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Evolution of terra sigillata technology from Italy to Gaul through a multi-technique approach

Yoanna Leon[1,2], Philippe Sciau[1], Michel Passelac[3], Corinne Sanchez[3], Robert Sablayrolles[4], Philippe Goudeau[5] and Nobumichi Tamura[6]

[1] CEMES, CNRS UPS 8011, 29 rue J. Marvig, F-31055 Toulouse, France
[2] Université de Toulouse, UPS, 29 rue J. Marvig, F-31055 Toulouse, France
[3] Archéologie des Sociétés Méditerranéennes, UMR 5140, CNRS, Univ Montpellier 3, MCC, F-34000, Montpellier, France
[4] TRACES (UMR 5608), CNRS, UTM, Université de Toulouse, 5 allées Antonio-Machado, F-31058 Toulouse, France
[5] Institut Pprime, CNRS, Université de Poitiers, ENSMA, Bd Marie et Pierre Curie, F-86962 Futuroscope Chasseneuil, France,
[6] ALS, LBNL, 1 Cyclotron Road, Berkeley, CA 94720, USA

To understand how the terra sigillata technology was transferred from Italy to Gaul, a large corpus of samples from various worskshop was studied by standard laboratory techniques (Raman spectroscopy, SEM, electron microprobe and colorimetry). Based on these results, a few representative samples were selected and investigated by synchrotron radiation at ALS on the 12.3.2 microdiffraction beamline. The beamline is very adapted to the crystallographic study of thin layers and allows us to determine precisely the mineral composition of the sigillata slips. The set of findings revealed significant differences between the Italic and Gallic slips, which suggest a modification in the manufacturing process. The transfer of the sigillata technique in Gaul is associated to an increase of the firing temperatures due to the use of more refractory clay. This change has no significant influence on their esthetic appearance (brilliance and color) but modify their mechanical properties, resulting in a stronger resistance for the Gallic slips. The implication of these results in archeological context is discussed. In particular, we will try to propose assumptions on the reason of the change in the manufacturing process.

Introduction

Terra sigillata is certainly the most famous ceramic produced during the Roman period. It was massively manufactured in standardized shapes and its widespread distribution makes it one of the main groups of Roman potteries. This tableware is characterized by the redness of its body (or paste) and its slip (or gloss), similar to the color of the clay (*terra*), and by the use of stamps (*sigilla*) in many instances (*sigillatus)*. Theses characteristics are at the origin of the name (*Terra Sigillata*) given by the archeologist of 19th century to this type of potteries. Terra sigillata was often presented as semi-luxury dishes, in-between common pottery and luxury metal tableware (bronze or silver), replacing Campanian ware with black slips inspired from Greek tradition [1]. The use of moulds to produce decorated shapes links sigillata to the Greek vessels of Mégara or Samos from III° and II° century BCE. Such pottery also comes under the name of vasa samia, mentioned in ancient texts.

The manufacturing of Terra Sigillata ware started in central Italy during the first century BCE. The success of this technique quickly spread to the whole of the Italian peninsula and then to the Mediterranean coast [2]. From the very start of our era, great centers of production were set up in the south of Gaul. For more than a century, the main Gallic workshop (La Graufesenque) produced millions of vases and exported its products to a great part of the Roman Empire [3, 5]: a true industry was set up. The success of sigillata ware was mainly due to its brightness and its red color aspect, which is derived from the nature and the microstructure of its coating [6]. This slip was obtained through the vitrification of a Fe rich clay preparation under oxidizing conditions [3, 7, 8]. Indeed, the high gloss and very homogeneous red color of this pottery is due to the using of new kilns where the ceramic pieces were isolated from the flames and the products of wood combustion, such as smoke, soot and other unburned hydrocarbons [8, 10]. The surface treatments constitute, with the firing phase, the most delicate stage of the manufacturing process and the one that also presents most characteristic variabilities of the know-how of every workshop. That is why microstructural characterization of slips is a powerful way to bring information on the craft, to compare the productions of various workshops, and, more widely, to have a better knowledge of the context surrounding the appearance of the first sigillata workshops in Gaul.

The goal of this paper is to follow the evolution of this roman technology from Italy to Gaul through a comparative investigation between Italian and Gallic sigillata. For this purpose a hundred samples were studied by electron microprobe, optic and electron microscopies, X-ray diffraction (XRD), Raman spectroscopy and colorimetry. In order to obtain more information on the crystal size and distribution of the different phases, a small number of selected sherds were also investigated by combined micro X-ray fluorescence (μXRF) and μXRD at the Advanced Light Source of Berkeley National Lab.

Experimental details

Archaeological samples

To have a global vision of these sigillata productions, various sherds coming from sites of production (dump) where they were cast (ceramic wasters), but also from the sites of consumption (thus sold), were selected.

The Italic samples come from Narbonne, La Graufesenque (Millau) and Bram sites in France as well as from the archaeological museum of Arezzo (Italy). The sherds found in France were produced by the Pisa and Arezzo workshops, whereas the sherds provided by Silvia Vilucchi, curator of Arezzo museum come from the Arezzo workshop [11]. The Gallic samples, produced by the workshops of La Graufesenque [4], Montans [12] and Espalion [13], come from these production sites and from various site of consumption (Bram, Rodez, Brive, Iruna Veleia…). A detailed description of all samples can be found in the PhD thesis of Y. Leon [14].

The electron microprobe, electron microscopy and μXRD measurements were performed on the polished cross-sections. The sherds were cut with a diamond saw and the resulting sections were mounted in epoxy and mechanically polished [14]. The X-ray diffraction (XRD), Raman spectroscopy and colorimetry measurements were achieved on the surface of the sherds and/or using the microprobe cross-section samples.

Elemental composition

The quantitative analyses of slips were performed using the CAMECA SX50 microprobe of the Laboratory of *Géosciences Environnement Toulouse* (GET) of the Toulouse University. The operating conditions were as follows: accelerating voltage 15 kV, beam current 20 nA and analysed surface close to 2 x 2 μm^2. Twelve elements were measured. Between 30 and 40 measurements were made on each sample, at different positions from the slip surface. Chemical data were processed using statistical methods based on multivariate analysis (principal component analysis, PCA). Multivariate analyses were carried out using XLSTAT-Pro v. 7.5.2 for Windows.

Mineral composition

Mineral composition was investigated both by X-ray diffraction and Raman spectroscopy. Details of the Raman study is given in reference [15]. X-ray diffraction study was performed on laboratory, using a Seifert 3000 T diffractometer (General Electric, Bad Dürkheim, Germany) equipped with a post-sample graphite monochromator (λ = CuKα). A small number of selected samples was also investigated by micro X-ray diffraction at the Advanced Light Source (Berkeley, USA) on beamline 12.3.2 [16]. Each sample, mounted on a XY piezoelectric stage was step-scanned under a monochromatic microbeam (6 keV) that has been chosen to avoid excessive Fe fluorescence background in the diffraction patterns as well as to allow for low penetration depth [17]. At each step, fluorescence signals (step 2x2 μm^2) as well as diffraction patterns (step 2x4 μm^2) were collected using respectively a high-purity Ge solid state detector and a MAR 133 CCD detector. The typical X-ray beam size on the sample surface was about 2 to 4 μm^2. The X-ray incident angle was 30° whereas the angular swing position of the CCD camera was 70°. The distance between the sample surface and the detector was about 79 mm. The diffraction patterns obtained (Debye–Scherrer ring pattern) were analyzed using the XMAS software to determine size range and orientation distribution of the grains for the major crystalline constituents of the sigillata slip [18].

Microstructure and color

The observation of microstructure and body/slip interphase was conducted by electron microscopy with a JEOL JSM 6460 LV, in backscattered electron mode with a 15 kV accelerating voltage and a probe current of about 50 nA. For a few samples, observations at nanometer scale were realized by electron transmission microscopy in order to determine the nanostructure of the slips. These HREM observations were carried out at CEMES laboratory on a CM30 Philips microscope operating at 300 kV equipped with a Super-TWIN objective lens and images were collected using a CCD camera (2048 x 2048).

The color study was conducted with a Konica - Minolta CM 2600d portable spectroradiometer analyzing light reflected by the sample. From the reflectance spectra, the chromaticity of slip was investigated using the International Commission on Illumination (CIE n° 15). Color coordinates were expressed in the CIE L*, a*, b* system where L is related to color lightness, while a* and b* are each determined by hue and saturation [14].

Results and discussion

Nature of the slips

Elemental composition

The analysis of the elemental compositions of bodies and slips performed on a wide panel of south-Gallic and Italic samples, confirms the previous results and conclusions obtained on a smaller corpus [19]. Both for Italic and south-Gallic productions, the slip (about 20 μm thick) was obtained from a non-calcareous clay (CaO>2.5 % in wt) while in two cases a calcareous clay was used to shape the body. All sigillata slips are characterized by significant rate of iron (8-12 % in wt) and potassium (5-10 % in wt). They present also a Al/Si ratio close to that of Illitic clays. Elemental average compositions of slips of various studied workshops are reported in Table 1. Each of the centers have their own characteristics and, for each of the south-Gallic workshops studied, there are no significant variations between the various samples, whatever the considered period. From the early first century CE until the second century CE, the potters of La Graufesenque, as those of Montans, used the same clay for the paste, and the same preparation of slip, which is very coherent with a collective organization of the craft. Furthermore it is sometimes difficult to differentiate the products of the satellite workshops of Rozier and Espalion of those of La Graufesenque: the elemental composition of both the bodies and slips are rather similar [20] (Fig 1).
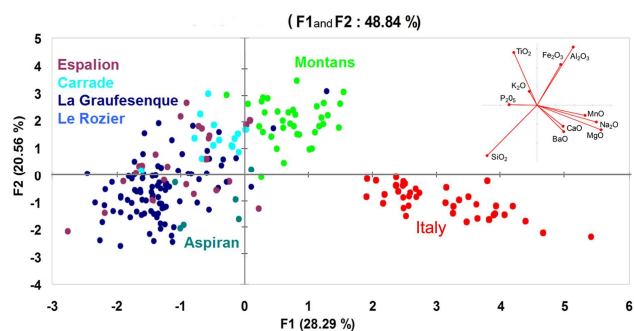
Fig. 1 Variables and scores of the sigillata samples of various studied workshops according to the elemental composition of their slip for the first two principal components (representing 48.84% of the total variability).

On the other hand, the analysis of the Italic sigillata slips are revealing chemical variations between the workshops of Pisa and Arezzo [14], and also between the productions of the various pottery-making firms of Arezzo (Table 1). Variations in potassium and aluminum contents allow us to distinguish between the products of "Ateius" (0 - 14CE) from the oldest ones of "Perrenius" (25BCE - 0). The chemical composition of the body of these sigillata also allows us to separate the two individual pottery-making firms [14]. The potters of Arezzo seem to work with more independence and freedom, taking advantage of an organization already establishes well before the implementation of the sigillata production.

If we observe now all the sherds of Italic sigillata, aretina and pisan, found in the workshops as well as on the various sites of consumption, it is clear that they all differ from south-Gallic slips with a larger amount of sodium and , above all, two to three times higher levels of magnesium (Table 1, Fig 1). As discussed in previous publications [15, 21], the magnesium plays a major role in this type of clay preparation and influences largely the microstructure of the slip.

Average chemical composition of slips	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	K$_2$O	CaO	TiO$_2$	MnO	Fe$_2$O$_3$	BaO
Graufesenque (n=78)	0.08 (0.06)	0.95 (0.22)	23.22 (2.37)	55.70 (2.79)	0.17 (0.04)	8.02 (0.85)	1.39 (0.87)	0.72 (0.10)	0.05 (0.01)	9.63 (1.00)	0.08 (0.02)
Le Rozier (n=3)	0.05 (0.01)	1.11 (0.08)	22.60 (0.15)	58.69 (0.63)	0.15 (0.01)	6.31 (0.06)	1.01 (0.05)	0.71 (0.01)	0.04 (0.01)	9.24 (0.19)	0.08 (0.01)
Espalion (n=36)	0.05 (0.02)	0.91 (0.16)	25.28 (3.05)	54.69 (3.79)	0.21 (0.06)	6.66 (0.60)	1.08 (0.39)	0.77 (0.10)	0.06 (0.01)	10.23 (1.06)	0.07 (0.02)
Carrade (n=13)	0.08 (0.04)	0.99 (0.22)	29.00 (3.19)	52.50 (3.43)	0.18 (0.04)	4.93 (0.50)	0.76 (0.20)	0.84 (0.15)	0.05 (0.01)	10.58 (0.83)	0.08 (0.01)
Aspiran (n=8)	0.87 (0.17)	1.43 (0.59)	22.49 (2.20)	55.81 (2.89)	0.17 (0.05)	7.63 (0.91)	1.17 (0.19)	0.71 (0.15)	0.04 (0.01)	9.61 (0.96)	0.07 (0.01)
Montans (n=37)	0.32 (0.14)	1.15 (0.22)	31.12 (1.39)	44.96 (1.39)	0.13 (0.09)	9.47 (1.60)	1.44 (0.63)	0.78 (0.15)	0.05 (0.01)	10.52 (1.43)	0.07 (0.02)
Italic (n=39) (Arezzo, Pise)	0.95 (0.37)	3.23 (0.45)	26.94 (0.60)	49.51 (0.77)	0.12 (0.02)	6.58 (0.90)	1.53 (0.48)	0.58 (0.08)	0.07 (0.02)	10.38 (0.61)	0.09 (0.02)
Arezzo «Ateius» (n=5)	0.94 (0.12)	3.70 (0.15)	26.23 (0.49)	48.67 (0.33)	0.11 (0.01)	7.07 (0.32)	1.89 (0.72)	0.51 (0.04)	0.07 (0.02)	10.71 (0.18)	0.09 (0.02)
Arezzo «Perrenius» (n=5)	0.55 (0.15)	3.33 (0.45)	27.26 (0.25)	50.38 (1.10)	0.13 (0.03)	5.58 (0.21)	1.12 (0.41)	0.62 (0.07)	0.07 (0.02)	10.87 (0.40)	0.09 (0.03)

Table 1 Average elemental composition of the sigillata slips of workshops studied (south-Gallic and Italic) obtained by electron microprobe in Laboratoire des Mécanismes et Transferts en Géologie (LMTG) of Toulouse University (France). The standard deviations are given in brackets and n is the number of samples.

Mineral composition

XRD investigations performed on a wide panel of Italic sigillata [14] have permitted to confirm the first results obtained from a few sherds [21, 22] : the slips of various Italic productions

have a similar microstructure, which differs from those of the south Gaul slips already described [20, 22]. While the Gallic slip is characterized by the massive presence of corundum nanocrystals and the almost entire absence of spinel crystals (< 2%), the Italian slips contain a proportion of spinel that exceeds 30% and corundum was not detected. In agreement with the conclusions obtained on the study of the clays [21], this is the 3 % of magnesium contained in the Italic sigillata slips which allowed the spinel formation: the spinel phase is formed directly from the decomposition of illite, which is thus favored, and allows the vitrification of the matrix at a lower temperature (<1000°C). These slips therefore require lower firing temperature than the slips which are poor in magnesium. Effectively, the antique Italian slips have a mineral composition very close to the Mg-rich illitic clays after firing in the temperature range of 950 - 1000°C [14]. In addition, the X-ray diffraction study of the mineral composition of the body indicates that the Italian sigillata were fired at lower temperatures than the Gallic, whose temperature was estimated to about 1050°C based on the mineral composition of the bodies [22] and dilatometry measurements [23]. Potters thus adapted firing with clay preparation. These differences of temperature lead to a number of variations: the south-Gallic slips poor in magnesium required a higher temperature which causes the formation of nanocrystals of corundum within the glassy matrix [24]. The main effect of corundum is to turn the slip into a mechanically very resistant coating. These temperature differences between the south-Gallic and Italic workshops induce other less obvious mineral variations that directly affect the color of the slip: Indeed as with the south-Gallic slip, the Italic slips are composed of a transparent glassy phase, which also contains quartz and, in particular, hematite crystals responsible for the red color of the slip.

The previous investigation by Raman spectroscopy [15] and electron energy loss spectroscopy using a transmission electron microscope [6] revealed that the hematite crystals contained in the slips are Al-and Ti-substituted. The study of phases transformations of various illitic type clays as a function of the temperature showed that, according to its crystallization, hematite grew gradually rich in aluminum and titanium; Raman investigations have shown that it was possible to evaluate the degree of substitution and the crystallinity of hematite (which depends directly on the temperature) from the Raman spectrum of the slip. Indeed, the results obtained on the Italic and south-Gallic workshops show that hematite contained in Italic slips has a lower degree of crystallinity and substitution than those of south-Gallic slips fired at higher temperatures [15].

To link chemical composition and mineral composition at the micron scale and accurately assess the size and distribution of different mineral phases contained in the slip, a synchrotron beamline dedicated to micro X-ray diffration was used. This line allows analysis in reflection mode of the cross section of the sherds, which is an advantage because the classical diffraction in the laboratory allows only surface analysis and the thickness of the slip is not always sufficient to distinctly

separate the signal of the slip from the signals of the paste. Moreover, the size of the beam on the order of 1-2 µm, can accurately probe a smaller volume than that allowed by a conventional instrument. It is therefore more suited to the heterogeneity of this type of material. The precise experimental geometry for all graphs were calibrated using quartz as an internal standard. Whatever the sample considered, for each point (Fig. 2a), the 2D diffraction patterns (Fig. 2b) made on the slip are very similar, indicating good homogeneity at this scale. Due to the often too small thickness of the slip (less than 20 µm), the XRD patterns obtained in the laboratory on a large number of sherds showed the presence of a variable but significant proportion of anorthite [22]. The few percent of calcium present in the slip can effectively allow the formation of a small amount of this plagioclase, however the synchrotron measurements confirm that this phase is sometimes present in negligible amounts in the gloss. The main phases detected are hematite and quartz and especially spinel and corundum present in different proportions according to the workshop considered (Fig. 2 and Fig. 3). Whatever the sample studied (Italic or south Gallic), the rings associated with hematite are relatively thin and continuous but also dotted with spots, which implies the presence of a large number of crystals of submicron size and a few of several micron size (Fig. 3). For south-Gallic slips that have a larger particle size, the number of these larger hematite grains is higher than in Italic slips. In these slips, quartz is associated with occasional and isolated diffraction spots implying the presence of crystals of micrometer size. On the 2D diagram of Italic slips, quartz is associated with very thin ring related to the presence of smaller crystals (Fig. 3). The spinel and corundum (C) are characterized by continuous rings which involve the presence of crystals of less than a few tens of nanometers. For Italic slips, rings associated to the spinel are relatively wide compared to the other phases, indicating a low crystallinity and thus very small grains. The ring corresponding to the 440 plane is often the one with the highest intensity (Fig. 2b). This is the only plane where the intensity is not uniformly distributed over the ring and focuses around $\chi = 0$, indicating a texturing of spinel crystals. A crystal orientation parallel to the surface could explain the higher intensity of the ring associated with this plane.
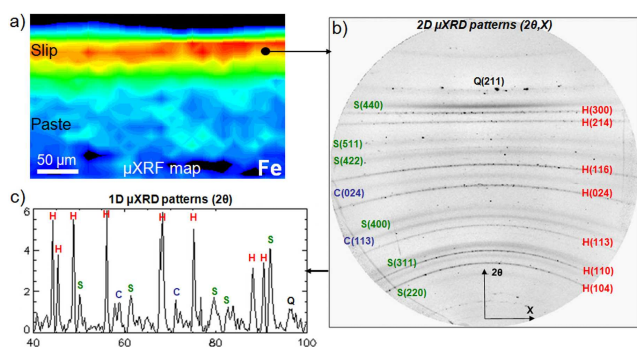

Fig. 2 XRF map of iron ($2 \times 2 \ \mu m^2$ pixels) performed in an italic sigillata cross-section (a), 2D (b) and 1D (c) µXRD patterns obtained in the slip of this sample ($2 \times 3 \ \mu m^2$ beam) (H: Hematite, S: Spinel, C: Corundum and Q: Quartz).

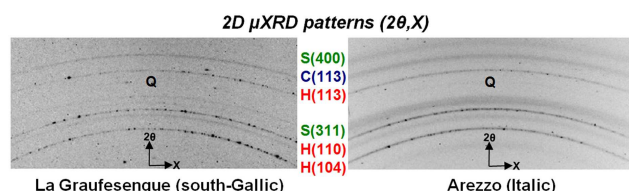**Fig. 3** 2D µXRD patterns obtained in the slip of south-Gallic and Italic sigillata samples ($2 \times 3 \ \mu m^2$ beam) (H: Hematite, S: Spinel, C: Corundum and Q: Quartz).

By integrating according to χ a ring of a phase for each recorded point, mineral mapping of the analyzed surface is obtained (Fig. 4): This map is characteristic of the distribution of the phase according to the (hkl) plane selected. Chemical maps clearly show the differences in composition between the paste and the slip which is characterized by a higher concentration of iron which is evenly distributed (Fig. 4). Corundum is very evenly distributed in south-Gallic slips and there are no variations between the different maps associated with this phase. For hematite this is not the case due to the presence of larger grains (Fig. 4a). For spinel of Italic slips, a particular crystal orientation is observed (Fig. 4b). The grains contained in the interface are however not textured and appear clearly on the mapping associated to the 311 plane. The distribution of spinel crystals in Italic slips is also more heterogeneous than corundum crystals in the south-Gallic. Indeed, contrary to the corundum which is formed in the glassy matrix, the spinel crystals appear in the clay from magnesium contained within it [21]. If this element is not evenly distributed, the crystals will not be either.

For Italic as south-Gallic sigillata, a systematic shift is observed between the lines of hematite of the paste and those of the slip. The profile lines shown in the Fig. 5, illustrate the changes in interplanar spacing between the paste and the slip: hematite contained in the body is characterized by the lattice parameters close to the reference crystal which contains uniquely iron. By contrast, those of the hematite crystals of the slip are smaller, in agreement with a substitution of iron atoms by aluminum and titanium atoms [6, 15]. However, the largest crystals of hematite detected particularly in south-Gallic slips have parameters closer to the reference crystal, implying that they were already present in the clay preparation before firing and were not eliminated during the various settling operations. Changes in interplanar spacing between the slip and the paste are more pronounced in south-Gallic sigillata: indeed, crystals in their slip have a lattice parameter smaller than in the Italic slips, corresponding with a higher substitution of hematite crystals caused by their higher firing temperature [15].
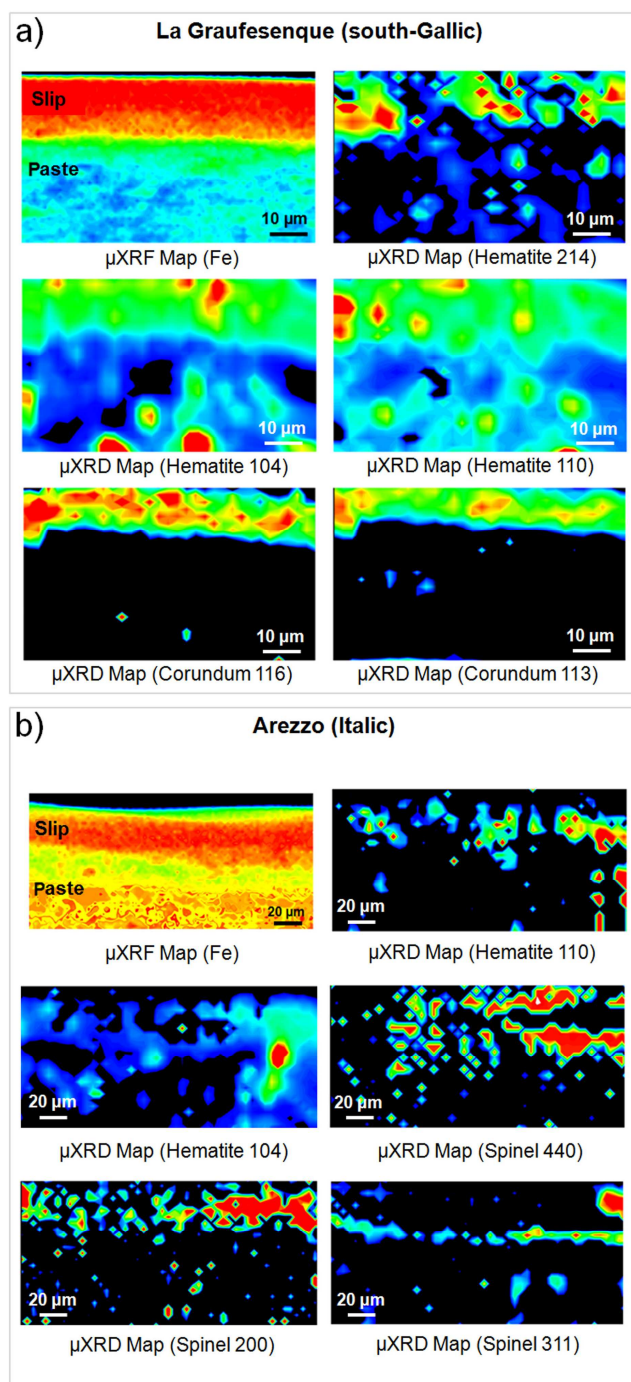
Fig. 4 XRF map of iron (2 × 2 µm² pixels) and corresponding mineralogical maps obtained by integrating the intensity over a given diffraction ring (hkl plane) for each phase, recorded at ALS (2 × 3 µm² beam) on the slip of a south-Gallic sigillata cross-section (a) and of an Italic sigillata cross-section (b) (H: Hematite, S: Spinel, C: Corundum and Q: Quartz).
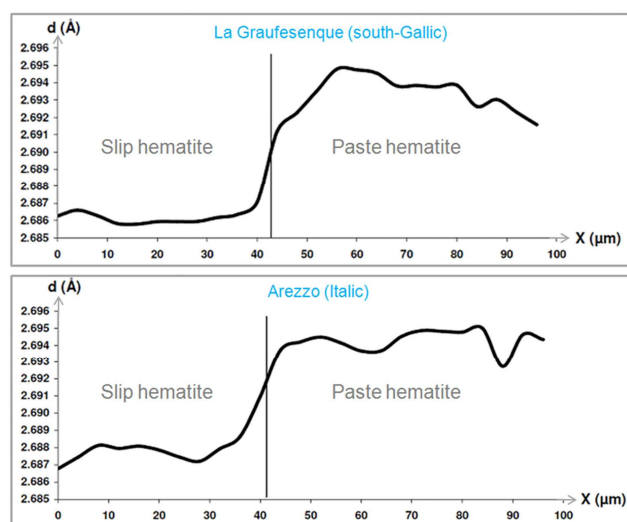

Fig. 5 Evolution of the interplanar distance (d spacing) of the hematite plane (104) on a profile line paste – slip performed on a south-Gallic sigillata cross-section and on an italic sigillata cross-section.

Microstructure

To assess more precisely the size, shape and distribution of the different phases contained within the slip on the submicron scale, thin sections taken from the slip of different sherds of Italic and south-Gallic sigillata were observed by TEM bright field. At this scale the sigillata slips consist of a glassy matrix where very small crystals of a few tens to a few hundred nanometers are dispersed (Fig. 6).

The distribution of hematite crystals in the slip is heterogeneous. The majority have an angular shape, and are not larger than 100 nm. We can see that some of them are more or less aligned parallel to the surface of the slip, which corresponds well with their formation within the layers of clay. The few crystals of hematite larger (greater than 200 nm) which occasionally appear have a more rounded shape. In Italic slips, spinel is in the form of small crystals of acicular shapes of only a few nanometers (Fig. 6b). As µXRD investigations have previously shown, these crystals are oriented parallel to the surface of the slip. This confirms the results obtained on experimental clays [14, 21]: the spinel crystals are formed in the clay layers from magnesium and aluminum that are alredy present and thus keep this orientation after the disappearance of the clay. In the south-Gallic slips, the corundum crystals never exceed 50 nm (Fig. 6a) and are always spherical in accordance with their formation within the glassy matrix, from the excess of aluminum in it [21]. They are randomly distributed in the glassy matrix. Occasionally a few crystals of orthoclase (potassium feldspar) and mullite have been identified in the slip of some sherds of sigillata of the workshop of Montans. As the study of different clay samples has demonstrated, mullite formation at these temperatures necessarily implies the presence of initial kaolinite, which is consistent with the high levels of aluminum measured in the sigillata slip of Montans [14].
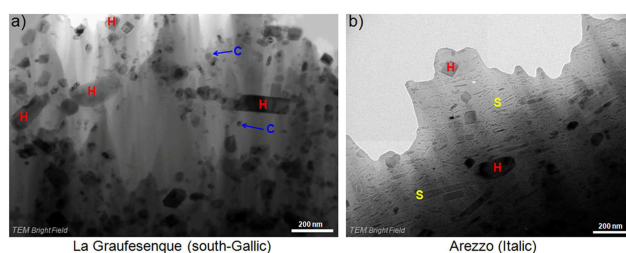
Fig. 6 TEM bright field images obtained on an italic sigillata slip (a) and on a south-Gallic (b) sigillata slip (H: Hematite, S: Spinel and C: Corundum).

Color

As seen, the temperature differences also lead to variations in the microstructure and also in the composition of hematite crystals. This double substitution of hematite crystals directly influences the color of the sigillata slips. The color study of the various sherds clearly shows that the workshop of La Graufesenque made a product with a redder slip and reached a level of gloss twice as high as that of the Italic slips (Fig. 7). The sigillata of the other south-Gallic workshops have a color which lies between that produced at La Graufesenque and in Italy, which probably show a less well controlled firing. None of them therefore equal a red and gloss as intense as La Graufesenque sigillata. The firing temperature reached by the potters of La Graufesenque is perfectly suited to this type of preparation which is poor in magnesium.
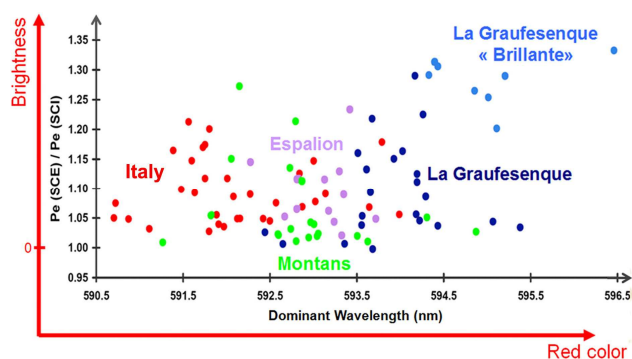

Fig. 7 Brightness (specular reflectance) according to the color (Excitation Purity Pe) of the sigillata samples of various studied workshops. The brightness is evaluated from the specular reflectance component measured by dividing the excitation purity obtained in the SCE mode (Specular Component Excluded) by the excitation purity obtained in the SCI mode (Specular Component Included).

Adherence Body/Slip

The observations of the texture of the body/slip set by scanning electron microscopy show a very low vitrification of Italic sigillata paste linked to the insufficient firing temperature, and a well-defined interface (Fig. 8b). The glassy slip and the non vitrified paste show differences in expansion coefficient, which are at the origin of mechanical strains. These constraints, by relaxing at the interface, can cause the delamination of the slip observed on most of the Italic sherds studied (Fig. 8a). For south-Gallic productions, fired at higher temperatures, the paste has a characteristic cell structure of calcareous clays fired at over 1000°C (Fig. 8c). It is due to CO_2 occurring during the decomposition of the calcite contained in the paste, and to its partial vitrification. The adhesion of the slip on the paste is stronger, which is a criterion of solidity and quality. Given the partial vitrification of the paste, the stress relaxation is exercised differently between the slip and the body, and produces the appearance of microcracks perpendicular to the plane of the interface (Fig. 8d). These microcracks are present in all samples studied, including those of very good quality. This phenomenon is general to all sigillata with a partially vitrified paste. The temperature differences which are imposed directly by the composition of the used clay preparation cause, therefore, indirectly significant variations on the interface which are quite visible.
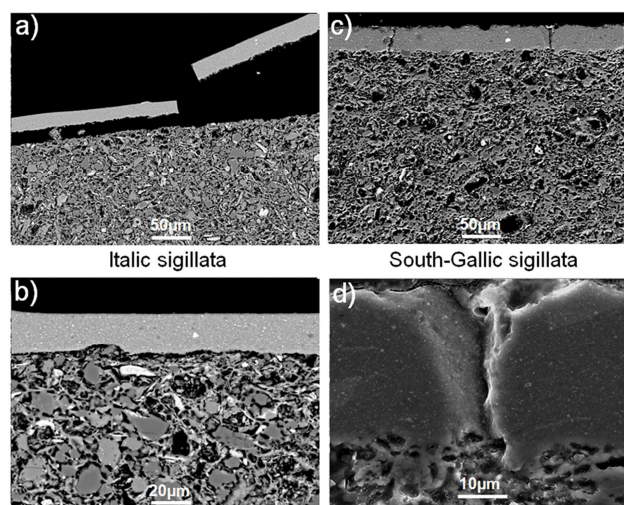

Fig. 8 SEM-BSE images performed in an italic sigillata cross-section (a, b) and in a south-Gallic (c, d) sigillata cross-section.

Conclusions

The microstructural analysis of sigillata has been performed in a wide range of scales (by means of complementary characterization techniques) giving us relevant information on the appearance context of the first south-Gallic workshops. From these data, it is now possible to identify the key conditions (nature and composition of the clay, temperature and atmosphere of firing) leading to specific types of slip microstructures and thus to bring to light the resemblances and the characteristics of different productions.

These results show that the production of sigillata in the southern Gaul does not arise from a simple technology transfer, thanks to the intervention of the Italian specialists, but it is also associated to an significant technological evolution.

The archaeological data showed [4] that the production of sigillata in southern Gaul begun suddenly (10-20 CE) and was associated with the arrival of Italian specialists. Previous archaeometric studies demonstrated that the imitations of Italic sigillata made in the Gallic workshops (30 BCE – 10 BCE) before the production of sigillata cannot be associated to an initial phase for the later sigillata production [14, 25, 26]. On the contrary these studies have revealed that the slip

composition was suitable to the firing protocol used for their manufacturing. The similitude in composition between the Italic and south-Gallic sigillata slips as well as the use of calcareous clay for the bodies, are in good agreement with the archaeological deductions. In both cases, a K-rich illitic clay with a Fe content around 10% (in wt %) was used to elaborate the slips. However the ship composition between these two production areas shows a systematic difference in magnesium content which modify the vitrification temperature of the slip and lead to increase the firing temperature by about 50-70° C for the Gallic productions. Thus, the transfer from Italy to Gaul came along with a different modification of the process of elaboration which confers a better mechanical resistance and adherence on slip and also improves its optical properties. Indeed in all the south-Gallic workshops studied, there is the systematic use of a slip which is poor in magnesium. The study of Italic sigillata imitations made in the La Graufesenque workshop revealed that the Gallic potters have used clays of various kinds, probably taken from nearby workshops and that all of these slips are also poor in magnesium [25]. Nevertheless the study of the clay resources of the various south-Gallic centers tends to demonstrate that it is not a particularity of local clays : indeed all the clays collected in compatible geologic levels (Permo-Triassic), nearby the La Graufesenque, Espalion and Montans workshops, have higher levels of magnesium, closer to Italic slips [14, 15]. This raises the question of the origin of the magnesium deficiency. Two scenarios are possible: either this feature is natural and specific to certain deposits or it is a direct consequence of the process used in the preparation of slips. In the first case, it involves a systematic search of magnesium-free clays which, if based on our geological investigations, seem rare. Even then it would be a voluntary selection adopted by all, and based on criteria difficult to identify. The second more likely assumption, implies some specificity in the slip preparation, common to all south-Gallic workshops and already adopted by the terra sigillata imitations workshops of La Graufesenque. With the beginning of commercialization of sigillata products, workshop potters used the same clay paste that was used for the production of sigillata imitations made just before in the same workshop [27]. Maybe they also retained certain processes relating to the preparation of the slip. Indeed it is possible that a particular treatment imposed on clay can help eliminate some of the magnesium. The clay was maybe put in tubs allowing the flow of water, which would allow the rainwater to leach the magnesium in the clay (by cation exchange with the H + ions) from the preparation and therefore eliminate a large part of it. Therefore it would be a difference in the preparation of the south-Gallic slip responsible for structural modification that results in improved optical and mechanical properties.

The use of illitic clay poor in magnesium requires a higher firing temperature, thus adding an additional cost [28] but also a better mastery of oxidizing firing. At 1050°C the hematite is more sensitive to the reduction than 980°C and it is critical that the oxygen rate is as high as possible (i.e. close to 21%). To obtain very high gloss red coatings, it is essential that there is no smoke around vessels, during the vitrification step. In a recent study, Fe^{2+} was found in the slip cores of the Italic sigillata, but not in the slip of La Graufesenque sigillata. This result is consistent with a better mastery of oxidizing firing by the Gallic potters, but the number of analyzed samples (4 in total) is small and further study is necessary for any definite conclusion. Although few firing structures have been found, the use of tubes (tubuli) is early attested at the site of La Graufesenque workshop. These tubes allow preventing the vessels from being into contact with exhaust fumes and fire. As the experimental firings show, these tubes would be more airtight than the various firing device (Saggars) that have most probably been used by the workshop of Arezzo in early sigillata production. However, we do not have enough archeological data on firing structures to explain the possible difference in the mastery of oxidizing firing.

In any event the potters of La Graufesenque and Montans adapted new processes (firing protocol) while keeping a certain know-how with regard to the preparation of the clay. This modification leads to an evolution of the product, which in turn provided a good response to an increased need for utilitarian vessels during this period. Even though we cannot really speak about a change of status of the sigillata, it is clear that this evolution in process runs parallel with the variations of political and economic context (Republique / Empire) which surround both of the productions considered (Italic and south-Gallic).

Notes and references

1   J.V. Noble, *The techniques of painted Attic pottery*, Watson-Guptill ed., New York, 1965.

2   M. Madrid Fernández, J. Buxeda i Garrigós, *A review of the archaeometric studies*, 5th European Meeting on Ancient Ceramics, ed. V. Kilikoglou, A. Hein, Y. Maniatis Archaeopress, 1999, pp. 287-297.

3   F. Oswald, T.-D. Pryce, G. Simpson, *An introduction to the study of terra sigillata*, New ed., Gregg Press, Farnborough, 1966.

4 D. Schaad, *La Graufesenque (Millau, Aveyron) ; Condatomagos, une agglomération de confluent en territoire rutène IIe siècle aC - IIIe siècle*, Editions de la Fédération Aquitania, Pessac, 2008, vol. **I**.

5 M. Genin, *La Graufesenque (Millau, Aveyron) ; Sigillées lisses et Autres Productions*, Editions de la Fédération Aquitania, Pessac, 2007, vol. **II**.

6 P. Sciau, S. Relaix, C. Roucau, Y. Kihn, *J. Am. Ceram. Soc.* 2006, **89**, 1053-1058.

7 M.S. Tite, M. Bimson, I.C. Freestone, *Archaeometry*, 1982, **24**, 117-126.

8 M.S. Tite, *Archaeometry*, 2008, **50**, 216-231.

9 A. Vernhet, *Gallia.*, 1981, **39**, 25-43.

10 M. Picon and A. Vernhet, *SFECAG, actes du Congrès de L'Escala-Empuries*, 2008, 553-566.

11 A. Oxè, H. Comfort, P. Kenrick, *Corpus Vasorum Arretinorum. A Catalogue of the Signatures, Shapes and Chronology of Italian Sigillata, Second edition completely revised and enlarged*, Bonn, Habelt, 2000, Antiquitas III, **41**.

12 Th. Martin, *Céramiques sigillées et potiers gallo-romains de Montans*, Ed. Centre de documentation, d'étude et de formation archéologiques de Montans "Élie Rossignol", 1996.

13 J.-L. Tilhard , *Les céramiques sigillées d'Espalion (Aveyron-France)*, ADRAHP et Fédération Aquitania, Périgueux, 2009.

14 Y. Leon, *Etude de la diffusion en Gaule d'une technique romaine d'élaboration de sigillées à travers l'analyse microstructurale des surfaces décoratives (ou engobes)*, Physique de la matière, Université de Toulouse, 2010.

15 Y. Leon, C. Lofrumento, A. Zoppi, R. Carles, E.M. Castellucci, P. Sciau, *J. Raman Spectrosc.*, 2010, **41**, 1260-1265.

16 M. Kunz, N. Tamura, K. Chen, A.A. MacDowell, R.S. Celestre, M.M. Church, S. Fakra, E.E. Domning, J.M. Glossinger, J.L. Kirschman, G.Y. Morrison, D.W. Plate, B.V. Smith, T. Warwick, V.V. Yashchuk, H.A. Padmore, E. Ustundag, *A dedicated superbend x-ray microdiffraction beamline for materials, geo-, and environmental sciences at the advanced light source*, Rev. Sci. Instrum, 2009, **80**.

17 P. Sciau, P. Goudeau, N. Tamura and E. Dooryhee, *Appl. Phys. A*, 2006, **83**, 219-224.

18 N. Tamura, in *Strain and Dislocation Gradients from Diffraction. Spatially-Resolved Local Structure and Defects*, eds. Barabash R. and Ice G., Imperial College Press (London), 2014, 125-155.

19 Y. Leon, P. Sciau, A. Bouquillon, L. Pichon, P. de Parseval, *PIXE (particle induced X-ray emission): A non-destructive analysis method adapted to the thin decorative coatings of antique ceramics*, Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms, 2012, **291**, 45-52.

20 Y. Leon, C. Dejoie, A. Bouquillon, R. Ciszak, P. de Parseval, P. Sciau, in *Les céramiques sigillées d'Espalion (Aveyron-France)*, ADRAHP et Fédération Aquitania, Périgueux, 2009, 59-77.

21 P. Sciau, S. Relaix, C. Mirguet, P. Goudeau, A. M. T. Bell, R. L. Jones and E. Pantos, *Appl. Phys. A*, 2007, **90**, 61-66.

22 P. Sciau, C. Dejoie, S. Relaix, D. Parseval, in *La Graufesenque (Millau, Aveyron) ; Sigillées lisses et Autres Productions*, Editions de la Fédération Aquitania, Pessac, 2007, vol. **II,** 23-36.

23 M. Picon, *Les mesures, par dilatométrie, des températures de cuisson des céramiques de La Graufesenque : principes et applications*, Annales de Pegasus, 1998, **3**, 32-40.

24 P. Sciau, P. Goudeau, N. Tamura and E. Dooryhee, *Appl. Phys. A*, 2006, **83**, 219-224.

25 C. Mirguet, C. Dejoie, C. Roucau, P. de Parseval, S. J. Teat and P. Sciau, *Archaeometry*, 2009, **51**, 748-762.

26 M. Passelac, Y. Leon and P. Sciau, *L'utilisation d'hématite broyée dans les revêtements de présigillées de Bram*, SFECAG, Actes du congrès de L'Escala-Empúries, 2008, 567-576.

27 M. Picon, in *Céramiques de la Graufesenque et autres productions d'époque romaine, hommages à Bettina Hoffmann*, Archéologie et histoire romaine, eds. M. Genin and A. Vernhet, éditions monique mergoil, Montagnac, 2002, 139–163.

28 M. Picon, *A propos des sigillées, présigillées et imitations de sigillées : questions de « coûts » et de marchés*, SFECAG, Acte du Congrès de Bayeux, 2002, 345-356.