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Micro-Raman investigation of *terra sigillata* slips: a comparative study of central Italian and southern Gaul productions[†]

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Terra sigillata is certainly the most famous fine ware of the Roman period, and for this reason it has been a subject of interest for both the archeology and archeometry communities. X-ray diffraction studies showed systematic differences in the mineral compositions between central Italian and south Gaul productions. All the slips contain hematite; the Gallic ones embody also a significant content of corundum, while the Italian productions contain a great proportion of spinel. Raman investigation fails to reveal directly these differences because the spectra are dominated by the hematite peaks. However, we originally demonstrate that, due to the occurrence of an upshift of bands, the Raman spectrum of these *sigillata* slips can be associated with a substituted hematite. This premise has been confirmed by comparing the crystallization of hematite in four annealed clays to that of the ancient slips. The results suggested that the presence of the strong additional Raman band at around 680 cm⁻¹ present in both clays and ancient slips could be associated with the recrystallization of hematite, occurring above 750 °C. It could also be due to the magnetite content, but this hypothesis is not supported by X-ray diffraction data. In addition, the reduction seems to take place only above 1050 °C, as suggested by the unveiling of hercynite as well as the darkening of the clay samples. Raman scattering is shown to be very sensitive to small variations in clays composition and to firing temperature, and it has been successfully used as an *in situ* sensitive probe for discriminating between Italian and south Gallic productions. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: micro-Raman spectroscopy; *terra sigillata*; slip; hematite

Introduction

Terra sigillata is certainly the most famous fine ware of the Roman period with characteristic decorations obtained by means of specially designed stamps (*sigilla*). This pottery was extensively produced in standardized shapes and was widely distributed across the Roman Empire. Archeologists demonstrated that it can be traced back to the industrial activity of a few specialized workshops.^[1,2]

Terra Sigillata pottery production originally started in the middle of the 1st century B.C. around central Italy, with the development of the high-gloss red coating obtained through vitrification under oxidizing atmosphere of a clay preparation rich in iron oxide.^[3] This coating technique quickly spread throughout the Italian peninsula and to the Mediterranean coast and resulted in the establishment of great centers of production in the south of Gaul from the very beginning of the 1st century A.D.^[4,5]

X-ray diffraction and microprobe analysis revealed systematic differences between the central Italian (Arezzo) and south Gaul productions (La Graufesenque), both in the elemental and mineral compositions.^[6–8] All the slips contain quartz and hematite; however, the Gallic ones embody a significant content of corundum nanocrystals, while the Italian productions contained a great proportion of spinel (MgAl₂O₄). In addition, the X-ray diffraction study of the mineral composition of the body indicates that the Italian *sigillata* was fired at lower temperatures than the Gallic ones. These differences resulted in a modification of their

mechanical properties. The adhesion of the south Gaul slips is better, and the presence of nanocrystals of corundum offers a better resistance to scratches. These modifications could indicate an evolution in the manufacturing process around the beginning of the 1st century A.D. In this context, a nondestructive and rapid technique capable of distinguishing between the two different processes would allow us to test this assumption on a more representative corpus including museum artworks.

Raman spectroscopy is a nondestructive and rapid technique particularly suitable to study the mineral composition of thin decorative surfaces. We wanted to explore the capabilities of the Raman technique to discriminate between these two different types of slips. The main difference between these two types concerns the

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nanocrystalline phases (corundum and MgAl_2O_4 spinel). Unfortunately, the hematite contribution to the Raman spectrum is very high in the *sigillata* slips and the detection of these nanometric phases is very difficult. For example, corundum was not detected in south Gaul *sigillata* slip.^[9,10] Also, in order to find another criterion to separate the two types of productions, the evolution *versus* firing temperature of several fine clays was carefully examined using Raman spectroscopy. These clays were ascertained as possible sources of raw material and were selected on the basis of chemical composition close to that of the antique slips.

Experimental

Raman spectroscopy

Micro-Raman measurements were performed at room temperature by means of a single-grating RM2000 Renishaw spectrometer equipped with a Peltier-cooled charge-coupled device detector. The Raman excitation was provided by an argon laser operating at 514.5 nm. A 100 \times microscope objective was employed to focus the laser beam and to collect the scattered light, providing a 1- μm -diameter laser spot. After verifying that the laser power did not have any influence on the hematite spectrum, we chose to record the spectra with a laser power of about 2 mW on the sample in order to optimize the signal/background ratio. Spectra were recorded in steps of 1.6 cm^{-1} , with an acquisition time of 30 s. The instrumental resolution, evaluated as the full width at half-maximum (FWHM) of an emission line of a He–Ne lamp, was 7 cm^{-1} . Wavenumber calibration was regularly verified by using the Raman peak at 520 cm^{-1} of a silicon crystal as a reference.

Archeological samples

The south Gallic *sigillata* samples as well as a part of Italian *sigillata* come from the La Graufesenque site. They were supplied by Alain Vernhet, who managed the excavations of this site for many years.^[11] The other Italian *sigillata* shards were provided by Silvia Vilucchi, curator of the archeological museum of Arezzo (Italy). Only samples with a homogeneous red color were selected. The samples showing reduction traces or firing problems (too low or too high firing temperatures) were discarded.

Clay samples

The studied clays come from the Permian and Triassic levels that surround the two main south Gallic workshops [La Graufesenque

(Aveyron, France) and Montans (Tarn, France)] and the smaller Espalion's workshop (Aveyron, France). These levels have been ascertained as possible sources of the raw material for the slips of these workshops.^[12] Four of the Fe-rich illitic clays were settled by the *Laboratoire des Mécanismes de Transfert en Géologie* of Toulouse III University in order to conserve only the fine fraction ($\leq 2 \mu\text{m}$).

Structural and chemical analysis

Analyses carried out by inductively coupled plasma atomic emission spectroscopy in the *Service d'Analyse des Roches et des Minéraux* (Vandoeuvre-Les-Nancy, France) confirmed that the fine fraction had a chemical composition close to that of the antique slips (Table S1, Supporting Information).

Phase transformations *versus* temperature under oxidizing atmosphere (air) were investigated by X-ray diffraction. The main results are summarized in Table 1. The chemical process involved in the formation of spinel (MgAl_2O_4) and corundum (Al_2O_3) under oxidizing atmosphere has been discussed in a previous publication.^[7] Corundum can be grown only if the amount of Mg is not too high ($\leq 3\text{--}4 \text{ wt\%}$). In this case, the total decomposition of illite ($< 900^\circ\text{C}$) gives rise to the formation of an intermediate potassium aluminum silicate phase, which gets disrupted above 1000 $^\circ\text{C}$ giving a vitrified phase in which corundum nanocrystals grow. On the contrary, if chlorite is present in the raw clay so that the amount of Mg exceeds 3–4 wt%, this intermediate phase is not observed. The spinel phase is formed directly from the decomposition of illite and allows the vitrification of the matrix at a lower temperature ($< 1000^\circ\text{C}$). After firing in the temperature range 950–1000 $^\circ\text{C}$, the Mg-rich illitic clays (MON7, VA7) have a mineral composition very close to the antique Italian slip. To date, the studied clays seem to contain too much Mg (1.6 wt%, ESP4) to lead to a mineral composition lacking in spinel, as observed in the Gallic slips.

These raw clays have a red color, and low-crystalline hematite was identified in all non-fired samples. A recrystallization of hematite is observed in the temperature range 800–950 $^\circ\text{C}$. The intensity of broadened hematite X-ray diffraction peaks decreases (the intensity) sharply, and new thin peaks appear at slightly higher angular positions. The recrystallization is accompanied by a diminution of cell parameters, in agreement with the substitution of Al for Fe.^[13,14]

Above 1100 $^\circ\text{C}$, the intensity of the X-ray diffraction peaks due to hematite decreases. At 1200 $^\circ\text{C}$, only very small peaks are observed

Table 1. Mineral compositions determined by XRD of the studied clays, before firing and after firing at 1050 and 1200 $^\circ\text{C}$

Studied clays	Mineral composition		
	Present phases before firing	Present phases after firing at 1050 $^\circ\text{C}$	Present phases after firing at 1200 $^\circ\text{C}$
ESP4	Illite , kaolinite , quartz and hematite	Hematite , corundum and spinel (MgAl_2O_4)	Mullite , hercynite , corundum and hematite
VA7	Illite , chlorite , kaolinite (?), quartz, hematite and calcite	Hematite , spinel (MgAl_2O_4), corundum and anorthite	Mullite , anorthite and hematite
MON4	Illite , quartz, hematite	Hematite , corundum and spinel (MgAl_2O_4)	Hercynite and corundum
MON7	Illite , chlorite , quartz, hematite, albite and dolomite	Hematite and spinel (MgAl_2O_4)	Hercynite
The main phases are given in boldface.			

in the ESP4 and VA7 samples. In the same temperature range, an increase of the intensity and a shift to small angles are observed for spinel peaks. At 1200 °C, the spinel peaks are close to the peak positions of hercynite (FeAl_2O_4). Mullite was also identified in the ESP4 and VA7 samples.

Raman Investigations

Fired clay samples

The measurements were made at room temperature on the fired clay samples previously studied by X-ray diffraction. Figure 1 shows

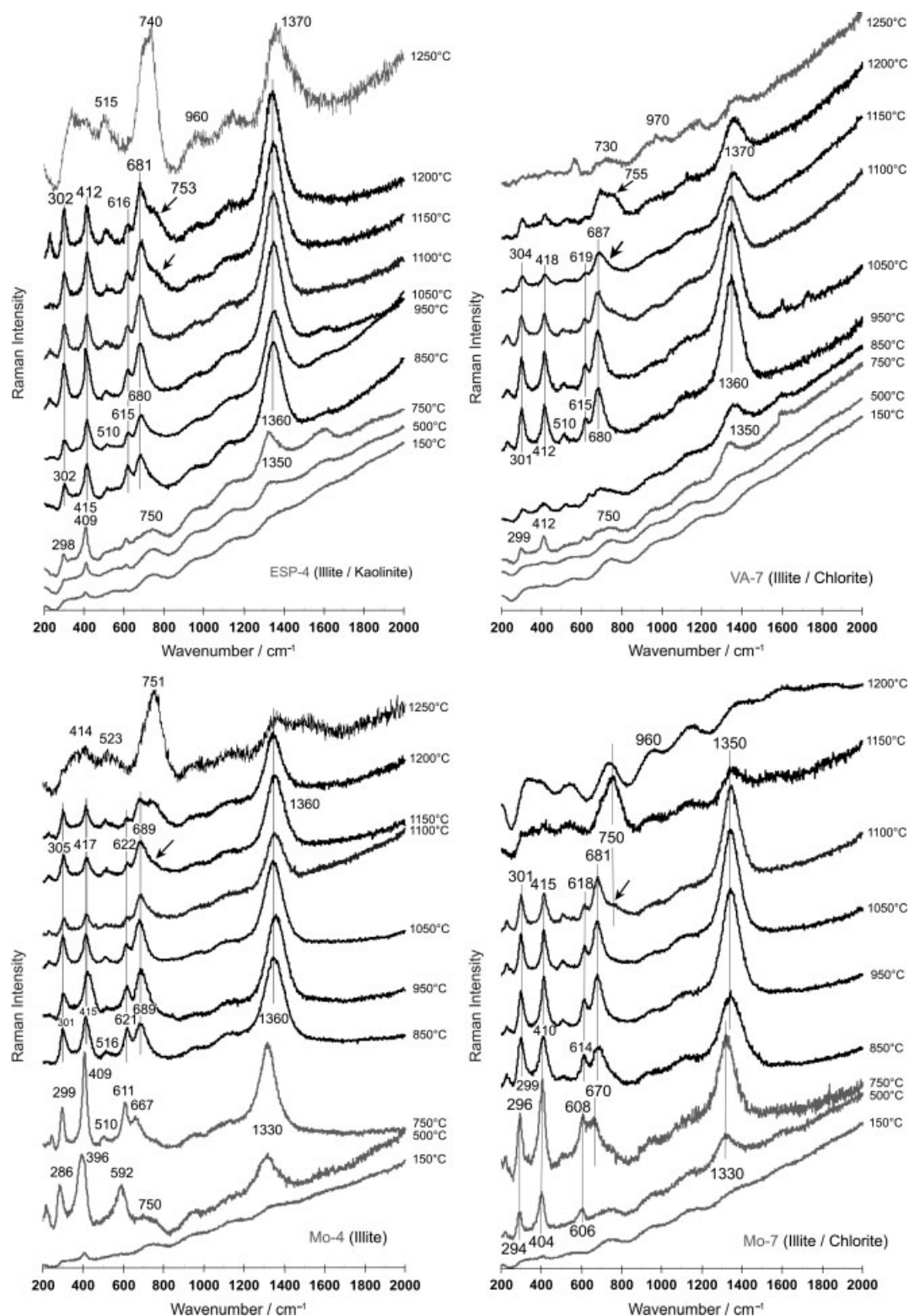


Figure 1. Raman spectra (normalized) obtained at room temperature on samples of clay, previously settled (fine fraction lower than 2 μm) and heated for 15 h under oxidizing atmosphere at different temperatures.

the evolution of Raman spectra *versus* the annealing temperature after normalization with the total scattered intensity.

The same remarks can be made for the four clay samples. From 150 to 750 °C, some characteristic bands of the hematite spectrum are present, but rather badly defined, testifying the low crystallinity of hematite as revealed by X-ray diffraction in this temperature range. For ESP4 and MON4, the E_g mode at 412 cm⁻¹ associated with the O–Fe–O bending interactions is already present at 150 °C. The three E_g modes (299, 412 and 615 cm⁻¹) become visible at 500 °C, except for the VA7 and MON7 samples for which these peaks appear only at 750 °C. In addition to the hematite peaks, the Raman spectra show a broad band at 750 cm⁻¹, which could be attributed to the illite clay.^[15] For the four samples, this band disappears above 750 °C, in agreement with the illite decomposition observed by X-ray diffraction.

Above 800 °C, an abrupt change is observed in the spectra. All the hematite peaks are now present, and the characteristic strong second-order band at 1350 cm⁻¹ assigned to a two-magnon scattering is clearly seen.^[16] However, the peaks are slightly upshifted and broader compared to pure hematite, and an additional broad peak at 680 cm⁻¹, systematically observed in antique slips (Fig. 2), is also present. It can be noted that this drastic change takes place earlier (than 750 °C) for MON4 and MON7. The wavenumber shift and the broadening of the hematite peaks above 800 °C is in agreement with the abrupt structural change observed in this temperature range in X-ray diffraction. The broadening and the shifting toward higher wavenumber are both well explained by a partial substitution of iron by a lighter atom, which is in good agreement with the decrease of the cell parameters of hematite revealed by X-ray diffraction. In a Raman study of natural ocher, similar spectra were found and the peak at 680 cm⁻¹ was attributed to magnetite.^[17,18] However, in our case magnetite was not found by X-ray diffraction. In addition, the Raman signal of magnetite is much weaker than that of hematite, and only a large magnetite amount could explain such an intense peak at 680 cm⁻¹,^[16,18] and that should be easily detected in the X-ray diffraction patterns. The spinel that appears in the X-ray patterns above 900 °C is not detectable in the Raman spectra, as well as the corundum which grows above 1000 °C.

Above a certain temperature, depending on the sample type, a new band appears at around 750 cm⁻¹, while the Raman spectrum of hematite begins to disappear. In the spectra of the samples fired at 1250 °C, hematite is no longer detected. The band at 750 cm⁻¹ is a characteristic band of the spinel structure. It could be due to the 8Al₂O₃ · 2SiO₂ spinel,^[19] as expected from clay decomposition before mullite formation or hercynite (FeAl₂O₄), as found by X-ray diffraction. In some samples (Table 1) fired at this temperature, mullite was also identified. The broad band at 950 cm⁻¹ could be attributed to mullite. However, some broad bands could also be due to the vitreous matrix that constitutes the major part of samples fired above 1050–1100 °C.

In the temperature range 850–1100 °C, the Raman spectra of all the samples are very close to those of the antique slips shown in Fig. 2. The only difference among the four clays is the temperature range over which no strong evolution is observed. For the pure illitic clay (MON4), the domain is very wide (from 750 to 1200 °C), whereas it is more restricted for the three other clays: from 750 to 1100 °C for the illite–chlorite clay (MON7) and from 850 to 1200 °C for the illite–kaolinite clays (ESP4 and VA7).

In order to quantify the evolution of Raman spectra of the clay in this temperature range, the maximum intensity of each peak was measured from the normalized spectra. By considering the

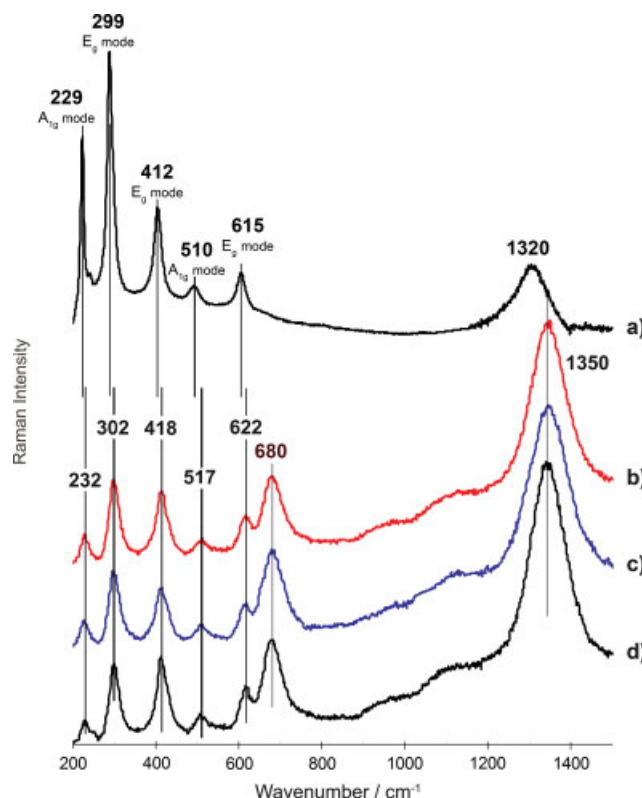


Figure 2. Typical Raman spectra (normalized) of a reference sample of pure hematite (a), an Italian *sigillata* slip (b), a south Gallic *sigillata* slip (c) and MON7 clay fired at 1050 °C (d).

intensity ratio, all the standard peaks of the hematite phase evolve in a similar way with regard to temperature. The main evolution concerns the intensity of the additional peak at 680 cm⁻¹, which increases more quickly than the others. All the clays show the same evolution. The intensity of the 680 cm⁻¹ peak increases from the hematite structural modification temperature, reaches a maximum before slightly decreasing as the band at 750 cm⁻¹ appears. Figure 3 shows the evolution of the ratio (680/620) in accordance with the ratio (680/415) until the complete disappearance of hematite signal. The effect of temperature is evident. The dots corresponding to the lower firing temperatures are on the left of the graph, while those of higher temperatures are on the right. The influence of the nature of the clay is less easily observable. However, an in-depth comparison reveals that the ratios do not present the same evolution for all the clays. In the 850–1050 °C temperature range, the (680/620) ratio is nearly constant for ESP4 with only an increase of the (680/415) ratio. In the same range, both of these ratios rise for the three other clays.

Antique slips

The spectra recorded on the antique slips confirm the great similarity between the Raman signal of Italian and Gallic *sigillata* slips (Fig. 2), even though their mineral composition differs in MgAl₂O₄ spinel and corundum content, respectively.^[7,14] In ionic structures such as corundum or MgAl₂O₄ spinel, the Raman signal is weaker than in hematite. In addition, the fact that the crystals of these phases have a nanometric size points to a more diffuse response. Consequently, because of the predominance of the hematite signal, corundum and spinel nanocrystals cannot be detected in the antique slips.

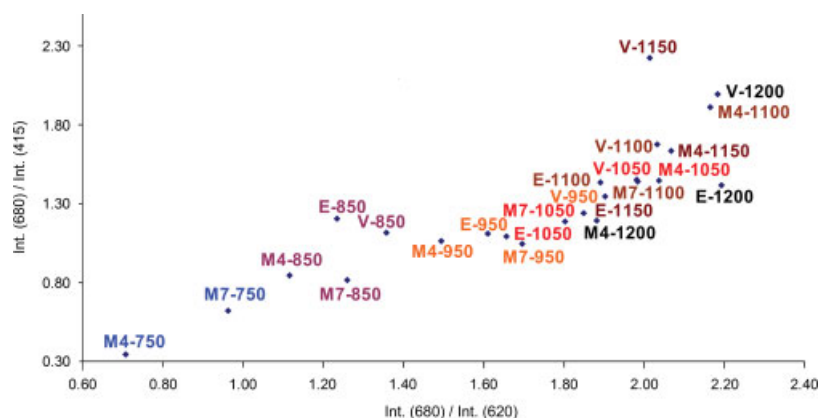


Figure 3. Diagram representing the intensity ratio (680/620) according to the intensity (680/415) for different firing temperatures (E: ESP4, M4: MON4, M7: MON7 and V: VA7).

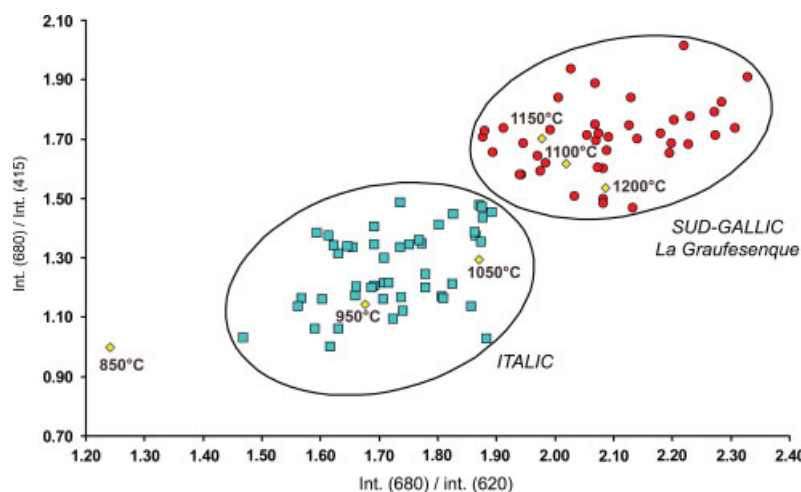


Figure 4. Diagram representing the intensity ratio (680/620) according to the intensity (680/415) of Italic (■) and south Gallic (●) *sigillata* slips as well as of studied clays for different firing temperatures (♦). Only the average values of the four clays for every temperature are represented. The number of analyzed samples is 40 and 48 for La Graufesenque and Italian workshops, respectively.

These spectra are very close to those recorded from the clay samples fired under an oxidizing atmosphere. They show the same wavenumber upshifts and the simultaneous presence of the additional band at 680 cm^{-1} . As for firing the clays, some of ancient slips were analyzed by X-ray diffraction to check for the presence of possible magnetite phase correlated with the 680 cm^{-1} band, but magnetite was never detected.^[7,20] Thus it seems highly questionable that this band is due to magnetite. Complementary investigation by electron energy loss spectroscopy using a transmission electron microscopy revealed that the hematite crystals contained in the Gallic slips are Al- and Ti-substituted.^[14] Al substitution involves an upshift and a broadening of hematite bands.^[17,21] However, Al substitution does not involve a strong band at 680 cm^{-1} . Only a weak band was observed for the compositions close to the end of $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$ solid solution.^[21] On the other hand, the 680 cm^{-1} band is the most intense band of ilmenite (FeTiO_3),^[22,23] whose structure is similar to that of hematite, in which half of the Fe atoms are replaced by Ti ones. It is also the main band of other iron titanium oxides such as ulvöspinel (Fe_2TiO_4) or pseudobrookite (Fe_2TiO_5). In fact, when Ti–O bonds are present, they are the most prominent features in the Raman spectrum, thanks to their higher polarizability.^[23] Even a small amount of Ti in the hematite structure could explain

the strong activation of this mode. We thus assume that hematite double substitution could be at the origin of the global upshift and the presence of the 680 cm^{-1} band.

This present study of clay has demonstrated the notable effect of the firing temperature on the Raman spectrum and in particular on the intensity of the additional band at 680 cm^{-1} . Spectra were recorded on 88 antique slips (40 and 48 from La Graufesenque and Italian workshops, respectively) and the maximum intensity of each peak was measured. Figure 4 shows the graph of the ratio (680/415) versus the ratio (680/620). The dots are well separated into two groups according to their origin. A principal components analysis was also performed taking into account the maximum intensity, the associated wavenumber and the FWHM of every peak. The results led to the same conclusions: the dots associated with the Italian and the south Gallic productions are well separated (Fig. S1, Supporting Information). The south Gallic slips are located near various clays fired above 1050°C , while the Italian slips are close to the clays fired at around 950°C , in agreement with their respective firing temperatures estimated from the mineral composition of their body.^[6,7] Separation of the two productions using Raman spectroscopy is clearly due to the firing temperature difference rather than the chemical composition variation.

Conclusion

In this work, we have confirmed that the Raman spectra of Italian and south Gallic production are very similar, although their chemical and mineral compositions present some differences. The characteristic Raman spectrum of these *sigillata* slips is attributed to a substituted hematite, causing a global upshift of the bands. The attribution of the additional highly intense band around 680 cm^{-1} is not clear yet. The study of clays fired under oxidizing conditions shows that this band can be associated with the recrystallization of hematite, which occurs above $750\text{--}850^\circ\text{C}$ depending on the nature of clay. We propose that substitution of hematite with Ti atoms is responsible for the appearance of this intense band.

Although the spectra are very similar, an in-depth analysis shows that Raman spectroscopy can be an efficient probe for slip discrimination between Italian and south Gallic productions. Since the selected parameters depend on the firing temperature, this approach applied to a greater number of samples from other Italian and Gallic workshops would allow us to verify whether these differences in the manufacturing processes between Arezzo and La Graufesenque are systematic and whether they can be extrapolated to changes in the manufacture of *sigillata* around the beginning of the 1st century A.D.

Similar approaches can be also considered in other complex, multicomponent materials in which the Raman signature of a given phase could be used as an internal probe for local structural and chemical modifications. For example, the Raman signal of hematite in Iznik red glass could be used to obtain some information on the raw materials and the manufacturing processes.

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Supporting information

Supporting information may be found in the online version of this article.

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