	//	xx	x	x	//	//	//	x	//	//
32	weakly anisotrope	brown	serial	thin layer red-brown (0.01 mm)	0.01-0.3	very low	xxx	x	xx	x	x	//	tr	//	x	xx	//
33	weakly anisotrope	light brown	serial	thin layer red-brown (0.01 mm)	0.01-0.2	very low	xxxx	x	xx	//	x	//	//	//	//	//	//
34	isotrope	brown	serial	thin layer red-brown (0.02 mm)	0.01-0.2	very low	xxxx	xx	xx	//	xx	//	//	//	//	//	//
35	isotrope	reddish brown	serial	thin layer red-brown (0.01 mm)	0.01-0.3	very low	xxx	//	xx	//	x	//	tr	//	//	//	//
36	isotrope	dark brown	serial	thin layer red-brown (0.01 mm)	0.01-0.1	very low	xxx	//	xx	x	x	//	//	//	//	//	//
37	isotrope	dark brown	serial	thin layer red-brown (0.01 mm)	0.01-0.1	very low	xxx	//	xx	x	x	//	//	//	x	//	//
38	weakly anisotrope	dark brown	serial	thin layer red-brown (0.02 mm)	0.01-0.5	very low	xxx	//	xx	tr	x	//	tr	//	x	//	//
39	weakly anisotrope	brown	serial	thin layer red-brown (0.01 mm)	0.01-0.1	very low	xxx	//	xx	tr	x	//	//	//	x	xx	//
40	weakly anisotrope	light brown	serial	thin layer red-brown (0.01 mm)	0.02-0.1	very low	xxxx	x	xx	//	x	//	(x)	//	//	//	//

Abbreviations: Qz, quartz Feld, feldspar w-Mica, white mica b-Mica, brown mica Ox, oxides Cpx, clinopyroxene. xxx = predominant, xxxx = abundant, xx = frequent, x = sporadic, tr = traces, // = not present.

Table 3. Abundances of minerals in the XRD analyses taken for TS samples.

Sample	Quartz	Feldspar	Calcite	Mica	Diopside	Goethite	Gehlenite	Gypsum
4	xx	x	xx	x		tr		
5	xx	xx	x	x	x	tr	x	
6	xx	xxx	x	x	x	x		
9	xx	xx	x	x	tr	x	x	
10	xx	xx	x	x		tr	x	
11	xx	x	x	xx	tr	x		
18	xx	x	tr	x	x	tr		
21	xx	xx	tr	x	x	tr		
25	xxx	xx	xx	x	x	x		x
30	xx	xxx	x		x	x		
32	xxx	xxx	xx	x	x	x		
33	xx	xx	x	x	x	tr	x	
34	xx	xxx	x		x	tr	x	
35	xx	xx		tr	x	x		
36	xx	xxx			x	x		
37	xxx	xxx	tr	tr	x	x		
38	xxx	xxx	xx		x	x		
39	xx	xxx	tr		x	x		
40	xx	xx	x	x	x	tr	tr	
CAL1	xxx	xx	xx	x	x			
CAL2	xxx	xx	xx	x	x			
CAL3	xxx	xx	xx	x	x			
CAL4	xxx	xx	xx	x	x			

xxxx = predominant, xxx = abundant, xx = frequent, x = sporadic, tr = traces

quantities and just one sample in thin section (traces in sample 4) thus, considering the significant amount pointed out in XRD, it should be considered a later phase formed after the firing process (over 850 °C) (Grifa et al., 2009a).

In BG spacers calcite occurs in significant amount; clinopyroxene, rarely observed in thin sections, again should be regarded as a phase newly formed after heating.

Gehlenite was detected in samples 5, 9, 10, 33, 34 and 40. Calcite is ubiquitous (except for samples 35 and 36). The occasional occurrence of gypsum could be considered as efflorescences affecting the surface of sample 25.

Clay samples (CVR1 and CVR2) mainly consist of illite-smectite mixed layers, kaolinite and chlorite along with abundant quartz and calcite, with minor feldspar and dolomite.

#### *XRF analyses*

The analyses of major (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> in wt.%) and trace elements (Ni, Rb, Sr, Y, Zr, Nb, Sc, V, Cr, Ba, La, Ce, Nd in ppm) are reported in Table 4.

Major elements vary in a very narrow range (SiO<sub>2</sub>: 51.9-60.7 wt.%; Al<sub>2</sub>O<sub>3</sub>: 14-17 wt.%; K<sub>2</sub>O: 2.5-3.4 wt.%; TiO<sub>2</sub>: 0.7-0.9 wt.%) except for



CaO along with LOI which show wider ranges (8.2-16.1 wt.% and 1.1-9 wt.%, respectively).

The trace elements reflect the behaviour of major elements. In particular, Ni (63-106 ppm), Cr (110-197 ppm) and Rb (121-188 ppm) show quite narrow ranges, whereas Sr (282-457 ppm) and Ba (337-612 ppm) account for higher variability.

The chemical composition of four kiln refuses (CAL 1, 2, 3 and 4; Table 4) generally reflects the range observed for all TS fragments.

The chemical composition of the two investigated clays (CVR1 and CVR2) are quite similar. They both show a high CaO content (15.6-17.6 wt.%). Silica ranges between 53.4 and 54.9 wt.% whereas alumina between 13.3 and 15.1 wt.%. K<sub>2</sub>O never exceeds 2.7 wt.%, Na<sub>2</sub>O is always below 0.6 wt.% and Fe<sub>2</sub>O<sub>3</sub> content ranges between 5.9 and 6.5 wt.%. As far as trace elements are concerned Rb is higher in CVR1 (153 ppm vs. 116 ppm); by contrast, Sr is higher in CVR2 (431 ppm vs. 379 ppm). Ba, Zr, Ni and Cr display in similar amounts in both samples (Table 4).

Chemical variations within the whole set of chemical data are reported in Figure 3 where the samples TS from Northern and Central Italy, the supposed Calenian fragments, kiln refuses and CVR1 and CVR2 clays are plotted.

The CaO vs. SiO<sub>2</sub> diagram (Figure 3a) evidences the CaO-rich character of all the samples; also, it should be remarked the chemical similarity between the supposed Calenian fragments and the kiln refuses, whereas the two clays show the highest CaO values (up to 18 wt.%). A negative correlation between Fe and Ca is evidenced in the diagram of Figure 3b (Fe<sub>2</sub>O<sub>3</sub> vs. CaO diagram). Relevant information are provided by Ti/Zr vs. Ba (Figure 3c) and Cr vs. Ba (Figure 3d) diagrams for TS samples that seem to arrange according to their area of presumed provenance.

#### *DTA analyses*

DTA analyses largely confirm the loss of

weight determined with L.O.I. (Tables 4 and 5) that ranges between 0.3% (sample 21) and 8.2% (sample 10). The endothermic effect at about 800 °C due to calcite dissociation accounts for the largest portion of weight loss along with a less pronounced effect (ca. 470 °C) likely due to hydroxyl ions release (Moropoulou et al., 1995).

### **Discussion**

All fragments show tiny grains of quartz, feldspar, white mica, brown mica and oxides set in very fine pastes. The most significant differences among all the investigated samples are the grain content, with packing values that never exceed 10% and, subordinately, the colour of the matrix, which varies from light brown, to reddish brown, brown, and dark brown. However, the colour and optical activity of the sintered clay matrix is conditioned by the firing temperature. Calcite was also observed as fossils and crystals remains, as late deposition of microcrysts on shards surfaces or as filling of voids. A high CaO content of the starting raw materials can be further testified by the crystallization of Ca-bearing phases only detected by XRD analyses which can be used as markers of the firing temperatures. On this account, all samples definitely experienced high firing temperatures, but the presence of prograde and neoformation phases allowed to narrow the temperature ranges. In particular, firing temperatures can be estimated by the occurrence of new forming Ca-bearing phases (diopside and gehlenite) and by the persistence of mica.

In spite of its abundance revealed by XRD, calcite cannot be considered as a useful thermal indicator. In fact, the presence of both calcite and diopside is not consistent with the lack of gehlenite, as described by firing reaction dynamics of Ca-rich phases, starting from CaO rich clayey raw materials (Cultrone et al., 2001; Grifa et al., 2009). Most of the analyzed samples, in fact, show calcite and diopside association, thus

Table 4. Major (wt.%) and trace (ppm) elements for TS samples, kiln refuses and clays (V, La, Ce and Nd not detected). The major oxide analyses are recalculated to 100 wt.% LOI-free.

Samples	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	sum	LOI
4	56.0	0.7	14.2	6.2	0.1	3.9	15.0	0.2	3.4	0.3	100	9.0
5	57.0	0.8	15.6	7.3	0.2	3.7	11.9	0.5	2.8	0.3	100	4.1
6	55.5	0.8	15.6	7.2	0.2	4.0	13.1	0.6	2.7	0.3	100	3.8
9	58.0	0.8	15.6	7.1	0.2	3.3	11.3	0.3	3.1	0.3	100	6.3
10	57.0	0.7	14.0	6.1	0.1	3.6	15.1	0.3	3.0	0.2	100	7.5
11	57.3	0.7	15.2	6.7	0.1	4.2	12.1	0.3	3.2	0.3	100	6.1
18	56.8	0.9	16.7	8.0	0.2	4.7	9.6	0.2	2.7	0.2	100	2.1
21	55.3	0.8	16.1	7.5	0.2	4.8	11.7	0.7	2.6	0.2	100	1.1
25	55.5	0.9	17.0	8.0	0.2	4.9	9.9	0.4	3.0	0.2	100	2.8
30	51.9	0.7	14.6	6.7	0.2	4.3	16.1	0.2	2.5	2.7	100	3.3
32	55.4	0.7	15.5	6.9	0.2	4.0	14.1	0.2	2.8	0.3	100	3.9
33	56.0	0.7	15.1	6.6	0.2	3.8	13.8	0.7	2.8	0.3	100	5.1
34	60.7	0.7	14.6	6.5	0.2	3.5	10.0	0.6	2.5	0.8	100	3.6
35	55.6	0.8	16.4	7.2	0.2	3.4	12.7	0.6	2.8	0.3	100	4.0
36	55.7	0.8	15.7	6.9	0.1	4.6	12.7	0.3	2.9	0.4	100	1.5
37	54.6	0.8	15.9	7.4	0.2	4.5	12.5	0.5	2.6	1.0	100	1.9
38	55.5	0.8	14.9	7.1	0.2	4.2	13.8	0.6	2.8	0.3	100	4.9
39	58.1	0.9	16.1	8.3	0.2	4.1	8.2	0.8	2.9	0.3	100	1.9
40	57.0	0.8	15.4	7.0	0.1	4.7	11.3	0.3	3.1	0.3	100	4.6
CAL1	55.8	0.8	16.2	6.9	0.1	4.6	11.9	0.4	3.1	0.3	100	1.6
CAL2	56.6	0.7	15.0	6.3	0.1	4.6	12.9	0.6	2.9	0.3	100	3.1
CAL3	57.2	0.7	14.3	6.1	0.1	3.6	14.3	0.3	2.9	0.5	100	5.5
CAL4	55.7	0.7	15.5	6.5	0.1	4.3	13.5	0.2	3.0	0.5	100	3.7
CVR1	53.4	0.8	15.1	6.5	0.1	5.3	15.6	0.5	2.7	0.1	100	17.1
CVR2	54.9	0.7	13.3	5.9	0.1	4.3	17.6	0.6	2.5	0.1	100	16.7

Samples	Rb	Sr	Y	Zr	Nb	Ba	Cr	Ni	Sc	V	La	Ce	Nd
4	136	348	26	150	17	353	110	63	18	104	41	63	28
5	173	377	34	191	17	586	143	88	20	107	45	107	45
6	156	360	32	162	16	536	154	94	21	115	43	83	40
9	170	409	34	202	20	585	132	77	16	105	70	127	49
10	153	338	29	150	18	337	121	67	15	92	32	61	22
11	149	324	28	162	16	377	139	64	17	126	41	88	31
18	142	298	30	146	19	423	183	99	22	143	45	84	35
21	134	318	34	141	18	441	179	93	21	136	45	75	32
25	150	307	33	141	20	449	197	106	20	147	53	70	32
30	125	372	29	122	15	459	166	88	24	111	32	70	37
32	166	436	33	175	20	556	143	88	21	102	54	85	29
33	166	414	32	185	19	536	128	77	17	98	45	111	42
34	156	457	34	199	17	558	133	77	17	90	43	93	39
35	188	429	36	238	21	612	136	82	18	115	67	118	45
36	132	406	30	137	20	365	147	74	20	142	44	89	38
37	139	317	28	129	18	398	175	93	17	135	46	81	43
38	121	374	25	140	15	343	141	84	17	114	38	72	27
39	133	282	32	153	18	338	158	85	19	118	50	85	41
40	149	349	32	162	19	375	132	71	15	110	42	76	29
CAL1	144	379	31	168	17	366	154	83	18	144	45	64	26
CAL2	148	381	34	171	19	366	138	79	16	120	37	73	40
CAL3	143	367	34	168	14	380	132	75	15	107	42	60	24
CAL4	174	389	38	174	19	420	134	84	16	113	45	70	37
CVR1	153	379	30	144	14	270	147	53	28				
CVR2	116	431	26	140	12	273	129	37	33				

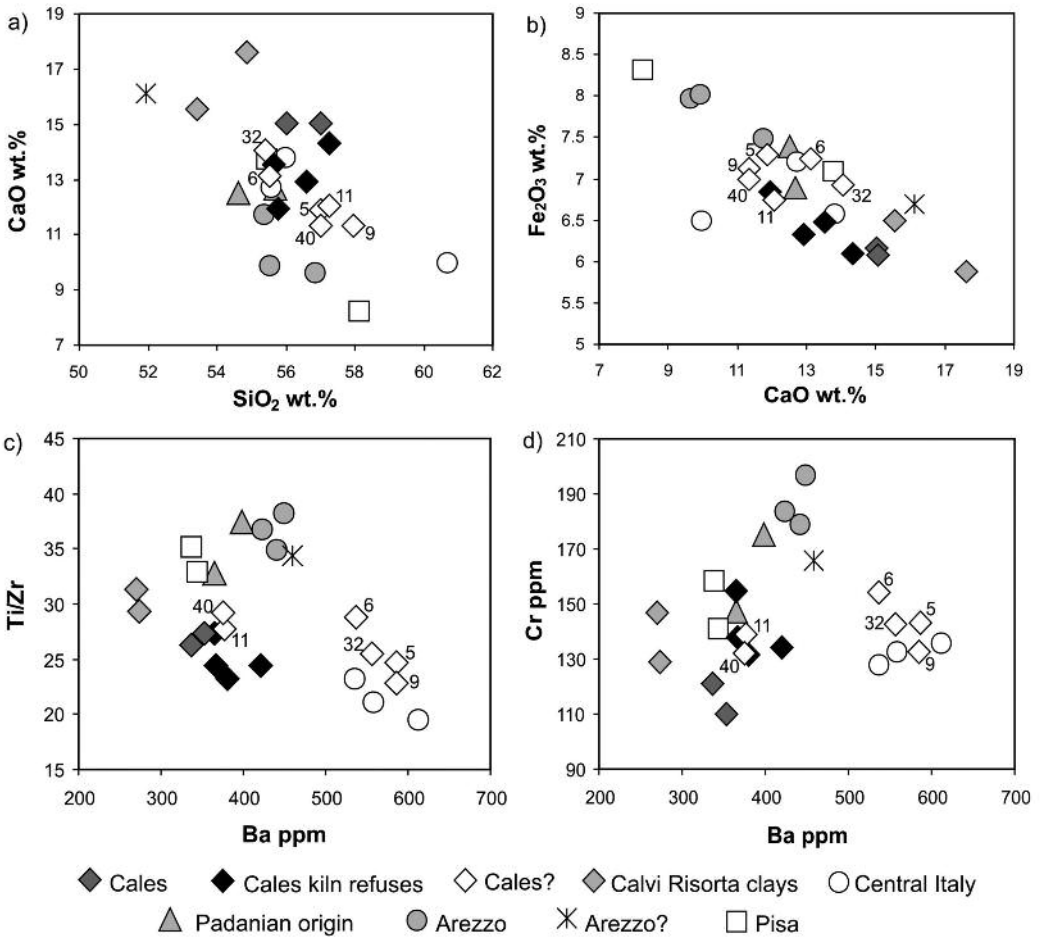


Figure 3. Different variation diagrams for Italian TS samples, kiln refuses and clays.

permitting to assert a secondary origin of calcite, often observed in thin sections as microcrystalline deposition. Significant post-burial weathering is testified by the presence of goethite (Secco et al., 2011). This hydroxide was likely responsible of the endothermic effect between 450 and 500 °C evidenced by DTA-DTG analyses.

Samples characterized by a light brown matrix (4, 5, 11, 12, 33, 40) along with the occurrence of gehlenite (5, 12, 33 and 40) account for firing

temperatures ranging from 850-900 °C; sample 11 was likely affected by lower temperatures (800-850 °C) because of the strong anisotropic matrix along with the lack of gehlenite and a higher amount of mica.

Samples with a brown matrix (18, 21, 30, 32, 34, 39) have as main firing indicator diopside, that accounts for the highest temperatures observed (1000-1100 °C); the occurrence of mica in sample 21 indicates slight lower

Table 5. DTA-DTG analyses for TS samples.

Samples	Provenance	Loss of weight (%)	Endothermal effect (°C)
4	<i>Cales</i>	6.80	800
5	<i>Cales?</i>	3.8	750
10	<i>Cales</i>	8.2	470-780
11	<i>Cales?</i>	4.0	760
18	<i>Arezzo</i>	1.1	710
21	<i>Arezzo</i>	0.3	
25	<i>Arezzo</i>	2.0	730
30	<i>Arezzo?</i>	3.0	750
33	<i>Central Italy</i>	5.2	460-780
34	<i>Central Italy</i>	4.2	470-700
36	<i>Padanian origin</i>	0.5	
38	<i>Pisa</i>	4.9	470-800
39	<i>Pisa</i>	1.5	720
40	<i>Cales?</i>	4.4	700

temperatures (950-1000 °C). It should be remarked that mica lamellae, observed in thin section also for samples affected by high temperatures, could have preserved their morphology and lost their crystalline framework (Cultrone et al., 2001).

Reddish brown matrix samples (6, 9, 25, 35) account for firing temperatures ranging from 950 to 1000 °C due to the presence of both mica and diopside; the occurrence of gehlenite in sample 9 leads to estimate a lower temperature range (850-900 °C).

Samples with dark brown matrix (36, 37, 38), also show a medium to high firing temperature range (950-1000 °C), with the only exception of sample 38 which accounts for higher temperatures (1000-1050 °C) due to the presence of diopside and the lack of mica.

Temperatures lower than 850 °C are attested for sample 4, due to the high amount of calcite and the lack of diopside whereas, taking into account the presence of gehlenite and diopside in sample 34, a temperature range of 850-1000

°C can be hypothesized. The temperature estimated for sample 10 on the only basis of the presence of gehlenite is 800-900 °C.

Kiln refuses (CAL 1, 2, 3 and 4) as expected, also show high temperatures (950-1000 °C) typical of a diopside and mica association.

OM and XRD data do not allow to distinguish, except for slight textural differences and firing temperatures range (Table 6), the Calenian products from the foreign ones. By contrast, relevant information can be achieved by the chemical composition of the shards if compared with production indicators (the BG spacers). This comparison can be fully considered, as Cales productions have been recorded in some ceramic dumps that covers the entire transition between BG and TS productions. On this account, the chemical likeness among these samples attests a high specificity in the ceramic technology of such fine ware production. It is hypothesized the use of CaO-rich clayey deposits probably after the removal of the coarser fraction. Moreover, some trace elements describe the slight

differences among samples. In particular, the *Arezzo* group, signed by *Umbr(icius)*, *Soter A. Sesti* and *C. Gavi* stamps, accounts for higher Ni-Cr pair content; the sample 37 (of supposed Padanian origin) and sample 30 (*Arezzo*) can be clustered to this group.

The analyses confirmed a Calenian origin for the two samples stamped by *Satri(us)* (4 and 10) as verified by their chemical composition very close to BG spacers. A Calenian production can be also proved for samples 11 (stamped by *Actus*) and 40 as showed in Ti/Zr vs Ba diagram (Table 6).

This aspect confirms the hypothesis proposed by Soricelli (2004) and Pedroni and Tasser

(2002) which suggested, based on diffusion and circulation of *Satrius* stamps in Northern Campania, a possible Calenian origin (Table 6).

Ti/Zr vs Ba diagram (Figure 3c) also enables to distinguish a group formed by 3 samples of Central Italy provenance (33, 34 and 35; *Iucu(ndus) Valeri Tyranni*, *Notus* and *Pistus* stamps) along with 3 presumed Calenian shards (6, 9 and 32) and the Calenian sample (5) stamped by *Theopil(a)* confirming for these samples (6, 5, 9 and 32) a provenance of Central Italy. This group is characterized by the highest barium content, ranging from 536 ppm up to 612 ppm. Barium is one of the most mobile elements

Table 6. Inferred provenance and firing temperature ranges of TS samples.

Samples	Stamps	Provenance	Accerted Provenance	Firing Temperature
4	<i>Satri(us)</i>	<i>Cales</i>	<i>Cales</i>	< 850°C
5	<i>(T)heophil(a)</i>	<i>Cales?</i>	<i>Central Italy</i>	850-900°C
6	<i>Darn(...)</i> <i>Vecil(ius)</i>	<i>Cales?</i>	<i>Central Italy</i>	950-1000°C
9	<i>Cra(...)</i> <i>Meno(laus)</i>	<i>Cales?</i>	<i>Central Italy</i>	850-900°C
10	<i>Satri(us)</i>	<i>Cales</i>	<i>Cales</i>	800-900°C
11	<i>Auctus</i>	<i>Cales?</i>	<i>Cales</i>	800-850°C
18	<i>Umbr(icius)</i>	<i>Arezzo</i>	<i>Arezzo</i>	1000-1100°C
21	<i>Soter A. Sesti</i>	<i>Arezzo</i>	<i>Arezzo</i>	950-1000°C
25	<i>C. Gavius</i>	<i>Arezzo</i>	<i>Arezzo</i>	950-1000°C
30		<i>Arezzo?</i>	<i>Arezzo</i>	1000-1100°C
32	<i>Cupitus</i>	<i>Cales?</i>	<i>Central Italy</i>	1000-1100°C
33	<i>Iucu(ndus) Valeri Tyranni</i>	<i>Central Italy</i>	<i>Central Italy</i>	850-900°C
34	<i>Notus</i>	<i>Central Italy</i>	<i>Central Italy</i>	850-1000°C
35	<i>Pistus (or Iastus)</i>	<i>Central Italy</i>	<i>Central Italy</i>	950-1000°C
36	<i>Agath(us)</i>	<i>Padanian origin</i>	<i>Padanian origin</i>	950-1000°C
37		<i>Padanian origin</i>	<i>Padanian origin</i>	950-1000°C
38	<i>L.(ucius) R.(asinius) P.(isanus)</i>	<i>Pisa</i>	<i>Pisa</i>	1000-1050°C
39	<i>Cra(...)</i> <i>Meno(laus)</i>	<i>Pisa</i>	<i>Pisa</i>	1000-1100°C
40		<i>Cales?</i>	<i>Cales</i>	850-900°C
CAL1		<i>Cales</i>	<i>Cales</i>	950-1000°C
CAL2		<i>Cales</i>	<i>Cales</i>	950-1000°C
CAL3		<i>Cales</i>	<i>Cales</i>	950-1000°C
CAL4		<i>Cales</i>	<i>Cales</i>	950-1000°C

and in ceramic samples its content could be strongly increased by post-burial effects (Maggetti, 2001). It should be remarked however, that this element is particularly high only in samples of this group and not evidenced for all the other samples for the same site; moreover, the  $P_2O_5$  and MnO content, other elements easily affected by contamination, is comparable for the entire set of investigated samples and definitely accounts for a distinctive character of this group.

Menchelli et al. (2001) studied from archaeological and archaeometric point of view, the TS productions from Pisa area, attributing the *L.(ucius) R.(asinius) P.(isanus)* stamp to local workshops. They show in the northern area of Pisa the existence of different products, both for the features of stamps and for mineralogical and chemical characteristics, due to a long period of production and the wide diffusion on several sites. On this basis, in our opinion the two samples 38 and 39, despite the chemical differences (Figure 3), could have been produced in Pisa area.

The last sample showing *Agath(us)* stamp cannot be univocally associated to any group described so far, also because this stamp likely suggests a padanian origin of the shard.

The compositional differences observed in the variation diagrams between the clay and the Calenian samples (4, 10, 11 and 40) are expected to be due to the purification of clays, in order to obtain a very fine paste suitable for this highly specialized and characteristic ceramic production. This process aimed at removing the coarser particles definitely modifies the chemical composition of the clay (Eramo et al., 2004); this process could be invoked for Calenian TS samples characterized by the lack of coarse – very coarse sand in ceramic paste, by contrast occurring in high quantities, about 30%, in clay samples (De Bonis, 2011).

Calenian samples (4, 10, 11 and 40) were fired at lower temperature ranges (800-900 °C, Table

6), thus not reflecting the technological characteristics of the highly sintered slip TS, which was fired up to maximum temperatures in excess of 900 °C (Mirti et al., 1999). On the contrary, other fragments of this study, due to the estimated firing temperature ranges (850-1100 °C) and the frequently observed optical inactivity of clay matrix, might be characterized by an extensive vitrification (Maniatis and Tite, 1981), more similar to the TS produced in the *Arretino modo* (Cuomo di Caprio, 2007). Unfortunately, SEM observations which may confirm such hypothesized vitrification stage could not be performed due to the lack of material.

### Conclusions

This preliminary study pointed out the high technological performances of the ancient workshops producing TS from Northern to Southern Italy. The whole data set accounts for standard procedures in terms of clayey raw materials (high CaO clays, probably after the removal of coarser fraction), firing temperatures (950 °C, on average) and at least stylistic devices (repertory perfectly comparable) which make difficult to distinguish a production centre from another. The stamps, whenever linked with specific production markers (furnace structures, kiln wastes, etc.) can indicate a centre of production. However, in many cases the provenance related to the stamps are only presumed on the basis of distribution. Just following this assumption the *Satrius* stamps were assigned to a Cales workshop (Soricelli, 2004; Pedroni and Tasser, 2002); the analytical data on the samples stamped by this craftsman inferred a Calenian provenance, thus confirming the archaeological data. The products of this workshop will be precisely tested by further analyses on a larger sampling in order to better characterize the production. Possibly, other workshops were active on Calenian territory acted other workshops as testified by samples very

close to BG spacers and *Satrius* stamped samples.

Of course, Cales for its position on ancient Appia was also a territory of exchanges as showed by the presence of foreign TS fragments (for which no data are available, so far), and likely due to this strategic site, along with the vessels, recipes and material culture travelled from other production centres.

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