Raman Study on Pompeii Potteries: The Role of Calcium Hydroxide on the Surface Treatment

ARTICLE *in* JOURNAL OF SPECTROSCOPY · DECEMBER 2014

Impact Factor: 0.54 · DOI: 10.1155/2014/435026

Daniele Chiriu
Università degli studi di Cagliari

P.C. Ricci
Università degli studi di Cagliari

Andrea Polcaro
Università degli Studi di Perugia

Davide Nadali
Sapienza University of Rome

Hindawi Publishing Corporation
Journal of Spectroscopy
Volume 2014, Article ID 435026, 10 pages
http://dx.doi.org/10.1155/2014/435026

Research Article

Raman Study on Pompeii Potteries: The Role of Calcium Hydroxide on the Surface Treatment

Daniele Chiriu,[1] Pier Carlo Ricci,[1] Andrea Polcaro,[2] Paolo Braconi,[2] David Lanzi,[2] and Davide Nadali[3]

[1] *Dipartimento di Fisica, Università di Cagliari, s.p. n 8 Km 0.700, Monserrato, 09042 Cagliari, Italy*
[2] *Dipartimento di Lettere-Lingue, Letterature e Civilta' Antiche E Moderne, Università di Perugia, Via Armonica 3, 06123 Perugia, Italy*
[3] *Dipartimento di Scienze dell'Antichità, Sapienza Università di Roma, Via dei Volsci 122, 00185 Roma, Italy*

Correspondence should be addressed to Pier Carlo Ricci; carlo.ricci@dsf.unica.it

Received 28 October 2014; Accepted 17 December 2014; Published 31 December 2014

Academic Editor: Petre Makreski

Pottery samples from the Pompeii archaeological site were investigated by IR Raman spectroscopy and EDAX measurements. The analysis of the Raman spectra of the surfaces reveals the presence calcium hydroxide (peak at about 780 cm^{-1}) while the calcium carbonate is totally absent. The comparative studies on the carbonation effect of the surfaces were performed on laboratory grown samples of calcium hydroxide. The samples were treated at high temperature and exposed to different ambient conditions, and the analysis suggests that the original surfaces of Roman pottery were scattered by calcium hydroxide (limewash) before the cooking process in the furnace. The result of this surface treatment not only permits a vitrification of the surfaces but also seems to reduce the content of CO_2 in the furnace atmosphere and then obtain a more oxidant ambient during the cooking of the pottery. These results give new insights on the real degree of knowledge of the Romans about the art of ceramics and more generally about chemistry and technologies.

1. Introduction

Nowadays the use of technological experimental techniques in the field of cultural heritage is widely accepted and diffused. The amount of information that a joint approach between physics, chemistry, and archeology is sensibly increased and the efforts in this direction are always growing. The problem that is emerging with the diffusion of technologies is the needed of "pure" sample, intending the study of samples that were not altered after their recovery. This trivial consideration increases its importance when we are dealing with samples that were found decades or centuries ago when the treatment for restoration was not so accurate and they were not deeply studied with particular regard to their influence on the same samples with time. In this sense one example is the use of Paraloid. Paraloid is an acrylic resin which used a stabilizing of the samples that intensify the colors and the brilliance of the surfaces and at the same time decreases the effect of environmental at the surface. However the use of Paraloid in some sense decreases the possibilities to perform further analysis on the treated samples. In this sense the use of untreated samples is mandatory to gather new information in cultural heritage in particular in well-known archaeological excavations [1, 2].

This paper displays the results of studies on different samples, founded during the excavations guided by Perugia's University among 2004 and 2008 for the "Regio VI" project (Figure 1) in the framework of the project "time through colors" funded by the Italian Ministry of University and Scientific Research within the national grant "Futuro in Ricerca" 2012. Studies on production's scraps come to know some technical details related to the so-called "Production's Archaeology." These technical details specifically concern the heat treatment's temperature of ceramic wares, the composition of clay, the type of coating, and the type of ambient generated during the heat treatment (oxidative

Figure 1: Comprehensive view of the archaeological site of Pompeii (Region VI).

Figure 2: Furnace situated below the triclinium of domus VII, 15, 9-10.

or reductive). Part of the samples consists of production's scraps of two manufacturing centres, now located below the foundations of domus VI, 5, 9–19 and domus VII, 15, 9-10. The other part consists instead of plasters, founded in different stratigraphical units of domus VII, 15, 1-2, also known as "Casa del Marinaio."

During the 2004 excavations a furnace was found among the foundations of domus VI, 5, 9–19 (furnace VI). This furnace was built with a twin praefurnium and a quadrangular combustion room. This manufacturing centre dates back to a period between the end of the IIIrd century b.C. and the half of the IInd century b.C., as evidenced by production's scraps. The production consists mainly of dolia, large containers, some kinds of "olla" in common ware, and pans in internal red slip ware.

The furnace situated below the triclinium of domus VII, 15, 9-10 (furnace VII) produced instead amphora, cooking ware, common ware, and internal red slip ware (cumanae testae). All the samples can be dated at the beginning of the IInd century b.C. (Figure 2).

Studies on plasters take moves to verify the chemical and physical transformations caused by the thermal shock due to Vesuviu's eruption of 79 A.D. Plasters were founded in 2007 on a trench inside the second atrium (amb. I) of the so-called "Casa del Marinaio."

In this paper we report the Raman spectra, the vibrational analysis, and the EDAX measurements on the above mentioned archeological samples and for comparison with samples grown and treated specifically in laboratory.

Being applied in archaeology only in the recent years, Raman spectroscopy is becoming increasingly important as an analytical tool in conservation science [17, 18]. Its relevance is given by the intrinsic properties of the technique; actually Raman spectra are obtained by excitation with low energy radiation; by contrast with common "archaeology" experimental techniques such as Mossbauer spectroscopy and Electronic Spin Resonance, Raman spectroscopy is completely not destructive and does not need any pretreatment of the samples. Moreover, thanks to the advances in the technology devices in the recent years, it is possible to collect excellent experimental data in situ, by means of optical fiber coupled devices with small and compact dispersive apparatus. The possibilities to utilize an excitation wavelength at 1064 nm and collect an efficient Raman signal are of particular relevance in untreated samples, where the luminescence signal often overlaps and masks the weak Raman signals.

A deep scientific study by means of nondestructive and technologically advanced techniques on untreated pottery samples from the archeological excavation of Pompeii can give new light on the pottery manufacturing methods of Romans and, more in general about the art of ceramics in Roman's age.

2. Materials and Methods

Raman scattering measurements were carried out in back scattering geometry with the 1064 nm line of an Nd:YAG laser. Measurements were performed in air at room temperature with a compact spectrometer BWTEK i-Raman Ex integrated system with a spectral resolution of about 9 cm^{-1}. Chemical analysis was carried out by using EDAX microanalysis system of a Dual Beam FEI Nova.

Different samples originating to mention two furnaces (furnace VI and Furnace VII) in Pompeii were analyzed. For sake of clarity and brevity we choose as representative of the different samples the fragments denoted by VII59B11 and VI59B7Z for the furnaces VII and VI, respectively (Figures 3(a) and 3(b)). However, if it is not explicitly indicated, no differences in the measurements performed were observed with respect to other samples with the same provenience or inside the same sample itself. Moreover the sample 659A14730 (Figure 3(c)), a clear waste of production, was used as comparative sample.

Raman analysis interested also two different plaster's samples:

(i) the first sample (sample HT) was a IVth style painting exposed to the heat of the eruption. This sample was originally situated on the US 1, at 35,003 meters a.s.l.;

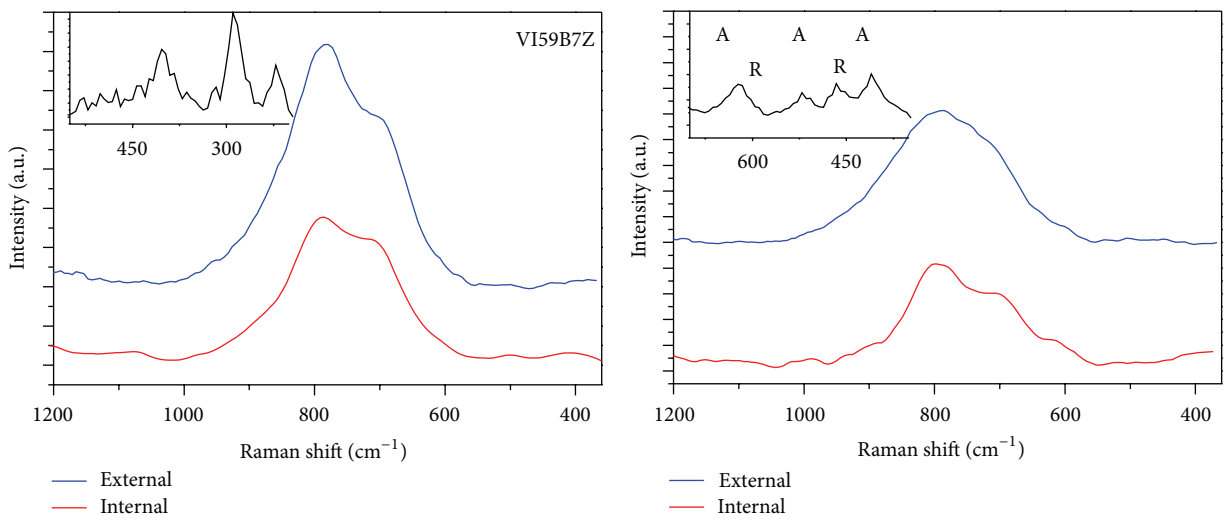
(ii) the second sample (sample LT) was instead a Ist style painting, dated to the IIIrd century b.C. and not exposed to the heat of the eruption. This sample was in fact situated on the US 22, at 33,803–33,863 meters a.s.l, and was covered by 1,4 meters of ground during the eruption.

3. Experimental Results

The internal and external faces of the VI 59B7Z sample were analyzed by Raman spectroscopy, EDAX measurements,

(a) (b) (c)

Figure 3: Images of the samples VII59B11 (a), VI59B7Z (b), and 659A14730 (c).



(a) (b)

Figure 4: Raman spectra of the external and internal surface of samples VI59B7Z (a) and VII59B11. The inset in the (a) section is an enlarged view of the external surfaces of sample VI59B7Z. The inset in the (b) section reports the Raman spectrum form the cross section of sample VII59B11. The peaks are identified as TiO_2 in the anatase (indicated with A) and rutile phase (R).

and SEM images; the Raman Figure 4(a) reports the Raman spectra: a large band between 600 and 900 cm^{-1} centered at about 780 cm^{-1} is present in both the spectra, and no other peaks are easily distinguishable in the spectrum relative to internal surface. On the contrary, the Raman spectrum of the red external surface of the sample VI 59B7Z present also peaks at 226, 292, and 411 cm^{-1} assignable to the hematite phase of the iron oxide (inset, Figure 4(a)) [19]. Actually, the use of iron oxides in different polymorph as red pigments is widely stated [18, 20, 21]. The Romans achieved different colours from deep red to purple through the grinding of hematite crystals. The particle size affects the colour where very fine particles on a nanometer scale gave purple.

According to [22, 23] the large peaks at 780 cm^{-1} can be assigned to the presence of *calcium oxide and calcium hydroxide*. As a confirmation the EDAX analysis (Figure 5) was taken along the different surfaces: the peaks of calcium and Iron are well evident; several elements have also been detected in the samples probably arising from natural minerals present in the proximity of the excavation site such as quartz (SiO_2), feldspars, leucite ($KAlSi_2O_6$), and kaolinite ($Al_2Si_2O_5(OH)_4$) [24, 25].

To better observe differences between the clay and the surface of the pottery, the samples were analyzed also in the cracks of the surfaces and in cross section: the Raman spectrum does not reveal any presence of calcium hydroxide and the EDAX analysis reveals a small and reduced presence of calcium, while the relative presence of different elements remains almost unaltered (Table 1).

In the sample VII59B11 (furnace VII), the Raman spectra taken along the cross section randomly present peaks at 395, 450, 517, and 635 cm^{-1} (see inset in Figure 4(b)). Three of them are easily assignable to the presence of TiO_2 in the anatase phase, while the peak at 450 cm^{-1} and the enlargement of the band at 635 cm^{-1} suggest the presence of TiO_2 in the rutile phase [26, 27]. It is worth noting that these elements are present only as trace with respect to jumble and the relative high intensity of the Raman signal is due to the high efficiency of these materials and phases [26, 27]. In most of the other samples these peaks were not observed suggesting the random presence of titanium oxide in the starting material. Again, the Raman signal arising from the surfaces is dominated by the large by assigned to the presence of calcium oxide/hydroxide (Figure 4(b)).

Table 1

(a)

Element	Wt%	At%	K-ratio	Z	A	F
C K	15,99	28,76	0,0481	1,0720	0,2805	1,0005
O K	38,12	51,46	0,0780	1,0531	0,1943	1,0003
Mg K	1,23	1,09	0,0053	1,0085	0,4310	1,0012
Al K	1,60	1,28	0,0088	0,9784	0,5614	1,0019
Si K	3,04	2,34	0,0208	1,0079	0,6754	1,0019
K K	0,37	0,20	0,0032	0,9572	0,8983	1,0257
Ca K	18,09	9,75	0,1643	0,9789	0,9245	1,0034
Fe K	10,15	3,92	0,0886	0,8913	0,9776	1,0024
Pb L	11,41	1,19	0,0719	0,9181	1,0189	1,0000
Total	100,00	100,00				

(b)

Element	Wt%	At%	K-ratio	Z	A	F
C K	15,26	25,15	0,0331	1,0540	0,2058	1,0004
O K	41,31	51,10	0,1138	1,0355	0,2661	1,0003
Mg K	1,50	1,22	0,0082	0,9920	0,5523	1,0044
Al K	6,83	5,01	0,0448	0,9625	0,6778	1,0055
Si K	14,60	10,29	0,1061	0,9900	0,7328	1,0011
K K	2,09	1,06	0,0183	0,9395	0,9214	1,0117
Ca K	7,05	3,48	0,0638	0,9608	0,9391	1,0027
Fe K	6,19	2,19	0,0537	0,8717	0,9939	1,0017
Pb L	5,16	0,49	0,0315	0,5993	1,0185	1,0000
Total	100,00	100,00				

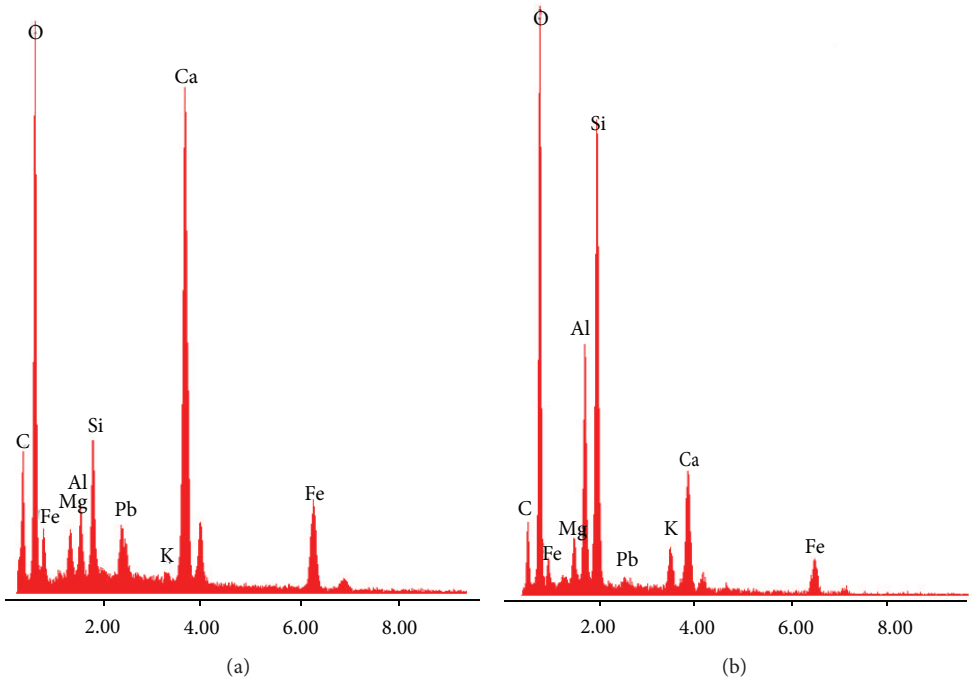


Figure 5: EDAX spectra from VI59B7Z sample taken on the surface (a) and cross section (b).

4. Discussion

The presence of the calcium oxide and hydroxide on the internal and external surfaces of the samples as well as the contemporary absence in the analysis of the cross sections and in the cracks strongly suggests that the calcium hydroxide was not accidental on the surface but on the contrary it was spread intentionally over both the surfaces of the potteries.

On the other hand the use of limewash as binder of different pigments is widely proved and accepted in antiquities and, in particular, in ancient Roman walls [21, 28, 29]. According to Vitruvius, intonaco is a set of finishing layers composed of lime and very fine-grained sand. In this technique the calcareous rock (mainly constituted by calcium carbonate ($CaCO_3$)) is first selected in base to their purity (small impurity can vary the final color of the powder) then was heated in oven at high temperature (more than 1000°C). In these conditions the calcium carbonate degrades in calcium oxide and carbon dioxide [21]:

$$CaCO_{3(S)} + \text{heat} \longrightarrow CaO_{(S)} + CO_{2(G)}. \quad (1)$$

Then, the calcium oxide was mixed with water forming calcium hydroxide:

$$CaO_{3(S)} + H_2O \longrightarrow Ca\,(OH)_2\,. \quad (2)$$

Finally, this compound (calcium oxide/hydroxide) was mixed again with calcium carbonate to obtain the so-called intonaco that was applied to the wall in order to obtain a smooth, polished surface that resembles marble. To this compound often mineral pigments were added to form different color on the wall. Different works based on Raman spectroscopy reveal the ill resolved double at 710–790 cm^{-1} due to the calcium oxide/hydroxide plus a narrow band at 1085 cm^{-1} from the calcium carbonate.

Some general and additional information can be deduced from the study of the Raman spectra of the intonaco; actually, the presence of the band from calcium carbonate is a clear indication that the samples were treated at high temperature; actually as previously stated at high temperature (above 550°C), calcium carbonate passes in calcium oxide (plus gaseous CO_2) that, being highly hygroscopic, forms naturally the calcium oxide/hydroxide (CaO(OH)). In general when the samples were treated at relative low temperature both the Raman signals from calcium carbonate and calcium oxide/hydroxide are present as in the case of Roman mural paints, being the mural paint not thermal treated. On the contrary in our samples, the absence of the band of carbonate, as reported in Figures 4(a) and 4(b), can be used as an indication of a thermal treatment of the pottery samples at high temperature.

An interesting proof of the above mentioned heat effect is evident in the Raman spectra of the mural samples (*casa del marinaio*). Both of them refer to mural paintings from Pompeii but only the first of them (sample HT) was in contact with the high temperature generated by Vesuvius's eruption and the Raman signal from this sample does not present the peak at 1085 cm^{-1} while the second sample (sample LT) pertains to a wall that was about three meters under the ground level at the time of the eruption, so the temperature was much lower and the calcium carbonate over the mural painting was preserved (Figure 6).

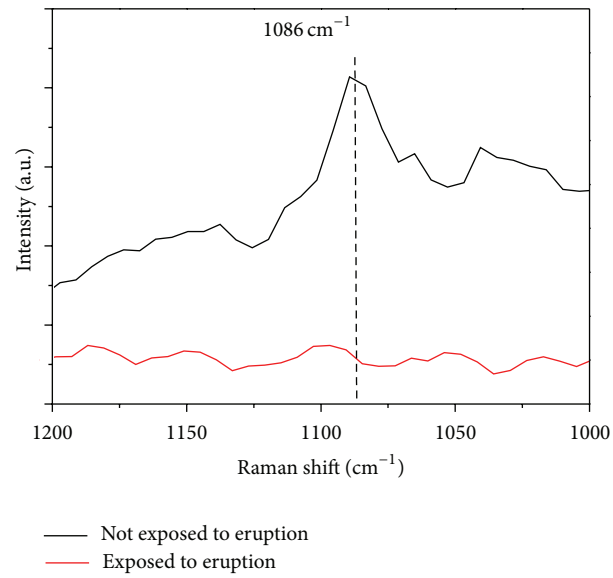


Figure 6: Raman spectra taken on mural samples from casa del marinaio (Pompeii), exposed and not exposed to Vesuvius's eruption. The band position relative to the strongest Raman band from the calcium carbonate is evidenced.

On the contrary in the pottery samples from Pompeii (see the spectra from the VII59B11, VI 59B7Z samples as representative in Figure 4) the band at 1085 cm^{-1} is always absent in all the measurements performed, suggesting that the limewash was spread over the pottery before the heat treatment in the furnace. As further indication of this hypothesis we report the Raman spectrum of the sample 659_A14730, a clear waste of production (Figure 7). Again the band at 780 cm^{-1} is evident, while the band of calcium carbonate is absent. The spectrum of the jumble registered in cross section does not reveal any peak of this phase, suggesting again that the limewash (calcium oxide/hydroxide) was spread over the surface before the heating treatment.

It can be interesting to try to answer the question, which is the function of the calcium oxide/hydroxide and why it was spread over the surface of the pottery before the heat treatment?

One hypothesis can be related to the same reason of the mural painting, that is, to smooth the surfaces and to use the intonaco as a binder of the inorganic pigment (that need a thermal treatment).

A second hypothesis can be associated to an improvement to the normal cooking process of the pottery. Actually, the addition of calcium oxide/hydroxide creates a layer over the surfaces that, during the heat treatment, remains highly oxygenated. The oxygen preserves the surfaces from carbonaceous waste that blacken the final good, moreover the oxygen permits to obtain a relative higher temperature at the surfaces favoring the vitrification process of the aluminosilicates,

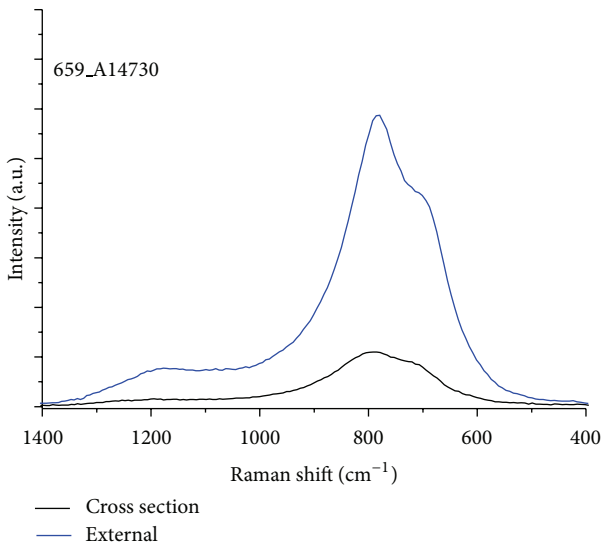


Figure 7: Raman spectrum of the sample 659A14730, a clear waste of production of the furnace VII, taken along the internal and external surfaces.

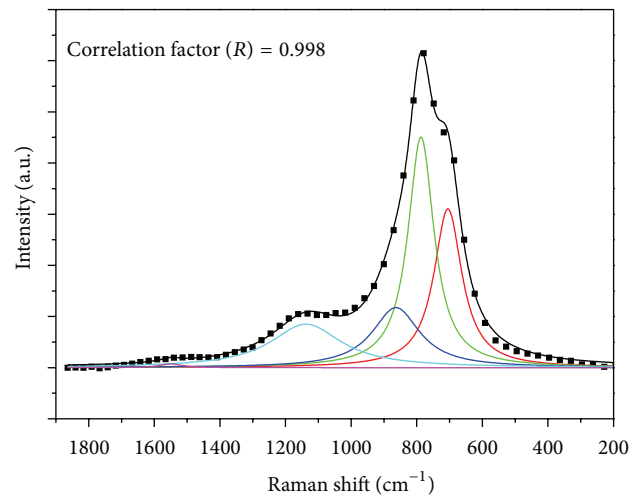


Figure 8: Raman spectrum of sample 659_A14730: deconvolutions with lorentzian profiles.

the hardening of the clay and decreasing the porosity of the surfaces [30, 31].

The high oxygenated ambient of these samples is indirectly suggested from the presence of TiO_2 in the anatase forms. Actually at temperature higher than 600°C the anatase phase naturally transforms to the more stable rutile phase; however highly oxygenated environmental conditions increase the temperature threshold for the phase transformation up to 1000°C [26].

As experimental proof of the thesis just illustrated, with the help of deconvolutions with lorentzian profiles, it is possible to analyze the Raman spectra in order to identify a degree of carbonation of the samples and then deep inside to the absorption process of CO_2 during the heat treatment of the pottery and justify the use of calcium hydroxide as getter of the carbon dioxide produced during the heat treatment. As indicated in [32, 33] the method of the carbonic dioxide sequestration (CDS) is well kwon and used especially in the case of the mineral carbonation of calcined calcium hydroxide (limewash) as indicated in the reaction:

$$\mathrm{Ca\,(OH)_{2(S)} + CO_2 \longrightarrow CaCO_{3(S)} + H_2O.} \quad (3)$$

In the case of heat treated pottery, the mentioned reaction takes place during the cooling process when the formation of calcium carbonate is allowed. Calcium carbonate can assume different crystalline phases as indicated by [11, 34]. The principal structures are indicated in Table 2 with Raman band and assignations.

Moreover, if the time of cooling is too fast it is possible to find a mixture of mentioned phases with an high probability to obtain the compound in amorphous conditions [12, 33, 35].

The deconvolution illustrates the effective position of the experimental Raman bands in the spectra collected on the ancient potteries (Figure 8 reports, as example, the deconvolution from the sample 659_A14730, waste of production). Raman bands are centered at 705 cm^{-1}, 787 cm^{-1}, 863 cm^{-1}, 1137 cm^{-1}, and 1549 cm^{-1}. An assignation of the peaks at 705 cm^{-1} 863 cm^{-1} and 1137 cm^{-1} is possible with the indications of Table 2, while the band at 787 cm^{-1} and 1550 cm^{-1} can be assigned to calcium oxide/hydroxide and vibration of hydroxyl molecule (O-H out of plane bending mode), respectively [15, 16].

The band at 705 cm^{-1}, in particular, could be assigned to Aragonite phase of calcium carbonate. The band at 863 cm^{-1} can be assigned to the ν_2 mode of $(CO_3)^{2-}$, which is Raman forbidden in the free ion, but remains weak after coupling to the cations in the lattice [8, 34]. The broad band at 1137 cm^{-1} can be assigned to the ν_1 mode due to the symmetric stretching vibration of the carbonate groups [15, 16].

The presence in the spectrum of the bands assigned to Aragonite and carbonate groups weakly bonded to the cations is significant for the happened sequestration of CO_2 by the samples during the heat treatment.

To better understand this phenomenon it is possible to explain each singular step of the process of carbonation in clays by using experimental archeological methods and reproducing the behavior of the sample.

Figure 9(a) shows the Raman spectrum of amorphous calcium hydroxide $Ca(OH)_2$ obtained heating calcite powders at the temperature of 1000°C for 1 h, with a ramp of temperature of 2°C/min, and after it reached the ambient temperature, mixed with water. No other peaks assignable to other stable or metastable crystallographic phases were found.

The bands at 796 cm^{-1}, 913 cm^{-1}, 1187 cm^{-1}, and 1650 cm^{-1} are associated to calcium hydroxide and water as indicated by [23, 34]. In particular the band at 913 cm^{-1} could be assigned to O-H out of plane bending mode according to Buzgar and Apopei [34].

After 24 h of exposition to the content of CO_2 present in the air at ambient temperature, the carbonation process

Table 2: (a) Fundamental vibrational modes of the carbonates according to [3, 4]. (b) Raman bands in some carbonates and hydroxyl-carbonates.

(a)

Mode	Symmetry	Selection rules	Frequencies (cm^{-1})
ν_1 Nondegenerate symmetric stretch	A′1	Raman	1064
ν_2 Nondegenerate asymmetric (out of plane) bend	A″2	IR	Near 800
ν_3 Doubly degenerate asymmetric stretch	E′	IR + Raman	1415
ν_4 Doubly degenerate symmetric (in-plane) bend	E′	IR + Raman	680

(b)

Calcite [5, 6]	Siderite [7, 8]	Aragonite [9–11]	Strontianite [10, 12]	Vaterite [13]	Azurite [7, 14]	Free CO_3^{2-} [15, 16]	Assignment [15, 16]
89					112		R (CO_3)
162	190			212	165 194		T (Ca, CO_3)
288	294	284	246	287	281		T (Ca, CO_3)
	506				540		T (Ca, Fe, CO_3)
716	731 742	701 705	701 711	750	739 764	680	ν_4-Symmetric CO_3 bending mode
		853	855		815 835	879	ν_2-Asymmetric CO_3 bending mode
					937 952		O–H out-of-plane bending mode
1092	1087	1085	1074	1090	1095	1063	ν_1-Symmetric CO_3 stretching mode
1437		1465 1547	1408 1447	1441	1421 1431 1462	1415	ν_3-Asymmetric CO_3 stretching mode
					1582		O–H bending mode
1754	1726 1733						$\nu_1 + \nu_4$

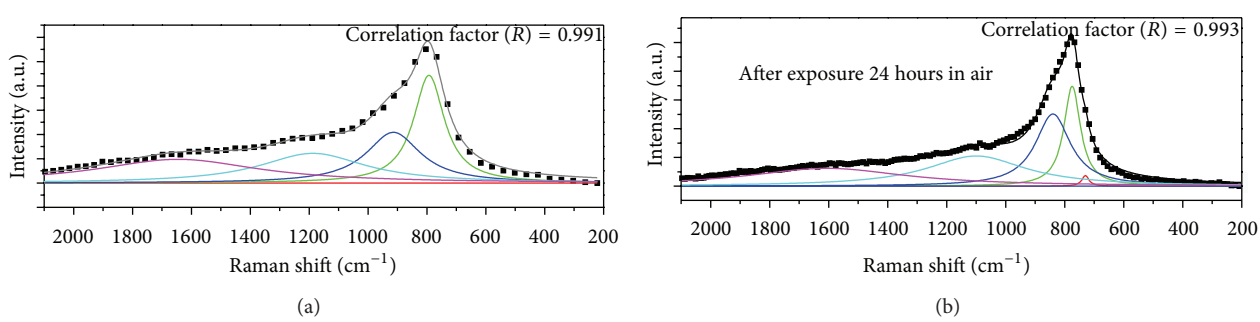


Figure 9: Raman spectrum of calcium hydroxide obtained heating at 1000°C $CaCO_3$ powders.

takes place and, in the spectrum shown in Figure 9(b), it is possible to observe the presence of different bands associated to the carbon dioxide sequestration. The band at 913 cm^{-1} disappears (the band was present in the spectrum taken at the beginning of the process, Figure 9(a)), while it is possible to observe the presence of the band at 863 cm^{-1} which could be associated to the mode ν_2 of the carbonate ions weakly bonded to the cations. In addition a new band at 740 cm^{-1} can be observed and assigned to the ν_3 symmetric CO_3^{2-} bending mode in Vaterite, suggesting favorable conditions for this metastable form (μ-$CaCO_3$) [13].

By wetting the same calcium hydroxide powders used in the previous experiment the "limewash" was realized with the purpose to reproduce the ancient technique probably used in Pompeii. The limewash was mixed with hematite and used to cover the surface of two samples of clay, indicated as A and B, differentiated by the presence of calcite into the mixture (sample A) and no presence of calcite (samples B) into

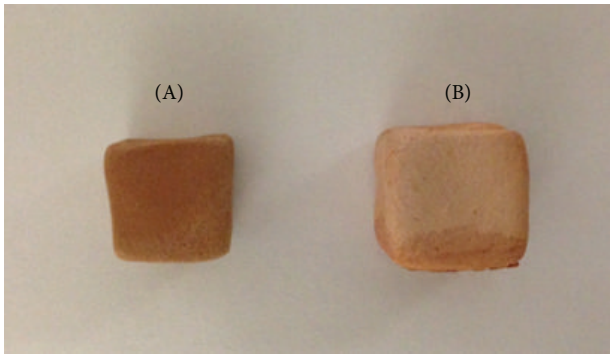


Figure 10: Laboratory samples: sample A: calcite in the mixture of the clay; sample B: absence of calcite in the clay. Both the samples were covered with Fe_2O_3 powder (hematite phase) and treated at 1000°C.

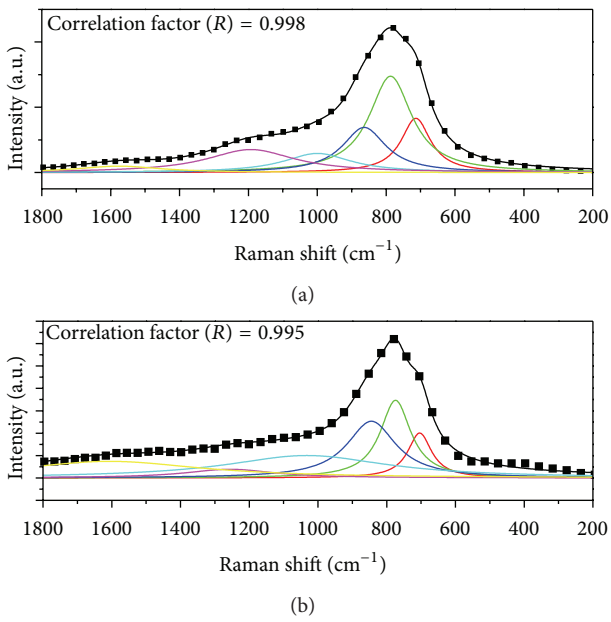


Figure 11: Raman spectrum with deconvolutions of samples (a) and (b).

the mixture (Figure 10). Each sample was treated at 1000°C with the same temperature treatment used in the previous calcite sample. As shown in Figure 10 the samples B present a different color in the limewash covered surface.

Figure 11 reports the Raman spectra of the samples A and B with the relative deconvolutions with lorentzian profiles. It is possible to observe the presence of the bands assigned to calcium hydroxide, as indicated previously, the presence of the band around 860 cm^{-1} due to CO_3^{2-} weakly bonded to the cations, and the presence of the band at 705 cm^{-1} typical for the ν_4 frequency mode of carbonate in Aragonite phase [9].

Figure 12 reports the Raman spectrum of the sample A collected in a cross section of the sample not exposed to the atmosphere, at high temperature. In this case the

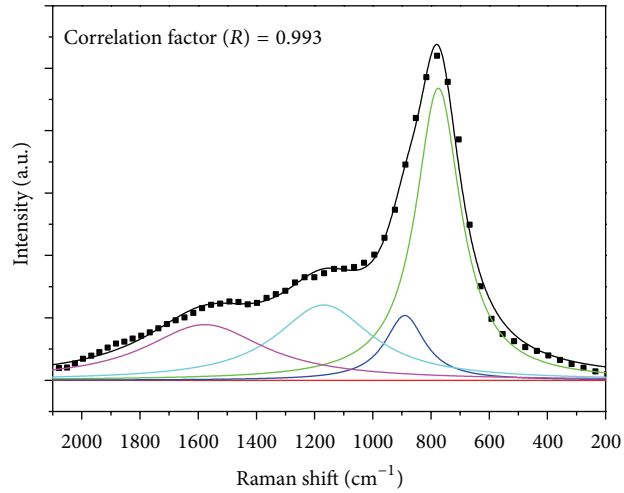


Figure 12: Raman spectrum of the cross section of sample A.

calcite present into the clay mixture has been transformed in calcium oxide/hydroxide due to the high temperature and the residual humidity of the clay. From the analysis of the Raman spectrum it is possible to observe the phenomenon of carbonation as indicated by the absence of the band at 705 cm^{-1} (Aragonite phase) and a slow contribution of the band at 860 cm^{-1} is shown (associated to the presence of carbonate ions weakly bonded to the cations) [9].

These results seems to indicate an high degree of knowledge of the cooking process of the pottery in the Roman age and in particular the use of calcium hydroxide as a tool to reduce the content of CO_2 in the furnace atmosphere and then obtain a more oxidant ambient and reach higher temperature close to the at the pottery surfaces.

5. Conclusions

In this study a characterization of different type of pottery samples and painted fragments of wall belonging to Pompeii has been performed by means of EDS microanalysis and Raman spectroscopy. The principal results obtained concern the use of calcium hydroxide above the surface of analyzed samples before cooking the clay. This technique of surface treatment seems to be not justified only for the use of a vitrification additive or sealant, but through this study it is possible to suggest that calcium hydroxide could be used as "getter" of CO_2 during the heat treatment. The result of this operation is to reduce the content of CO_2 in the furnace atmosphere and then obtain a more oxidant ambient when cooking the pottery. In these conditions, as illustrated in this study, the metallic oxides used as pigments on the surface, or contained in the clay mixture, could be preserved in the higher state of oxidation, providing a better esthetical result (in terms of color).

In any case, these findings give new light on the pottery manufacturing techniques of Romans and in particular open new questions about the real degree of knowledge of the

Romans about the art of ceramics and more general about chemistry and technologies.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This study has been supported by the Italian Ministry of University and Scientific Research (MIUR) within the national grant "Futuro in Ricerca" 2012 TIME THROUGH COLOURS. Analysis of painted artifacts in their archaeological, historical and sociological contexts (RBFR12405A_002).

References

[1] S. P. Koob, "The use of Paraloid B-72 as an adhesive: its application for archaeological ceramics and other materials," *Studies in Conservation*, vol. 31, no. 1, pp. 7–14, 1986.

[2] S. Chapman and D. Mason, "Literature review: the use of Paraloid B-72 as a surface consolidant for stained glass," *Journal of The American Institute for Conservation*, vol. 42, no. 2, pp. 381–392, 2003.

[3] L. Burgio and R. J. H. Clark, "Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 57, no. 7, pp. 1491–1521, 2001.

[4] F. A. Cotton, *Chemical Applications of Group Theory*, Wiley-Interscience, Richardson, Tex, USA, 3rd edition, 1990.

[5] S. Gunasekaran, G. Anbalagan, and S. Pandi, "Raman and infrared spectra of carbonates of calcite structure," *Journal of Raman Spectroscopy*, vol. 37, no. 9, pp. 892–899, 2006.

[6] N. Koura, S. Kohara, K. Takeuchi et al., "Alkali carbonates: Raman spectroscopy, ab initio calculations, and structure," *Journal of Molecular Structure*, vol. 382, no. 3, pp. 163–169, 1996.

[7] E. Mattei, G. de Vivo, A. de Santis, C. Gaetani, C. Pelosi, and U. Santamaria, "Raman spectroscopic analysis of azurite blackening," *Journal of Raman Spectroscopy*, vol. 39, no. 2, pp. 302–306, 2008.

[8] E. B. Scheetz and B. W. White, "Vibrational spectra of the alkaline earth double carbonates," *American Mineralogist*, vol. 62, pp. 36–50, 1977.

[9] J. E. Parker, S. P. Thompson, A. R. Lennie, J. Potter, and C. C. Tang, "A study of the aragonite-calcite transformation using Raman spectroscopy, synchrotron powder diffraction and scanning electron microscopy," *CrystEngComm*, vol. 12, no. 5, pp. 1590–1599, 2010.

[10] D. Krishnamurti, "The Raman spectra of aragonite, strontianite and witherite," *Proceedings of the Indian Academy of Sciences A*, vol. 51, no. 6, pp. 285–295, 1960.

[11] J. Urmos, S. K. Sharma, and F. T. Mackenzie, "Characterization of some biogenic carbonates with Raman spectroscopy," *American Mineralogist*, vol. 76, no. 3-4, pp. 641–646, 1991.

[12] M. Charles, R. Jeanloz, and R. J. Hemley, "Spectroscopic and x-ray diffraction studies of metastable crystalline-amorphous transitions in $Ca(OH)_2$ and serpentine," *Geophysical Monograph Series*, vol. 67, pp. 485–492, 1992.

[13] R. W. Gauldie, S. K. Sharma, and E. Volk, "Micro-Raman spectral study of vaterite and aragonite otoliths of the coho salmon, *Oncorhynchus kisutch*," *Comparative Biochemistry and Physiology A*, vol. 118, no. 3, pp. 753–757, 1997.

[14] R. L. Frost, W. N. Martens, L. Rintoul, E. Mahmutagic, and J. T. Kloprogge, "Raman spectroscopic study of azurite and malachite at 298 and 77 K," *Journal of Raman Spectroscopy*, vol. 33, no. 4, pp. 252–259, 2002.

[15] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry*, John Wiley & Sons, New York, NY, USA, 1997.

[16] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry*, John Wiley & Sons, Hoboken, NJ, USA, 6th edition, 2009.

[17] G. D. Smith and R. J. H. Clark, "Raman microscopy in archaeological science," *Journal of Archaeological Science*, vol. 31, no. 8, pp. 1137–1160, 2004.

[18] D. Bersani and J. M. Madariaga, "Applications of Raman spectroscopy in art and archaeology," *Journal of Raman Spectroscopy*, vol. 43, no. 11, pp. 1523–1528, 2012.

[19] L. Stagi, J. A. De Toro, A. Ardu et al., "Surface effects under visible irradiation and heat treatment on the phase stability of γ-Fe_2O_3 nanoparticles and γ-Fe_2O_3 -SiO_2 core-shell nanostructures," *The Journal of Physical Chemistry C*, vol. 118, no. 5, pp. 2857–2866, 2014.

[20] D. Hradil, T. Grygar, J. Hradilová, and P. Bezdička, "Clay and iron oxide pigments in the history of painting," *Applied Clay Science*, vol. 22, no. 5, pp. 223–236, 2003.

[21] I. Aliatis, D. Bersani, E. Campani et al., "Pigments used in Roman wall paintings in the Vesuvian area," *Journal of Raman Spectroscopy*, vol. 41, no. 11, pp. 1537–1542, 2010.

[22] H. G. M. Edwards, D. W. Farwell, D. L. A. de Faria et al., "Raman spectroscopic study of 3000−year−old human skeletal remains from a sambaqui, Santa Catarina, Brazil," *Journal of Raman Spectroscopy*, vol. 32, no. 1, pp. 17–22, 2001.

[23] T. Y. Kwon, T. Fujishima, and Y. Imai, "FT-Raman spectroscopy of calcium hydroxide medicament in root canals," *International Endodontic Journal*, vol. 37, no. 7, pp. 489–493, 2004.

[24] R. L. Frost, "Fourier transform Raman spectroscopy of kaolinite, dickite and halloysite," *Clays & Clay Minerals*, vol. 43, no. 2, pp. 191–195, 1995.

[25] I. C. Freestone, "Applications and potential of electron probe micro analysis in technological and provenance investigations of ancient ceramics," *Archaeometry*, vol. 24, no. 2, pp. 99–116, 1982.

[26] P. C. Ricci, C. M. Carbonaro, L. Stagi et al., "Anatase-to-rutile phase transition in TiO_2 nanoparticles irradiated by visible light," *Journal of Physical Chemistry C*, vol. 117, no. 15, pp. 7850–7857, 2013.

[27] P. C. Ricci, A. Casu, M. Salis, R. Corpino, and A. Anedda, "Optically controlled phase variation of TiO_2 nanoparticles," *Journal of Physical Chemistry C*, vol. 114, no. 34, pp. 14441–14445, 2010.

[28] S. Sánchez-Moral, L. Luque, J.-C. Cañaveras, V. Soler, J. Garcia-Guinea, and A. Aparicio, "Lime-pozzolana mortars in Roman catacombs: composition, structures and restoration," *Cement and Concrete Research*, vol. 35, no. 8, pp. 1555–1565, 2005.

[29] H. G. M. Edwards and D. W. Farwell, "The conservational heritage of wall paintings and buildings: an FT-Raman spectroscopic study of prehistoric, Roman, mediaeval and Renaissance

lime substrates and mortars," *Journal of Raman Spectroscopy*, vol. 39, no. 8, pp. 985–992, 2008.

[30] C. M. Sinopoli, *Approaches to Archaeological Ceramics*, Springer, Boston, Mass, USA, 1991.

[31] R. Newcomb Jr., *Ceramic Whitewares—History, Technology and Applications*, Pitman Publishing, New York, NY, USA, 1947.

[32] W. J. J. Huijgen and R. N. J. Comans, "Carbon dioxide sequestration by mineral carbonation: literature review," ECN Report ECN-C-03-016, ECN, 2003.

[33] W. Gu, D. W. Bousfield, and C. P. Tripp, "Formation of calcium carbonate particles by direct contact of $Ca(OH)_2$ powders with supercritical CO_2," *Journal of Materials Chemistry*, vol. 16, no. 32, pp. 3312–3317, 2006.

[34] N. Buzgar and A. I. Apopei, "The Raman study of certain carbonates," *Geologie*, vol. 15, pp. 97–112, 2009.

[35] S. Ekbundit, K. Leinenweber, J. L. Yarger, J. S. Robinson, M. Verhelst-Voorhees, and G. H. Wolf, "New high-pressure phase and pressure-induced amorphization of $Ca(OH)_2$: grain size effect," *Journal of Solid State Chemistry*, vol. 126, no. 2, pp. 300–307, 1996.