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REVIEW

Ceramic technology: how to characterize *terra sigillata* ware

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Abstract
As part of the Topical Collection on the archaeometric study of ceramics, this paper focuses on *terra sigillata* ware. The main aims are to provide a review on the state of the art of the studies and to provide a guide to the most suitable analytical techniques. The text is divided into four main parts: (1) a brief archaeological introduction on the ancient production of *terra sigillata*; (2) a summary of the archaeometric studies carried out to date; (3) a reasoned list of the most suitable techniques for the investigation of the ceramic body and (4) an in-depth discussion on the most effective techniques for the study of the coating. The application of both destructive and non-destructive techniques is critically evaluated as well as the advantages and disadvantages provided by the different instrumentation, in terms of sample preparations and expected results.

Keywords *Terra sigillata* · Red coating · Ceramic mass production · Roman ceramics · Provenance and technology

Premise

This paper contributes to the Topical Collection (TC) "*Ceramics: Research questions and answers*" aimed at guiding researchers in the study of archaeological ceramics from excavation to study and preservation in museum collections.

Each contribution has a tutorial approach covering one of the main issues pertaining to the study of ceramics: research questions and sampling criteria (Gliozzo 2020a); the chemical (Hein and Kilikoglou 2020) and mineralogical-petrographic (Montana 2020) investigation of raw materials; the technological character and suitability of raw materials (Gualtieri 2020); the processing (Eramo 2020) and modelling (Thér 2020) of clays; surface finishing (Ionescu and Hoeck 2020) and ceramic firing (Gliozzo 2020b); the investigation of different coatings such as black glass-ceramic (Aloupi-Siotis 2020), *terra sigillata* (this paper) and glazes (Pradell and Molera 2020); the isotopic study of particular types of products such as Chinese high fired ceramics (Henderson et al. 2020); the identification of post-burial transformations (Maritan 2020); the dating of ceramics (Galli et al. 2020); and the restoration and musealisation of ceramics (de Lapérouse 2020). This Topical Collection concludes with a tutorial on statistical data processing (Papageorgiou 2020).

This article is part of the Topical Collection on *Ceramics: Research questions and answers*

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Introduction

The term *terra sigillata* (sealed earth) can refer to different materials.

In the pharmacological field, *terra sigillata* indicates stamped troches and pastilles made of particular clays with presumed healing properties (see, e.g., MacGregor 2013; Photos-Jones et al. 2016). The ancient literary sources[1] frequently reported on the therapeutic properties of Lemnos, Chios, Samos and Kimolos earths. However, none of these

[1] To give only a few examples: *Hippocrates* (*Epidemics*) in the 5th–4th century BC, *Dioscorides* (*Materia Medica*) in the 50–70 AD), Pliny (*Naturalis*

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Fig. 1 *Terra Sigillata* vessel (type Dragendorff (1895) no. 29) from La Graufesenque workshop (France). This type was produced from the Tiberian period to ca. 85 AD and represents one of the major decorated forms of the South Gaulish sigillata. © Alain Vernhet

authors used the term "*terra sigillata*" and only indications such as those of a "*Lemium sigillum*" (the effigy of Diana) applied on the red and oily Lemnian earths can be found (e.g. Galen, *De compositione medicamento rum secundum locos* IX; Agricola, *De Natura Fossilium*, II). After the Roman Empire, the trace of these therapeutic earths is lost until the Middle Ages and the Renaissance periods[2] when the *terrae sigillatae* came again to be part of the regular pharmacopoeia (Spałek and Spielvogel 2019). In this field, the first explicit mentioning of "*terra sigillata*" dates back to Matthaeus Silvaticus (*Liber Pandectarum Medicinae*, no. 681; ca. 1480) and Paracelsus (first half of the 16th century AD) (Dannenfeldt 1984).

In the archaeological field, *terra sigillata* indicates a bright red (Fig. 1), highly standardized mass production of ceramic vessels designed to serve and consume food, dating from the 1st century BC to the 7th century AD and widespread in Europe, North Africa and the Near East.

The time when this denomination began to describe the well-known ceramic class is not known and, perhaps, not of particular importance. Although it is appealing to think that the term may in some way derive from or have any relationship with the medicinal red earths, there is no clear relation since the use of *terra sigillata* for this ceramic is not documented by ancient texts. To the best of our knowledge, the first mention in this field dates back to Dragendorff (1895).

Strictly speaking, this term should only be used for the vessels decorated with relief figures (*sigillum* = figurine) but the initial ambiguity between *sigillum* and *signum* (signature, stamp) has meant that the term was also used for plain vessels bearing the stamp (the latter should have been rigorously named "*terra signata*" instead of *sigillata*).

The use of signing the products with a stamp[3] was common in Italian *sigillata* and, beginning from the 1st century AD, was typically adopted also by Gaulish, Hispanic, Pannonian and, more rarely, oriental productions (Pucci 1993). This use lasted until the end of *sigillata* productions (i.e. mid 2nd century AD in Italy; end of the 3rd century AD in the above-mentioned provinces) and was rarely adopted by African workshops, although they lasted over a longer period (i.e. from the last 30 years of the 1st century AD to the 7th century AD) (Oxé and Comfort 1968; Pucci 1993; Mackensen 1998).

In the history of archaeological studies, the *terra sigillata* class firstly included moulded vessels with relief decorations, typically characterized by a shining, bright red, glossy coating. Over time, however, the denomination has started to include plain vessels made on the wheel, similarly characterized by red coatings, with variable tones and brilliance. Other names such as "Arretine ware"[4], "Samian ware"[5] (i.e. Gaulish *terra sigillata*), "*sigillata* made in the Italian manner" or "African red-slip ware" (in English) and Glanzton (gloss, in German)[6] are also used to indicate specific production centres or characteristics but without ever renouncing the common denomination of *terra sigillata*.

According to the current state of the art, the production began in Italy during the third quarter of the 1st century BC (or just over 30 years earlier, see Pedroni 1995; Oxé et al. 2000; Hayes 2008) and then spread throughout the Mediterranean. The early productions were mainly concentrated in Tuscany—corresponding to the ancient *Etruria*—in the ancient territories of *Arretium* (present Arezzo), *Clusium* (present Chiusi) and Pisa (Bruni 1995). In Arezzo—the first

[2] For instance, these earths are mentioned by Avicenna and Ibn al-Baitar at the beginning of the second millennium AD or in the "*Gart der Gesundheit*" dating back to 1470.

[3] Who stamped the *instrumentum domesticum* is an intriguing question, often debated. For *terra sigillata*, the reader is addressed to relevant literature: Pucci (1993, 2001).

[4] The most ancient quote referring to the *arretina vasa* is that of Isidore of Seville in the 6th–7th century AD (*Etymologiae*, XX, 4, 5): "*Arretina vasa ex Arretio municipio Italiae dicuntur, ubi fiunt*; *sunt enim rubra*". (Translation: Arretine dishes are named for the Italian city Arretium, where they are made, and they are red)

[5] The correspondence between the *Samia vasa* mentioned by Pliny and Isidore of Seville and the *terra sigillata* is generally taken for granted but, in reality, it is just a hypothesis. Isidore of Seville (*Etymologiae*, XX, 4, 3 and 6): "*Fictilia vasa in Samo insula prima inventa traduntur, facta ex creta et indurata igni; unde et samia vasa. Postea inventum et rubricam addere et ex rubra creta fingere (...) Samia vasa quidam putant ab oppido Samo Graeciae habere nomen. Alii dicunt cretam esse Italiae, quae non longe a Roma nascitur, quae samia appellatur*". (Translation from Barney et al. (2006): *Ceramic dishes are said to have been first invented on the island of Samos, made from white clay and hardened by fire, hence 'Samian dishes.' Afterwards it was discovered how to add red earth and to fashion vessels with red clay (...) Some think that Samian dishes got their name from Samos, a town of Greece. Others say that there is a white potter's earth from Italy, produced not far from Rome, that is called Samian*)

[6] The term glanzton corresponds to the English gloss and was "rediscovered" and applied to *terra sigillata* by Schumann, based on von Petrikovits (1951).

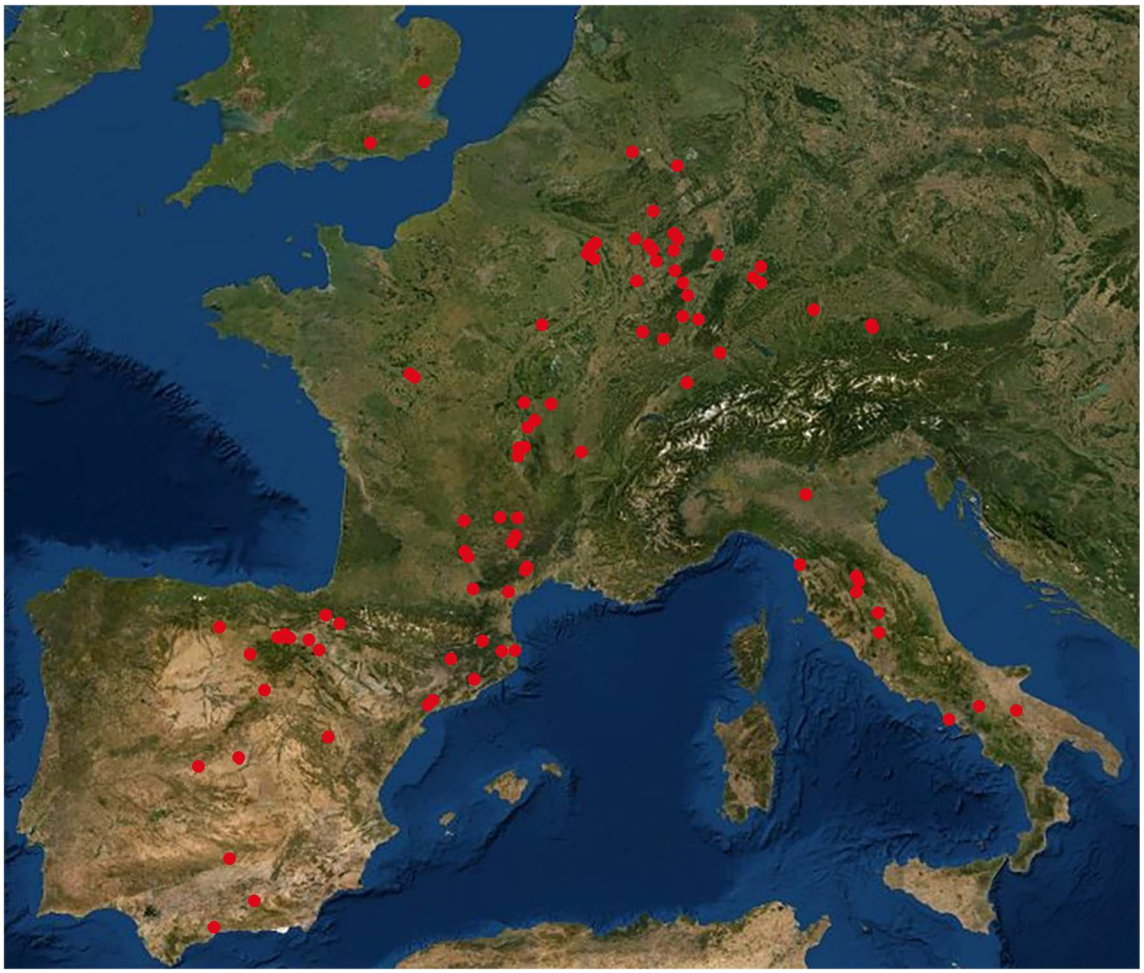


Fig. 2 The distribution of the *terra sigillata* production centres in the central and western Europe (data from http://potsherd.net/mapping/tskilns. Base map from Google Earth)

and largest manufacturing centre[7]—the production started during the years 30–25 BC with a series of plain (decorated by appliqués) and moulded vessels, variously inspired by the metal vessels, the Eastern *Sigillata* A, the central italic "Italo-megaresi" cups[8] and the local black gloss production (Mascione 1992; Pedroni 1995; Martin 2005).

From the Etrurian manufactures, *terra sigillata* production soon made its way across the peninsula (see Pucci 1985 on Italic *sigillata*) and further workshops were active both in southern (e.g. Cales, Naples, Pozzuoli, Scoppieto, Vasanello and Siracusa; see Sforzini 1990; Pedroni and Soricelli 1996; Roberts 1997; Bergamini 2003; Soricelli 2004) and in northern Italy (especially along the Po plain and Aquileia). The period of widest diffusion of Italic *sigillata* was between the end of the 1st century BC and the first decades of the 1st century AD. After that, the production began to decline and the workshops were converted to commercial products still decorated but aesthetically less refined, i.e. the so-called late Italic *sigillata* (Medri 1992). From the middle of the 2nd century AD the Italic production gave way to the Gaulish *sigillata* first and then to the African *sigillata*.

The South Gaulish workshops started their activity during the early Augustan age, producing smooth and undecorated vessels. Starting from Tiberius's reign, muffle kilns became widespread (the smoke was taken outside the firing chamber through tubules; see Picon 2002 and Heimann and Maggetti 2014, chapters 6–7 for an detailed overview) and triggered

[7] On the Arretine and Samian supremacy see also Pliny (*Naturalis Historia* XXXV, 160–161): "*Maior pars hominum terrenis utitur vasis. Samia etiam nunc in esculentis laudantur. Retinent hanc nobilitatem et Arretium in Italia et calicum tantum Surrentum, Hasta, Pollentia, in Hispania Saguntum, in Asia Pergamum. Habent et Trallis ibi opera sua et in Italia Mutina, quoniam et* sic *gentes nobilitantur et haec quoque per maria, terras ultro citro portantur, insignibus rotae officinis*". (Translated by Rackham (1952): *Among table services Samian pottery is still spoken highly of; this reputation is also retained by Arretium in Italy, and, merely for cups, Surrentum, Hasta, and Pollentia, and by Saguntum in Spain and Pergamum in Asia Minor. Also Tralles in Asia Minor and Mutina in Italy have their respective products, since even this brings nations fame, and their products also, so distinguished are the workshops of the potter's wheel, are carried to and fro across land and sea.*)

[8] Produced, for instance at *Ocriculum* (present Otricoli), *Mevania* (present Bevagna), *Tibur* (present Tivoli) and *Cosa* (Ansedonia, Grosseto).

mass production. The major centres were La Graufesenque (*Condatomagus*, see Bémont and Vernhet 1989), from which over 120 potters are known, followed by Banassac and their satellite centres (e.g. Le Rozier and Espalion) and Montans. The widest diffusion of South Gaulish *sigillata* throughout the Mediterranean was reached during the years 40–80 AD. After that short period, however, the production suffered a reduction in the years 80–120 AD and if, on the one hand, Mediterranean exports definitively ceased around 150 AD, on the other, exchanges within the Cisalpine region lasted until the beginning of the 3rd century AD (Bémont and Jacob 1986; Gabucci 2017). Some 10 years later, also the Central Gaulish workshops of Lezoux reached their production acme (during the 2nd century AD although imitations started around 10–15 AD; see Brulet et al. 2010). Initially, they covered long-range distances (esp. the legionary camps of Britain and the Rhine-Danubian limes) but, later, they scaled down their trade to regional and local markets (van Oyen 2016; Gabucci 2017).

As shown in Fig. 2, Gaulish *terra sigillata* workshops were widespread in the South (e.g. La Graufesenque and Banassac), Central (e.g. Lezoux, Vichy and Lyon; for the latter, see Desbat et al. 1996) and, beginning from the late 1st century AD or the early 2nd century, also Eastern Gaul (e.g. Chémery, La Madeleine and Trier). Among notable products the marbled *sigillata* deserves a further mention; in fact, this particular class developed in the last years of the reign of Tiberius (~ 30 AD) at La Graufesenque and showed the morphological repertoire of the plain Gaulish *sigillata*, combined with a characteristic marbled surface (see below for the archaeological investigation of this particular production).

Outside Italy and France, many other workshops were identified in Britain, Germany, *Raetia*, *Pannonia* (to mention only the major centres) and, especially, Spain and North Africa.

The Hispanic *terra sigillata* workshops (e.g. Abella-Solsona, Andújar, Granada, Arenzana, Bezares and Sabadell, Tricio) started just before the middle of the 1st century AD (~ 40–50 AD) and reached their apogee between the second half of the 1st century AD and the first half of the 2nd century AD. The decline started in the last years of the 2nd century; nonetheless, small productions lasted until the end of the 4th and the beginning of the 5th centuries AD (Mezquíriz Irujo 1985).

The production of African *sigillata* started by imitation of the above mentioned productions (esp. the Italic and South Gaulish products), in the second half of the 1st century AD. The North African workshops were mainly located in the *Africa Proconsularis* and their products were characterized by an orange or pinkish-red colour. Firstly, they joined the Italic and Gaulish productions on the Flavian age markets; then, their presence gradually increased until replacing the European ones during the 3rd century AD. As a matter of fact, African *sigillata* has had the largest and longest-lasting diffusion among the ancient ceramics and it was continuously produced until the 7th century AD (Carandini 1981).

Although this very brief introduction cannot be considered complete, it may have contributed to explaining the importance that this emblematic, highly standardized mass production has had in the ancient world. For the necessary in-depth investigations, we refer to the substantial body of literature available on this topic (in addition to those already quoted, see Hayes 1972, 1980; Carandini and Saguì 1981; Ettlinger et al. 1990; Mackensen 1993; Webster 1996; Tortorella 1998; Polak 2000; Kenrick 2002; Bonifay 2004; Poblome et al. 2004; Bes 2015; Sternini 2019).[9]

The archaeometric background

Archaeometric studies had a strong drive during the 1970s. Initially, they were mainly oriented towards the identification of the production groups while, only a few years later, an increasing number of systematic studies have focused on the production technology.

The provenance studies covered *terrae sigillatae* found in Italy, France, Spain, Switzerland, Germany and Britain (Table 1), as well as those from Greece (Daszkiewicz and Schneider 2011; Daszkiewicz and Baranowski 2011), Cyprus (Rautman et al. 1993, 2003; Rautman 1995; Gomez et al. 1996), Turkey, Syria and Jordan (Schneider 1995; Schneider 1996a, 1996b; Degryse et al. 2001; Poblome et al. 2001; Ladstätter and Sauer 2002; Mommsen and Japp 2009; Schneider and Japp 2009), Israel (Slane et al. 1993, 1994) and Tunisia (Taylor and Robinson 1996a, 1996b; Brun 2001, 2004; Mackensen and Schneider 2002, 2006; Baklouti et al. 2014, 2015).

Technological studies include some of those already mentioned and others that have dealt primarily with this aspect (Bimson 1956; Tite 1969; Tite et al. 1982a, 1982b; Gancedo et al. 1988; Mirti et al. 1999; Vendier et al. 2002; Sciau et al. 2006a, 2006b, 2011; Wang et al. 2016a) and whose main results are used for the description that follows.

Lastly, a small number of papers considered particular aspects such as the stamps (investigated by dual-energy computed tomography and X-ray imaging by McKenzie-Clark and Magnussen 2018) or the technological differences with respect to other red painted ceramic classes (see, e.g., the comparison with the Nabatean production in Tite et al. 2018).

[9] An online database is further available at https://www1.rgzm.de/ while basic information on types and distribution is provided by https://potsherd.net/atlas/Class/TS.

Table 1 Provenance studies performed on *terra sigillata* found in central, western and northern Europe

	Findplace	References
Italy	Adria	Maritan et al. 2013
	Aosta (*Augusta Praetoria*)	Mirti et al. 1990; Appolonia et al. 1992; Mirti et al. 1994, 1999
	Campania	Guarino et al. 2011; Grifa et al. 2019
	Etruria	Picon et al. 1971; Widemann et al. 1975; Ballié and Stern 1984; Menchelli et al. 2001; Gliozzo et al. 2003; Schneider and Daszkiewicz 2006
	Matera	Rella et al. 2016
	Po Valley	Schindler-Kaudelka et al. 1997
	Roma	Schuring 1988; Taylor and Robinson 1996b
	Sicilia	Cuomo di Caprio 1992
France	Lyon	Picon et al. 1971; Picon and Vichy 1974; Widemann et al. 1975; Ballié and Stern 1984;; Schneider and Daszkiewicz 2006
	Lezoux	Picon and Vertet 1970; Picon et al. 1971; Picon 1973; Ballié and Stern 1984; Argyropoulos 1995
	La Graufesenque	Picon et al. 1975; Ballié and Stern 1984; Lofrumento et al. 2004
	Montans	Picon et al. 1975
	Banassac	Picon et al. 1975
	Chemery-Faulquemont	Schneider and Hoffmann 1976
Spain	Zaragoza	Castillo et al. 1991
	Granada	Aranda et al. 2010
	Jaén	Serrano-Arnáez et al. 2016
	Tricio and Andújar	López et al. 2005
Switzerland	La Peniche	Küpfer and Maggetti 1978; Maggetti and Küpfer 1978; Maggetti et al. 1980
	Augst (Au*gusta Raurica*)	Jornet 1980
	Nyon	Zanco and Galetti 2001
Germany	Rheinzabern	Schneider and Hoffmann 1976
	Blickweiler	Schneider and Hoffmann 1976
	Pfaffenhofen	Picon 1974
	Schwabegg	Maggetti and Galetti 1993; Maggetti 1995
Britain	Colchester	Hart et al. 1987

Raw materials and production technology

As early as 1956, Mavis Bimson stated that "terra sigillata *red is (…) essentially the same as Greek black, the only difference being the higher state of oxidation of the iron it contains*" (Bimson 1956, p. 200) and, indeed, there are numerous analogies between intentional black and red glosses. In both cases, for instance, a CaO-poor and Fe-rich clay suspension was used to produce a highly sintered and coloured coating, although with different ratios of the main components.

From the point of view of material sciences, the *terra sigillata* is a composite material, consisting of a clayey ceramic body and a thin coating (Fig. 3).

The ceramic body generally shows a homogeneous colour (e.g. from light pink to light brown or light orange) and a fine grain size. The composition may be either non-carbonatic or

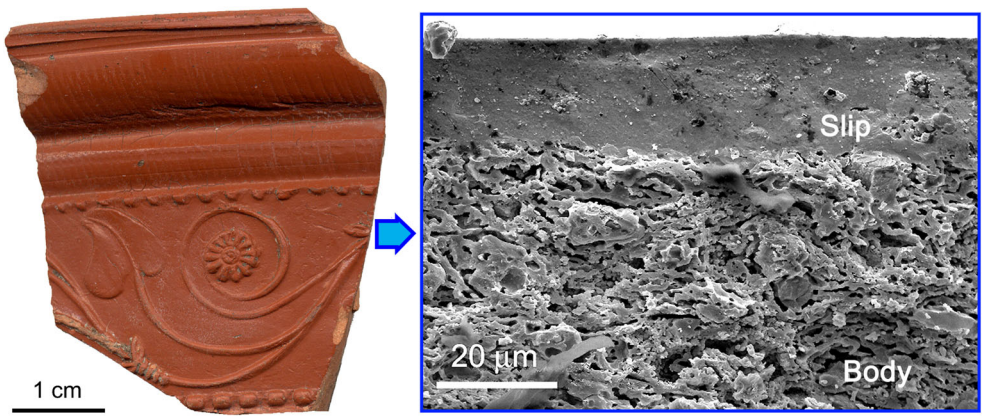


Fig. 3 Left: fragment of a Dragendorff (1895) type no. 29 (1st century AD) from the La Graufesenque workshop. Right: a cross-sectional SEM image in secondary electrons showing the different morphology of the slip and the body

carbonatic (e.g. 1 wt% CaO in a sample from Aosta in Mirti et al. 1999; 33 wt% CaO in a sample from Jaén in Serrano-Arnáez et al. 2016) and the mineralogical phases are embedded in a partially vitrified matrix.

The advantages of using a carbonatic clay have been clearly summarized by Heimann and Maggetti (2014), p. 203) in three main points: (1) the higher thermal expansion of a calcareous clay body ($4.5–7.0 \cdot 10^{-6}$ °C^{-1}) than that of a non-calcareous body ($2–3.5 \cdot 10^{-6}$ °C^{-1}) and its close comparability with the thermal expansion of the slip ($5–10 \cdot 10^{-6}$ °C^{-1}), which results effective in preventing cracking and delamination; (2) the high rigidity and compressive strength that a calcareous body can achieve due to newly formed phases; and (3) the wide range of temperatures at which it can be fired (850–1050 °C), facilitating potters work.

The coating (or slip) typically measures a few tens of microns and consists of a glassy matrix including micrometric and nanometric crystals (e.g. quartz, hematite, corundum, spinel).

There is general agreement that appropriate clay was required to promote sintering and develop different quality coatings. The use of illitic clay was first indicated by Rijken and Favejee (1941). Based on the high potassium contents (e.g. Tite et al. 1982a) and on the technological consideration that an illitic clay sinters at a lower temperature than a non-illitic clay (e.g. Mirti et al. 1999), this hypothesis has been frequently confirmed in several publications (Picon et al. 1971; Tite et al. 1982a, 1982b; Freestone 1982; Gancedo et al. 1988). Conversely, it still remains unclear whether the suspension corresponded to the finest fraction of the clays used for the ceramic bodies or to a different raw material. In this regard, even the possibility of resolving this issue has been questioned (see, e.g., Mirti et al. 1999).

For example, Tite et al. (1982a) suggested that both body and slip were possibly produced with the same clay, using different processing techniques. Conversely, Sciau et al. (2006b) found that different clays were used to prepare the body and the slip of the Gaulish *terrae sigillatae* they analysed. Gancedo et al. (1988) considered both hypotheses to be plausible for the *terra sigillata* found at Ampurias, Rosas and Mérida; however, they tended to differentiate the raw materials used for the ceramic paste from those used for the slip. Lastly, Walton et al. (2009) suggested the use of different sources for the Greek Attic "LCM coral red" and the "HCM coral red" coatings, respectively.

In any case, the vessels were coated by dipping and, after drying, they were subjected to a single firing in an oxidizing atmosphere. The maximum firing temperatures deduced from the investigation of ceramics fragments range from 850 to 1200 °C (e.g. 850–950 °C typical range in Maritan et al. 2013; 850–1000 °C in Lofrumento et al. 2004; 900–1000 °C in Gancedo et al. 1988; 950–1050 °C in Küpfer and Maggetti 1978; 1000–1200 °C in Tite 1969; 1020–1080 °C in Sciau et al. 2006a). Similarly, a maximum firing temperature of between 950 and 1050 °C was demonstrated by Maggetti (1995) for some fragments taken from the *terra sigillata* kilns at Schwabegg (Germany). Moreover, in line with previous findings, samples fired at temperatures below 550 °C were considered unintentional products, caused by an inhomogeneous heat distribution inside the kiln (Maritan et al. 2013; for thermal gradients inside the kiln, see Gliozzo 2020b in this TC).

Broadly speaking, these are the main characteristics of the *terra sigillata* and its production cycle but the examples provided below will illustrate how material sciences applied to the study of Cultural Heritage can provide a detailed microstructural, mineralogical and crystallographic characterization of both ceramic bodies and coating.

How to investigate *terra sigillata*

A systematic study of *terra sigillata* pottery requires a multiscale analysis. The bulk chemical and mineralogical composition is needed, as well as further dimensional and spatial information, regarding structure, size and distribution of both crystalline and amorphous phases and compounds. The investigations also include the study of physical properties such as the colour, the hardness, the porosity, the impermeability and the adhesion of coating.

The possibility of obtaining the information needed essentially depends on two factors: (1) the possibility of taking a sample—if the analytical technique is minimally or fully destructive—and (2) the possibility of accessing the instruments that can provide the most accurate result.

Without any doubt, these two factors are extremely important and must be carefully evaluated during the planning of the sampling campaign and the subsequent laboratory investigations.

The following text will separately illustrate how to investigate *terra sigillata* body and coating, based on the most recent advances made on the study of this significant ceramic production. Despite being primarily focused on the Gaulish *sigillata*, it can serve as a step by step guiding-tool for both sampling and analytical investigation of any type of *terra sigillata* pottery.

The investigation of the ceramic body

Macroscopic observations

The visual examination, possibly with a magnifying lens, represents the first step. In this phase, colour, textural homogeneity/heterogeneity and fracture can be described and broad groups can be macroscopically distinguished. Together with archaeological typology, this preliminary analysis will guide sampling because it will allow the researcher to

select representative samples. Moreover, the area to be investigated by means of physical and chemical analyses can be suitably selected and removed.

Elemental and chemical composition

The investigation of the chemical composition represents a second step. The analytical techniques available in this case are numerous and involve different sample preparations.

X-ray fluorescence spectroscopy (XRF) (Trentelman et al. 2010; West et al. 2010), particle-induced X-ray emission (PIXE) (Leon et al. 2012; Šmit 2013; Tamilarasu et al. 2016; Dasari et al. 2017) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (Goldstein et al. 2003) are three different spectroscopies based on X-ray emission. These techniques differ in the nature of the particle beam used to ionize the matter: photons for XRF, protons or alphas for PIXE and electrons for SEM-EDS. The nature of the beam is one of the main parameters defining the size of the analysed volume and the limit of detection. The smallest volumes are obtained with the electrons, thanks to their very low penetration and the ease with which they can be focused, while protons offer lower limits of detection. Other techniques routinely used for ceramic studies are represented by inductively coupled plasma mass spectrometry (ICP-MS) and neutron activation (NA). The former technique uses a plasma to ionize previously diluted samples while the latter involves a nuclear irradiation process.

Among all these techniques—and others that could be added to the list—there is no one better than the others in absolute terms. The parameters that vary are as follows: the destructive/non-destructive character and the area/volume to be investigated, the detection limits of the instrument and the accuracy of the result.

All the above techniques (except ICP-MS) can be used non-destructively and, in this latter case, accuracy can decrease (XRF and environmental SEM) or remain unchanged (PIXE, NA). However, for in situ techniques (environmental SEM, XRF, PIXE), the beam penetration is limited and usually cannot exceed the thickness of the coating; consequently, it is necessary to obtain a fragmentary find or purposely break it to expose the ceramic body. Neutron activation, XRF (in destructive mode) and ICP-MS, on the contrary, are bulk techniques (i.e. they investigate a volume instead of a surface) and, therefore, they do not present problems related to the investigated area (but NA makes the fragment radioactive for a certain period).

SEM-EDS represents a separate case because, on the one hand, it is rapid, widespread and relatively inexpensive but, on the other hand, it has the limitation of being an in situ (i.e. non-bulk) technique. To obtain reliable results, the sample must offer a flat surface (prepared on a thin section) and the number of analyses carried out on the single sample (usually squares $10–20 \times 50–100\ \mu m^2$) must be large enough to cover the compositional variability of the sample itself. Moreover, two further issues should be carefully considered. Firstly, the typical concentration accuracy is about 5–10% for element concentration superior to 1%; therefore, this method is only semi-quantitative for concentrations below that value. Secondly, due to the intrinsic resolution in energy of EDS detectors, the quantification of elements with close X-ray fluorescence lines can be problematic. For instance, this is the case of Ba and Ti elements for which the two lines (Ba-Lα and Ti-Kα) are too close to be separated by EDS. In these cases, a better energy-resolved method such as the wavelength dispersive X-ray fluorescence spectrometry (WDXS or WDS) should be used. In addition, using WDS, the detection limit is lower and amounts as low as 0.01% can be quantified.

In this regard, it is worth underlining that detection limits and accuracy are the fundamental parameters that determine the quality of the final result. Consequently, as far as the analysis of ceramic bodies is concerned, the bulk techniques (XRF, ICP-MS, NA) are preferable because they offer the possibility of measuring not only the major elements (i.e. the most abundant ones such as SiO_2, Al_2O_3) but also the minor and trace elements of a considerable volume of material. Minor and trace elements—sometimes better than major elements—can in fact provide fundamental discriminants for the provenance investigation.

Lastly, the availability of a specific instrumentation may require an additional organizational effort. SEM-EDS, XRF and ICP-MS are widespread techniques while PIXE and NA require a particle accelerator and the numbers of facilities dedicated to the study of Cultural Heritage are few.

Mineralogical composition

The investigation of the mineralogical composition represents a third step and, in this case, the options are less numerous. The first technique to be mentioned is optical microscopy (OM) which requires both the preparation of a thin section and a suitable preparation of the researcher in recognizing the various minerals' distinctive optical properties. This technique offers the great advantage of showing all main features of a ceramic sample: colour distribution, shape and percentage of porosity, grain size, clasts morphology, phase distribution, absence/presence of microfauna and of lithic fragments. Modal analysis can further allow the different phases to be quantified and the same thin section can be used for OM, SEM-EDS and other techniques such as electron microprobe analysis (EMPA). The only disadvantage can be represented by the preparation of the thin section which requires the destruction of a portion of the sample.

The second technique, which can be used alone or, even better, combined with OM is X-ray diffraction. Each

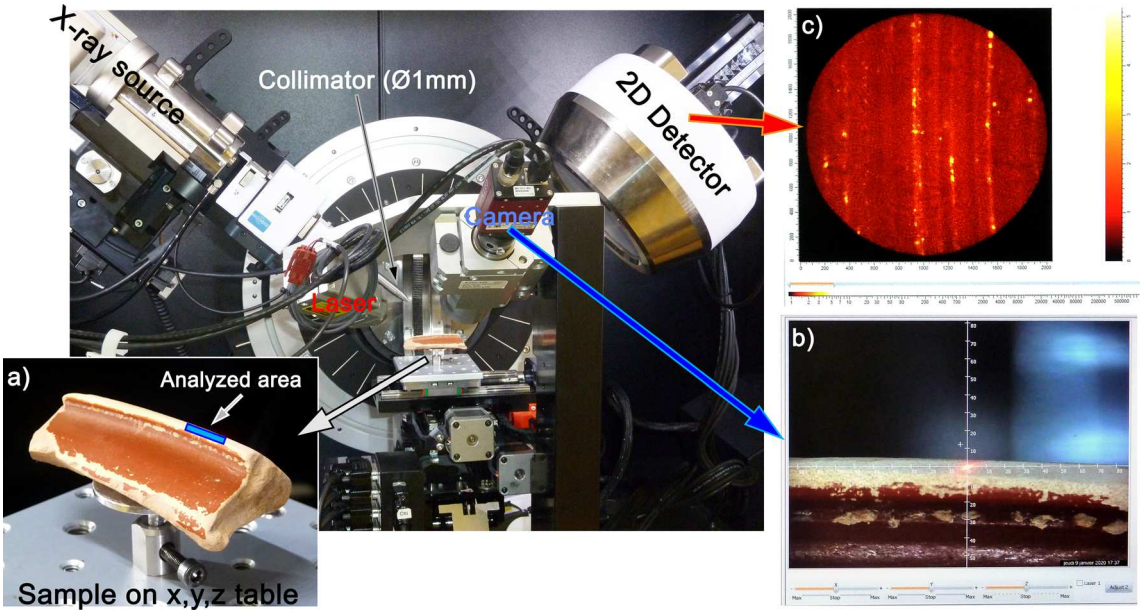


Fig. 4 The mounting of a *terra sigillata* fragment (diffractometer Bruker, D8 Discover). The sample is positioned on an x,y,z table (a) allowing us to select the analysed area using a laser and an optical camera (b). A 2D detector is used to record the pattern. The inset (c) shows an example of 2D image. The pattern is obtained by assembling a series of images recorded at different positions (Fig. 5). A collimator is used to define the beam size

crystalline phase has a specific diffraction pattern, which can be used to identify it (Klug and Alexander 1974). Different incident beams (X-rays, electrons, neutrons) can generate a diffraction pattern; however, X-ray diffraction is the easiest to implement, the most versatile and, consequently, the most widely used. The measurements can be performed on a powder obtained from the sample (bulk analysis) or directly on an edge of a sherd where the body is visible (in situ analysis).

The first solution requires collecting a small piece of the body, which must be finely ground in order to obtain a homogeneous fine-grained powder. The analysis by X-ray powder

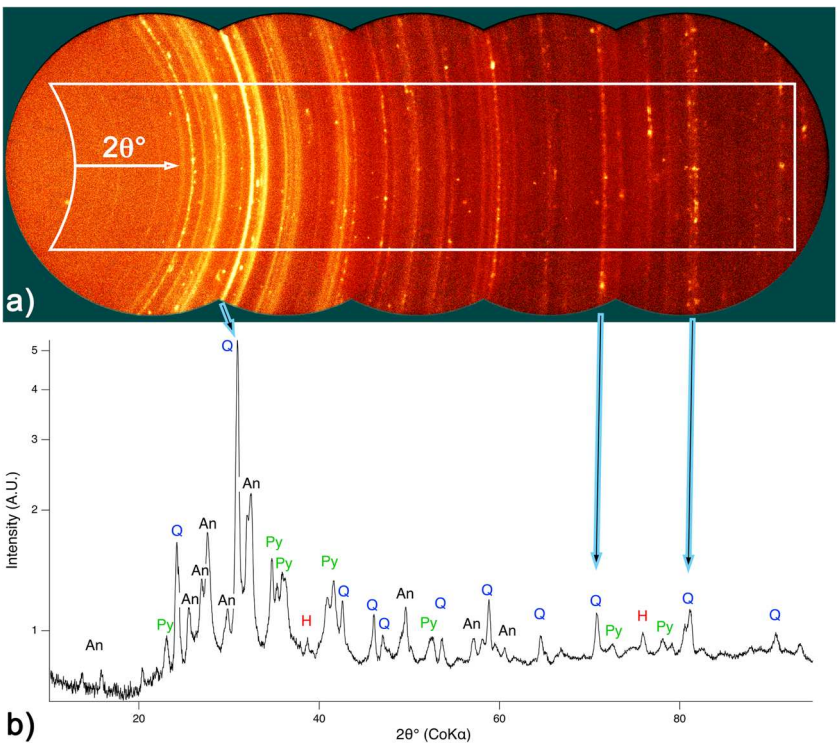


Fig. 5 (a) 2D pattern of *terra sigillata* body obtained from 5 images recorded every $\Delta 2\theta = 15°$ from $2\theta = 20$ up to 80°. (b) XRD pattern obtained after the integration of selected zone (white cursor) and indexed using the database: Q (quartz), Py (pyroxene type diopside), An (anorthite) and H (hematite)

diffraction is very efficient but it is also very sensitive to grain size and crystallographic orientation of grains. The best diffraction patterns are obtained from calibrated powder (1 μm ≤ grain size ≤ 5 μm) with randomly crystallographic orientations.

The second solution requires a diffractometer equipped with an X-ray beam small enough to collect diffraction patterns directly from the sherd (Fig. 4). The beam size is chosen depending on the size of the area to be analysed. In the example provided in Fig. 4, the incident beam was of 1 mm in diameter and oriented towards the uncovered edge of the rim. The fragment was oriented along the X-ray direction in order to take into account the expansion of the analysed area in this direction, following the 2θ angle. Neglecting the beam divergence, the analysed surface on the sample was around 1×5.8 mm^2 at the beginning ($2\theta = 20°$) and 1×1.6 mm^2 at the end ($2\theta = 80°$) of the diffraction pattern.

Most software delivered with diffractometers allow for diffraction pattern indexation, using the X-ray powder diffraction database (Fig. 5). However, automatic indexation must always be validated by the operator to avoid the risk of indicating phases which are actually absent. After phase identification, a quantitative analysis can be performed using the Rietveld method (see, e.g., Young 1995). In this regard, it is worth remembering that mineralogical phases can be (a) primary, i.e. originally contained by the clayey raw materials; (b) newly formed during firing (see Gliozzo 2020b in this TC) or (c) secondary, i.e. formed due post-burial transformations (Maritan 2020 in this TC). Therefore, phase identification should be suitably interpreted apart from being validated and quantified. As an example of what this means, it is possible to recall the case provided by La Graufesenque productions (South Gaul) whose mineralogical phases allowed the estimation of their firing temperature rather than providing useful provenance information (Sciau et al. 1992, Sciau and Vezian 2002). The authors studied the thermal transformation of a raw clay found, during the excavations, in a dump dated from the beginning of the 1st century AD. The results showed that the peak profile of the plagioclase (anorthite type) was a suitable parameter to estimate the maximum firing temperature and its ratios allowed a range indication of 1030–1080 °C.

Lastly, a third technique, which can be proficiently used for the determination of the mineralogical composition of a vessel, is represented by neutron diffraction (Bennington 2004). Similarly to neutron activation, the instrumentation requires a nuclear process and the specimen can retain radioactivity for some hours or days, depending on its composition. Differently, from all other techniques, the neutrons penetrate the entire volume of the vessel and the mineralogical investigation can be thus performed on the bulk without manipulating the sample. An entire vessel can be allocated in the chamber and the measurement will therefore be completely non-destructive but inclusive of the coating. Once collected the diffraction pattern, phase identification and quantification follow the same procedure as that used for X-ray diffraction.

The investigation of the slip

Macroscopic observations and colour measurements

Following a similar approach to that followed for the ceramic body, the investigation of the slip begins with the visual examination using a magnifying lens. This is a practical and quick way to highlight specific defects of some productions as shown in Fig. 6a. Information can also be obtained on slip homogeneity, glassy aspect and colour variations.

The colour of the coating is an important parameter which can be quantified. Several portable instruments (spectroradiometers) allow the light reflected by surface samples to be analysed; thus, the reflectance spectra are used to determine the principal wavelength and the colour coordinates, typically reported as L*, a* and b*. In the CIE[10] colour space L defines the lightness value from black (0) to white (100), the a* axis corresponds to the green-red component (with green in a negative direction and red in a positive direction), and the b* axis corresponds to the blue-yellow component (with blue in a negative direction and yellow in a positive direction). The typical reflectance spectrum of a *sigillata* coating is shown in Fig. 6b. Colour measurements were used to compare Italic and Gallic productions and highlight the redder and brighter appearance of La Graufesenque coatings (Leon et al. 2015).

Chemical composition

The determination of the chemical composition can be obtained (1) destructively, by means of scanning electron microscopy (SEM-EDS) or electron microprobe (EMPA), or (2) non-destructively, by analysing directly the surface of the vessel, by PIXE or portable XRF (with several limitations explained below).

The first type of approach is straightforward because the researcher has the image of the sample and can thus decide where to direct the beam for the measurement. The ceramic body and the slip are clearly distinguishable (Fig. 7) and the chemical composition can be easily determined (Fig. 8).

SEM-EDS can be also used to build elemental maps where the intensity of characteristic X-ray emission lines is assigned to each pixel (Fig. 9). Spectral data can also be processed in order to quantify the elemental composition at the pixel scale and thus to obtain quantitative maps; however, the spatial resolution of the element maps is rather low. Accelerating voltage and current can be lowered to increase the resolution

[10] CIE is the acronym of the Commission internationale de l'éclairage (International Commission on Illumination).

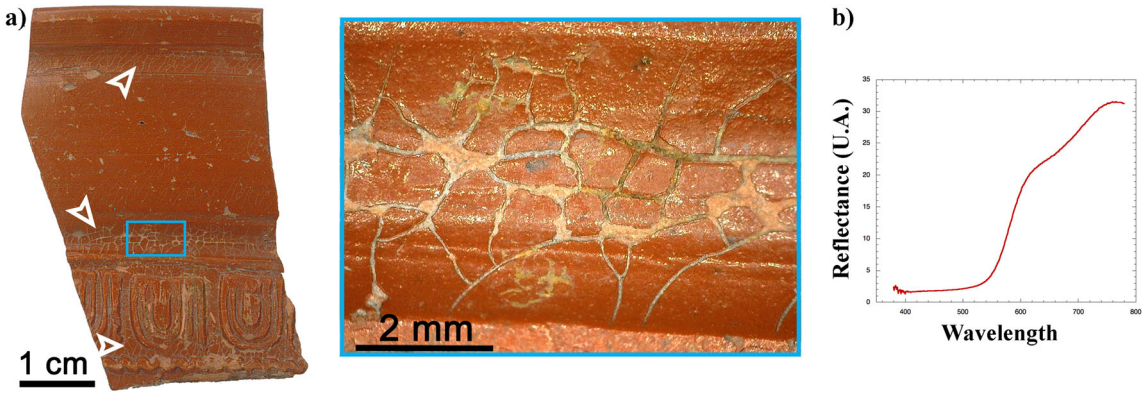


Fig. 6 (a) *Terra sigillata* sherd (1st century AD) from the workshop of Espalion (France) showing the network of cracks (white arrows and inset) characteristic of South Gallic productions. (b) Typical reflectance spectrum obtained from the slip of the *sigillata*. The colour parameters are L* 34.3, a* 30.0, b* 34.0, λd 595

but the accelerating voltage must be high enough to ionize atoms. In practice, these maps evidence compositional heterogeneities but the resolution is not high enough to determine the elemental composition of very small grains.

As demonstrated by the previous examples, the very small size of some grains may prevent an adequate investigation to be performed by means of SEM-EDS or EMPA. To overcome these difficulties, transmission electron microscopy (TEM) can be further used because it allows the investigation of small areas up to the atomic level. TEM requires a specific preparation because the sample must be thin enough to allow the transmission (i.e. the crossing) of the beam (Sciau 2016). For the same reason, TEM cannot be performed on the cross sections used for SEM-EDS or EMPA but it is possible to extract a thin foil using, for instance, a Dual Beam (FIB-SEM) system (Young and Moore 2005). This device incorporates both a focused ion beam (FIB) and a scanning electron microscope (SEM). This combination offers several advantages for sample preparation and microscopy applications; in fact, the ion beam is used for both material removal (FIB) and non-destructive imaging and analysis (SEM). SEM allows the position of the foil to be selected while FIB performs the extraction process. A detailed description of the process applied to the study of Italic and South Gallic *sigillata* is illustrated in Fig. 10 and described in detail in Sciau et al. 2006b, 2009), Leon et al. (2015) and Sciau (2016).

At low TEM resolution—i.e. at the nanometre scale—the main imaging method is the bright field (BF) mode, which places an aperture in the back focal plane in order to select only the transmitted beam to form the image. Scattering and diffracted beams are not involved in image formation; in fact, the diffracting zones appear dark while those regions that do not scatter the electrons appear brighter. Since the intensity of the transmitted electron beam depends on absorption, the thick zones (or those containing higher atomic numbers) are darker than the thin zones (or those containing light atoms). In the

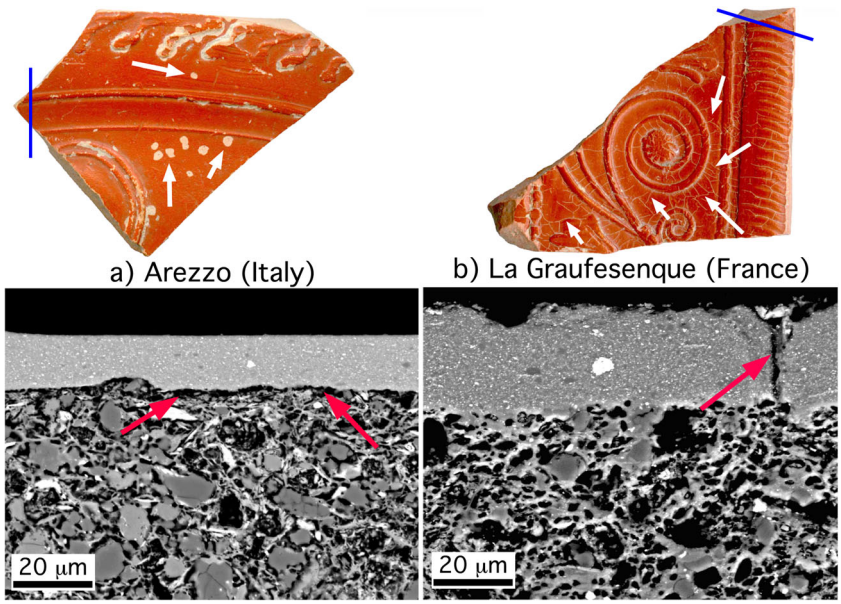
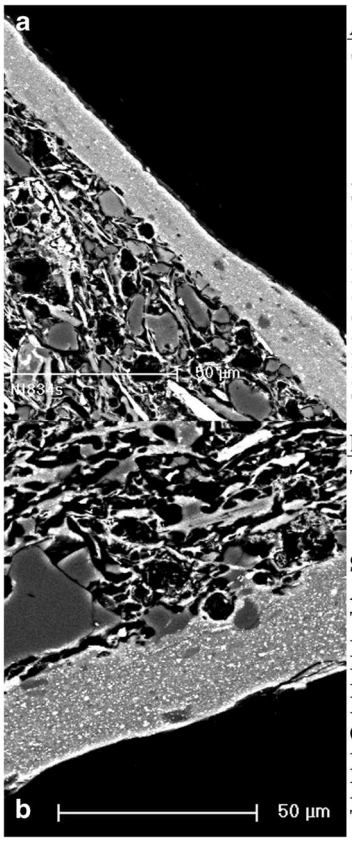


Fig. 7 SEM-BSE images showing different textures (body) and interfaces. The detachment of Arezzo coating (white arrows) is due to its low adhesion to the body (red arrows) while the cracks of La Graufesenque coating (white and red arrows) are due to the tight coating adhesion (data from Sciau et al. 2011)



A	ITALIC	
Thickness	min	max
	12	23
	n=10	sd
SiO_2	48.7	0.4
Al_2O_3	27.4	0.2
TiO_2	0.7	0.1
FeO	10.1	0.1
MnO	0.2	0.1
MgO	3.7	0.1
CaO	1.8	0.1
Na_2O	2.2	0.2
K_2O	5.1	0.1
Total	100.0	

B	HISPANIC	
Thickness	min	max
	16	36
	n=10	sd
SiO_2	48.8	0.1
Al_2O_3	29.5	0.1
TiO_2	0.7	0.2
FeO	7.9	0.3
MnO	0.2	0.1
MgO	2.4	0.1
CaO	1.3	0.1
Na_2O	0.9	0.0
K_2O	8.1	0.1
Total	100.0	

Fig. 8 SEM-BSE images of an Italic *sigillata* (Pucci type XXXV, 1st century AD) from the Marcianella workshop (A) and a Hispanic *sigillata* (Dragendorff 1895 type no. 27; 50–150 AD) from the archaeological site of *Thamusida* in Morocco. The chemical composition of the slip has been obtained on the basis of 10 square areas measured along the coating (EG unpublished data)

case of investigated *sigillatae*, BF images allowed hematite, corundum and spinel crystals to be observed in the glassy matrix and highlighted the differences between Gaulish and Italic samples in relation to the nature, the distribution and the orientation of nanometric crystals (see also Figure 6 in Leon et al. 2015). Moreover, these images demonstrated the strong orientation of spinel crystals in Italic samples and allowed their formation to be reconstructed during heating, after Mg- and Al-rich clay minerals. In the south Gallic coatings, the corundum crystals never exceeded 50 nm and they were always spherical in accordance with their formation within the glassy matrix, from the excess of aluminium. The measurements carried out by energy electron loss spectroscopy (EELS) further revealed that both corundum and hematite underwent substitutions (Fig. 11): corundum crystals contained around 6–8 wt% of iron ($Al_{1.86}Fe_{0.14}O_3$) while hematite crystals showed ~ 7–9 wt% of aluminium and 4–6 wt% of titanium ($Fe_{1.74}Al_{0.16}Ti_{0.1}O_3$). The discovery of these substitutions was of outstanding importance because they allowed for an explanation of the peak shifts observed in the Raman spectra of hematite, in addition to being consistent with the variation of the cell parameters (or interplanar distance) determined by both Lab and synchrotron XRD (see below for further details).

The second type of approach has the advantage of being non-destructive and the disadvantage of penetrating volumes that are not always measurable or determinable. For instance, the depth analysed by XRF is frequently higher than the thickness of the coating; therefore, this technique is not particularly

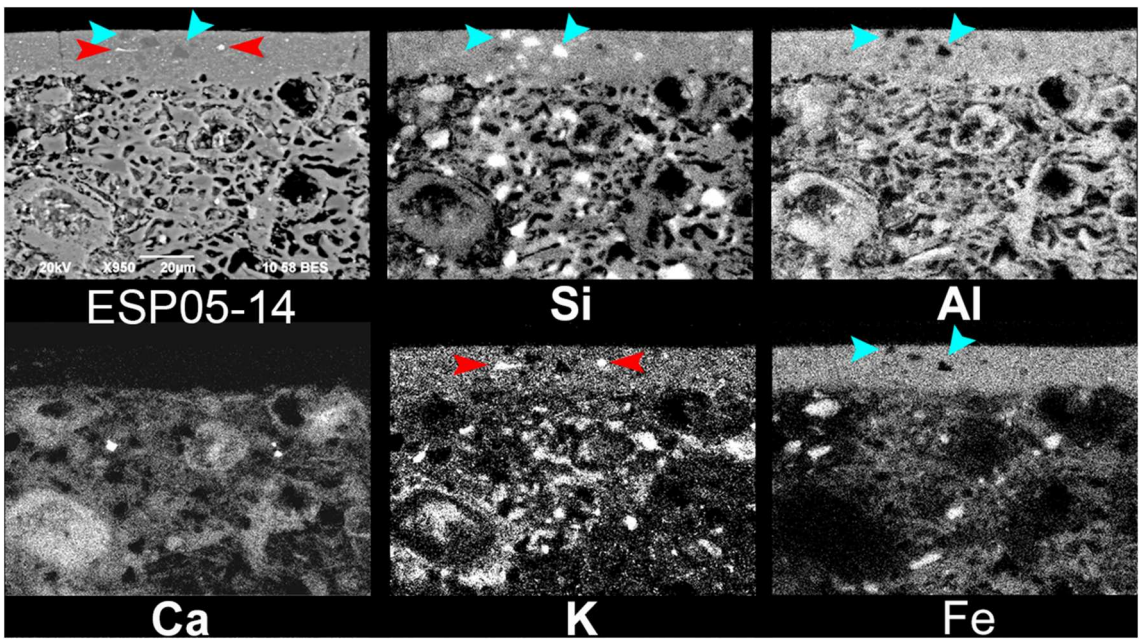


Fig. 9 An example of SEM-BSE image (top left) and elemental maps of a cross section (Espalion workshop). In this case, the spatial resolution was close to the micron and, in general, it is difficult to achieve a spatial resolution better than half a micron. An accelerating voltage of 15 kV was used in order to be able to use the Fe Kα line and get the Fe map. Grains such as quartz (blue arrows) can be easily distinguished and bright grains can show a variable composition (i.e. not only iron but also K-rich compounds as indicated by the red arrows) (Data from Sciau et al. 2011)

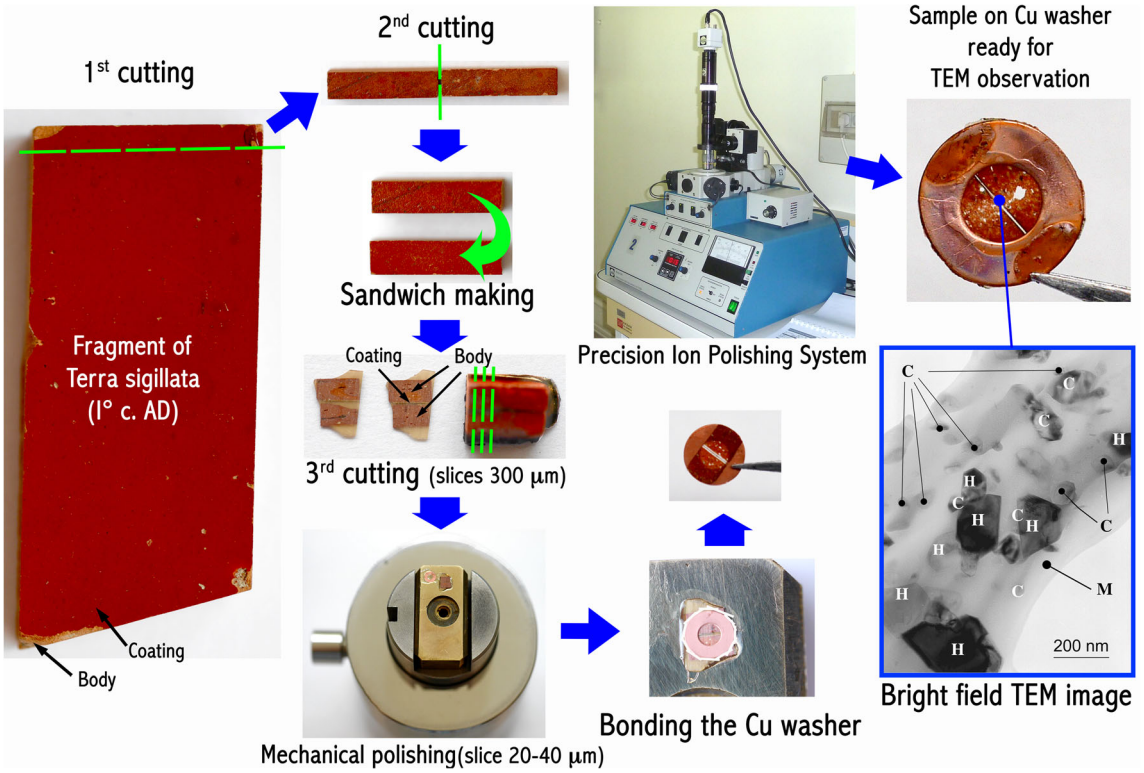


Fig. 10 The main steps of the TEM preparation of a *Terra sigillata* sample using mechanical and precision ion polishing: sawing steps using a wire saw; sandwich making using glue; sawing thin lamella (300 µm); mechanical polishing up to 20–40 µm; bonding (cyanolite) a reinforcing Cu washer; cutting sample around the Cu washer; unsticking the sample from the polishing holder; ion beam polishing (Gatan PIPS) to obtain a small hole in the centre of sample; sample ready for TEM study; a bright field image of a thin zone close to the hole (data from Sciau 2016)

well suited for surface analysis. Conversely, PIXE technique can provide excellent results and it has been shown that it is possible to limit the analyses to the coating by using a proton beam energy of 1.5 MeV. The study performed by Leon et al. (2012) highlighted that PIXE results are quite satisfactory as long as the coating is thicker than 15 µm. For very thin coatings, the energy of the proton beam can be decreased down to 1.3 or 1.2 MeV but, with these analytical conditions, the estimation of trace elements is no longer possible. Further advantages of this technique are represented by the small size of the

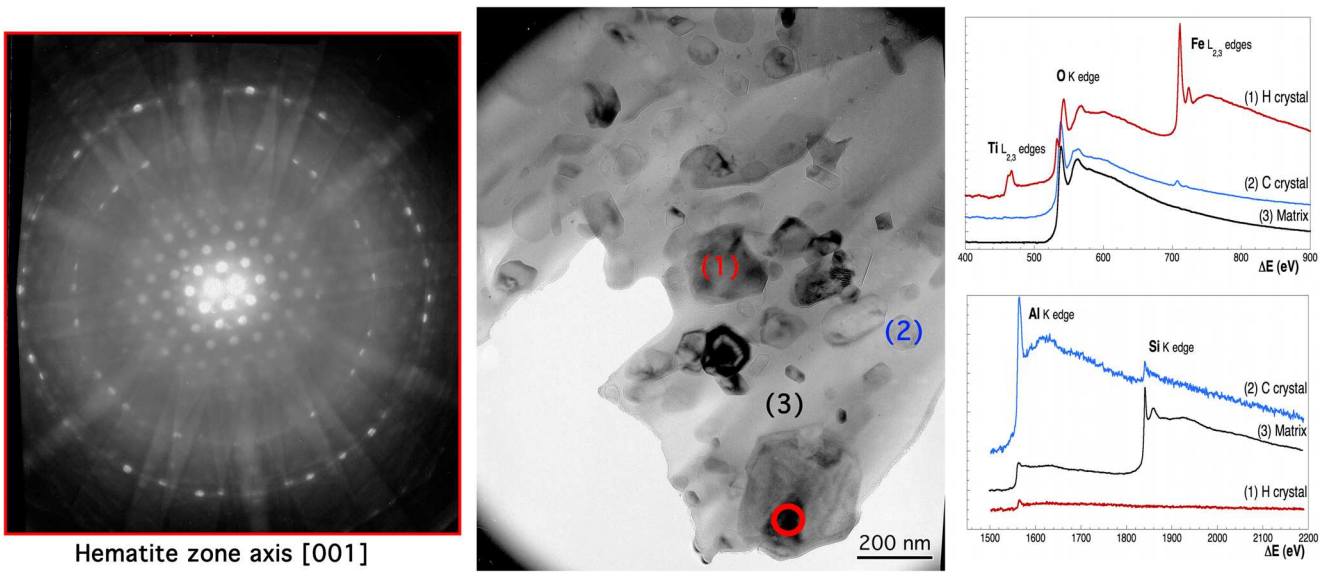


Fig. 11 Bright field image of La Graufesenque coating showing a glassy matrix containing submicrometric hematite and corundum crystals. The EELS spectra of the matrix (zone 3), corundum (1) and hematite (2) crystals are given on the right side while the electron diffraction pattern of a hematite crystal is given on the left (data from Sciau et al. 2006a)

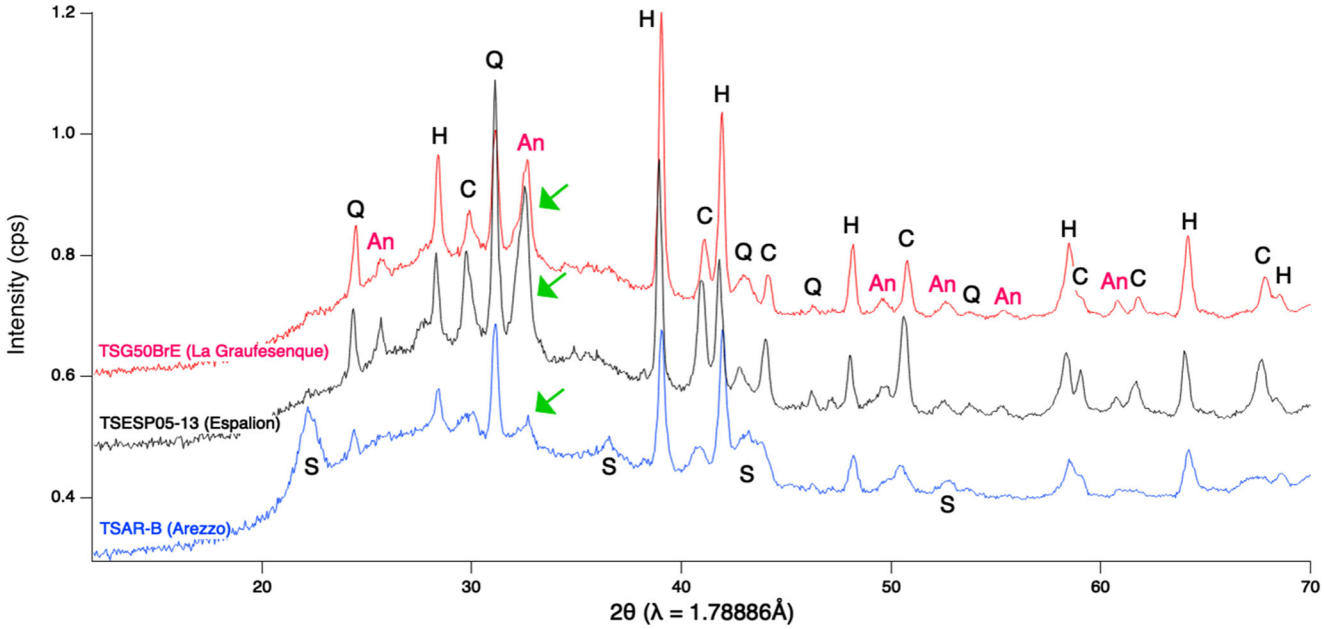


Fig. 12 XRD patterns, using the Kα line of Co. The main anorthite peaks (green arrows) are well observable also in the TSAR-B sample with a coating thickness close to 35 μm. Q, quartz; H, hematite; C, corundum; An, anorthite

beam and the capability of minimizing surface alteration problems. Conversely, the method is very sensitive to both the porosity and the heterogeneity of element distributions. Increasing the number of measurement points can attenuate the heterogeneity effect while a high porosity decreases the quality of results.

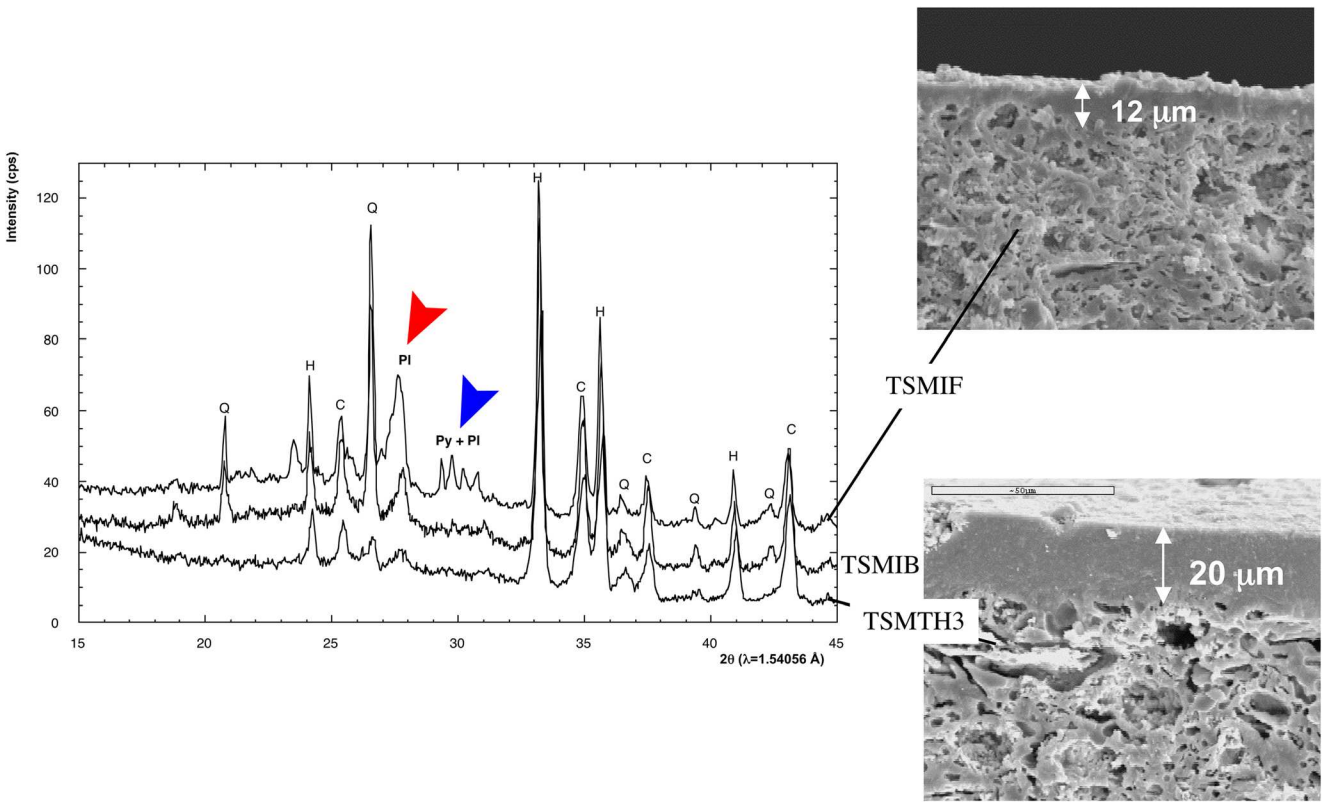


Fig. 13 XRD patterns of *terra sigillata* coatings (1st century AD) from Montans workshop (France) showing the correlation between the coating thickness and the intensity of main peaks of plagioclase (red arrow) and pyroxene (blue arrow). The TSMIB sample has a coating thickness of around 15 μm. Q, quartz; H, hematite; C, corundum; Pl, plagioclase Py, pyroxene (data from Dejoie et al. 2005)

The greatest disadvantage of this technique, however, is that it is not particularly widespread and, therefore, not easily accessible. The good news, on the other hand, is that the PIXE instrumentation held by the Louvre Museum, the Universities of Ljubljana and Oxford and Florence CNR laboratories have been often—if not exclusively—used for Cultural Heritage studies.

Mineralogical composition

The determination of the mineralogical composition of the slip can be performed by means of two main analytical techniques: X-ray diffraction and Raman microspectroscopy.

As mentioned before, X-ray diffraction is a powerful tool to determine the mineralogical composition of both ceramic bodies and coatings. The analysis can be performed directly on the sample without any preparation. In this case, the sherd, the laser and the camera have to be suitably positioned, in order to analyse only the area corresponding to the slip. Using the CuKα (1.54056 Å) X-ray wavelength, the depth of the analysed volume can be maintained below 20–25 μm (i.e. the average thickness of the *sigillata* coating) while CoKα wavelength is often recommended to study materials containing high iron amounts, in order to avoid the strong fluorescence which occurs with CuKα. Nevertheless, the fluorescence is correlated to the absorption and, consequently, a strong fluorescence is directly related to strong X-ray absorption. In the case where the main X-ray absorbent element is iron, the analysed depth is thus greater with Co than with CuKα. In practice, with Co X-ray source, the analysed depth can be higher than the thickness of the slip and several phases of the ceramic body can be observed in the XRD pattern, such as those of plagioclase in Fig. 12.

A similar example has been provided by Dejoie et al. (2005) who found that the body of italic and South Gaulish samples contained an anorthitic plagioclase which was absent in the coatings (Fig. 13).

When *sigillata* coating thickness is smaller than 20 μm, the researcher can decrease the penetration depth by changing the angle of incidence of the beam or exclude a posteriori the phases characterizing the ceramic body. However, several phases, such as quartz or hematite, can be present in both the body and the coating and their assignment to one or the other may not be straightforward. In these cases, the different ratios of the various phases combined with the information achieved by the other techniques can help to distinguish the relative contributions.

Raman spectroscopy is also often used to identify crystalline phases and the intensity of Raman spectrum strongly depends on the nature of the phase. In *sigillata* coatings, hematite is not the major phase but it typically shows the most intense spectrum, overwriting the other phases. Conversely, corundum (a major phase of Gaulish coatings) and spinel (one of the main phases of Italic coatings) are difficult to identify by Raman spectroscopy, although discrimination can be improved by using blue or green laser excitation.

In the study performed by Leon et al. (2010) on Italic and South Gaulish *sigillata*, Raman was used to focus on hematite. The results allowed the two types of production to be separated and provided information about their maximum firing temperature. Compared with natural and synthetized hematite, the hematite contained in *sigillata* coatings is characterized by a shift of Raman peaks and the presence of an additional peak around 680 cm^{-1} (Fig. 14). The up shift of the peaks is due to the substitutions mentioned above ("Chemical composition"), in fact, the high intensity of the additional peak (around 680 cm^{-1}) was attributed to a Ti substitution. Moreover, the experimental firing of several Fe-rich clays under oxidizing conditions showed that this peak was associated with the recrystallization of hematite (occurring above 750–850 °C depending on the clay) and that its intensity depended on the firing temperature. In conclusion, the intensity ratios between this peak and that of pure hematite were found to be a discriminant feature, able to distinguish the production technology of the Italic and Gaulish specimens investigated by the authors (Fig. 15).

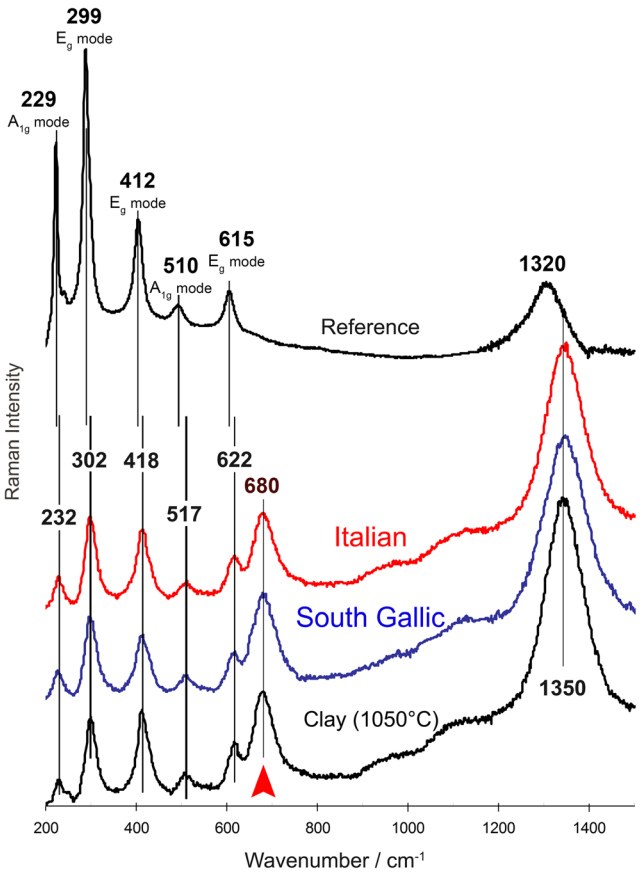


Fig. 14 Typical Raman spectra of hematite from an Italic *sigillata* coating (red), a South Gaulish *sigillata* coating (blue) and a clay preparation for slip fired at 1050 °C (black), compared with the reference Raman spectrum of hematite (data from Leon et al. 2010)

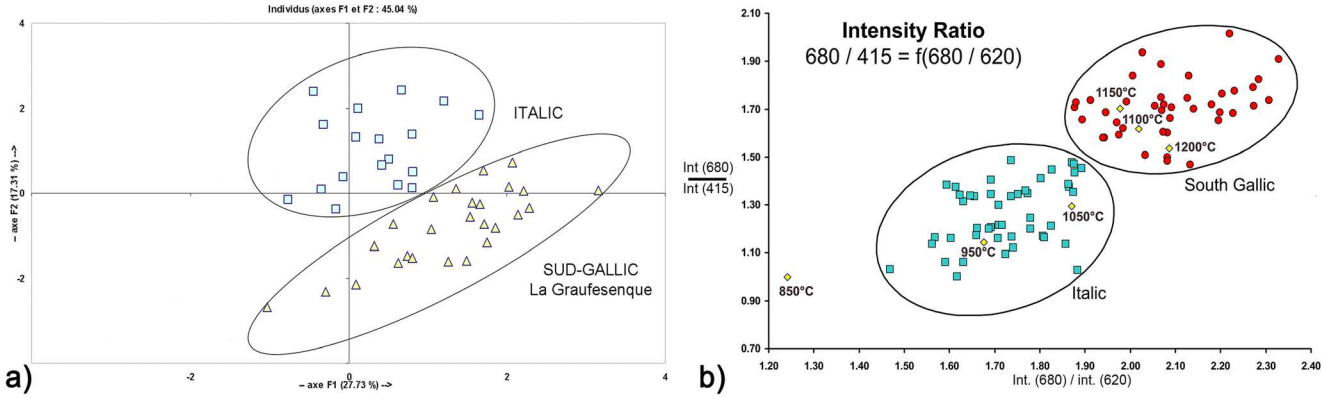


Fig. 15 Separation between Italic and Gaulish production can be obtained from a principal components analysis (a) taking into account the intensity, the position and the FWHM of every peak or from intensity ratios between peaks (b) (data from Leon et al. 2010)

The oxidation state

The evaluation of this parameter is of great importance when reconstructing firing technology. Iron plays a key role in the *sigillata* colour and the control of its valence state—Fe(II) or Fe(III)—is essential to obtain high-quality ceramics (i.e. desired colour aspect). To obtain a beautiful red colour, for instance, it is essential to have a prevalence of Fe(III). Several techniques allow the iron valence to be determined but the most used ones are Mössbauer spectroscopy and X-ray absorption spectroscopy (XAS). To the best of our knowledge, while several *sigillata* productions have been investigated by XAS (see below), Mössbauer spectroscopy has been used only twice (Gancedo et al. 1988; Castillo et al. 1991).

X-ray absorption near edge structure (XANES) involves the study of the fine structure of the absorption edge of an element and is a method for obtaining in-depth information on both its valence state and speciation. A proficient method to collect the X-ray absorption of bulk material is to measure the intensity of fluorescence as a function of the X-ray incident beam energy, the X-ray fluorescence (XRF) being proportional to the X-ray absorption. This technique thus provides an indirect way to measure the absorption of massive samples for which it is not possible to perform a measurement in transmission mode. In a first step, the experiment consists in recording the XRF maps. This procedure is performed by scanning the selected zone with a monochromatic X-ray microbeam with an energy close to the absorption edge of the atoms present in the material. Then, the

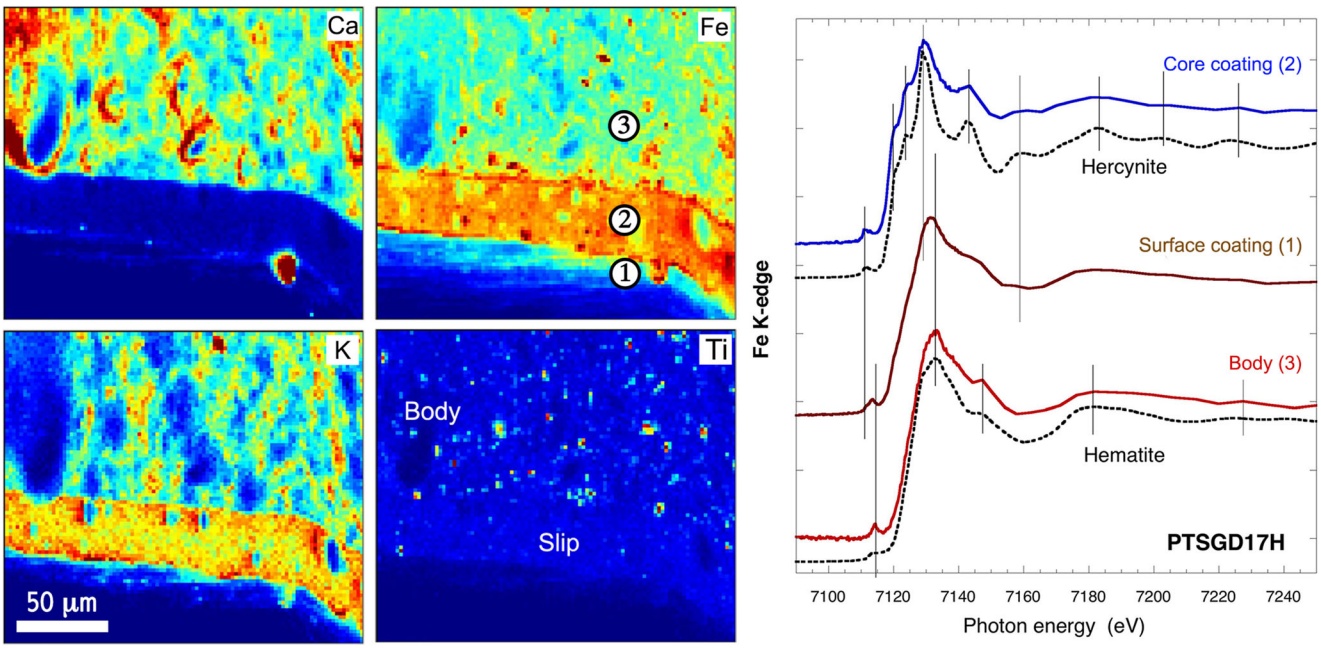


Fig. 16 Cross section of a pre-*sigillata* (La Graufesenque) analysed at SSRL (Stanford, USA) on beamline 2.3. Elemental map obtained with a beam size of 2.5 × 2 μm^2. On the right, XANES spectra recorded at the positions indicated on the Fe map. XANES spectrum from the core coating is close to the one of hercynite ($FeAl_3O_4$, Fe(II)) while the one from body is close to the one of hematite (Fe_2O_3, Fe(III))

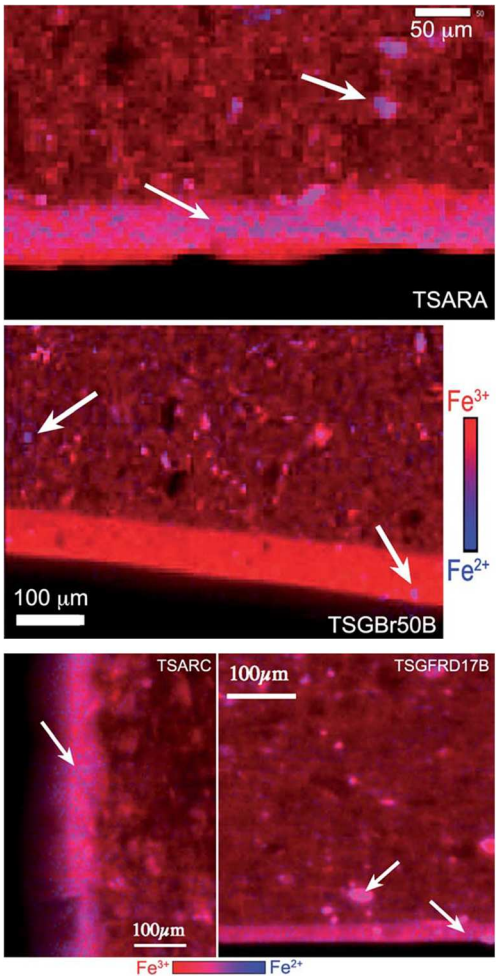


Fig. 17 Bicolor coded Fe valence state maps of Italic (TSARA and TSARC) and South Gallic (TSGBr50B and TSGFRD17B) *sigillata* recorded at the SSRL (Stanford) and ALS (Berkley): 100% Fe(II) in blue and 100% Fe(III) in red. Arrows point the major Fe(II) inclusions in Fe(III) (data from Sciau et al. 2011)

XANES spectrum is recorded at each point of interest by varying the energy of the X-ray microbeam around the absorption edge and by collecting, for each energy, the fluorescence of the element under investigation. When the coating is heterogeneous, the number of analyses should be increased in order to achieve a statistically representative result. Figures 16 and 17 show an example of this approach applied to the study of a pre-*sigillata* coating (Sciau et al. 2011).

In this case study, the iron fluorescence was measured for a few energies near the Fe K-edge and the Fe(II)-Fe(III) maps were extracted from the maps recorded at three different energies around the edge. Significant results were obtained on a few samples (Fig. 17) where Fe(III) was predominant in both the coating and the body.

Only a small amount of Fe(II) was found, mostly in the core of the coating and in some well vitrified area of the body (white arrow). The presence of Fe(II) in the coating core is likely the consequence of an unintentional shift to a reduction atmosphere during firing. Another notable piece of information obtained by that study was the fact that the difference in the Fe valence state distribution varied significantly among the samples. The Fe(II) rate was, in fact, lower in the *sigillata* sample TSG50BrB than in the others (TSARA, TSARC and TSGFRD). Applied to a significant corpus, this approach would allow not only an estimation of the efficiency of *sigillata* kiln from various workshops to be obtained but also to show the degree of control and proficiency of these artisans concerning this complex technology.

Another example on how X-ray absorption spectroscopy can be applied to the study of iron speciation investigations is provided by Wang et al. (2016a). In this latter study, instead of scanning the area of interest with a focused micro-X-ray beam, the area was entirely illuminated by a large X-ray beam. The 2D-XANES map of a selected element was obtained by recording a series of a few hundred X-ray radiographies at different energies and the energy was tuned using small steps (0.2–10 eV) across the absorption edge of the selected element. Then, a data pre-processing, including image alignment, normalization and several other corrections, allowed for the creation of the full-field XANES data set, i.e. a 3D radiography stack, consisting of a few hundred images recorded at different energies. In this way, each pixel contained a full high-resolution XANES spectrum and several maps—concentration, valence state and distribution of the phases—were extracted. Full-field XANES is a very powerful tool, which allows fast investigation to be performed on a large number of specimens. However, the measurements are carried out in transmission mode and, therefore, two requirements must be met at the same time: a specific sample preparation and a high concentration of the element of interest.

To conclude this excursus on X-ray absorption spectroscopy, it remains to be added that while the above examples all concern iron, the same speciation can be performed on other elements such as titanium, manganese or copper. Although these three elements may not be of primary importance in the study of *sigillata* pottery (except for Ti in marbled *sigillata*, see Wang et al. 2016a), the determination of their oxidation state can improve our understanding of the technological process which led to the production of black gloss (see Gliozzo et al. 2004, Aloupi-Siotis 2020 in this TC), glazes (see Wang et al. 2016b, Pradell and Molera 2020 in this TC) and glass (Santagostino Barbone et al. 2008; Gliozzo et al. 2010, 2013).

A brief guide to a good practice

As we have seen in the previous paragraphs, there is not a single technique that can provide all the answers while there

are many techniques that can provide complementary results to a single question.

Good practice requires that archaeometric questions are properly structured. After this fundamental step, the researcher can proceed with the visual examination of the ceramics and the sampling of the pieces deemed significant and representative. The choice of the analytical techniques must take place before taking a material sample because, as we have seen, a different sample preparation corresponds to a different analytical technique. Therefore, it is good to know which technique will be used for the analysis in order to limit to a minimum—if not to prevent—the destruction of the archaeological finds.

The choice of the analytical techniques to be used for the study should be based primarily on the accuracy that each of them is able to guarantee and will likely be diversified according to the area of investigation (surface or volume). In principle, it is good to privilege the bulk analysis for a massive volume such as that of a ceramic body and an in situ surface analysis for a volumetrically limited area such as that of the coating. Based on this reasoning, XRF, ICP-MS and NA will be the preferred techniques for the chemical analysis of the ceramic body (after mechanically removing the coating); OM and powder XRD for the mineralogical analysis of the ceramic body; SEM-EDS and EMPA for the chemical analysis of the coating; in situ XRD for the mineralogical analysis of the coating.

On the other hand, the use of portable instruments or SEM-EDS for obtaining the chemical composition of the ceramic body is a procedure that almost never finds a real justification in the conservation of the artifact and is therefore to be discouraged because it is less accurate than the bulk techniques.

The poor accessibility of instruments that require a nuclear process (such as NA and ND) or a synchrotron light (such as XAS and some types of XRD) must not discourage the researcher from their use; on the contrary, they must be enhanced for the resolution of specific problems.

Finally, if for conservative reasons, it is not possible to take a material sample, the researcher can make use of a set of analytical techniques capable of providing data similar to those usually obtained with conventional techniques (esp. PIXE and some non conventional techniques).

In this regard, however, it is worth specifying that there should be no fear of destroying a ceramic fragment when the expected result cannot be obtained in any other way and increases our knowledge significantly. The production of *terra sigillata*, like many other Roman productions, was a serial mass production and each type is often attested by hundreds of specimens. In most cases, therefore, the problem is not whether to take a sample or not, but only from which specimen to do it (i.e. not from a *unicum* or a fully preserved vessel).

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