

Raman imaging to quantify the thermal transformation degree of Pompeian yellow ochre caused by the 79 AD Mount Vesuvius eruption

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ABSTRACT: Most of the wall paintings from Pompeii are decorated with red and yellow colors but the thermal impact of 79 AD Mount Vesuvius eruption promoted the partial transformation of some yellow painted areas into red. The aim of this research is to develop a quantitative Raman imaging methodology to relate the transformation percentage of yellow ochre (goethite, α -FeOOH) into red color (hematite, α -Fe₂O₃) depending on the temperature, in order to apply it and estimate the temperature at which the pyroclastic flow impacted the walls of Pompeii. To model the thermal impact that took place in the year 79 AD, nine wall painting fragments recovered in the archaeological site of Pompeii and which include yellow ochre pigment were subjected to thermal ageing experiments (exposition to temperatures from 200°C to 400°C every 25°C). Before the experiments, elemental information of the fragments was obtained by micro energy dispersive X-ray fluorescence (μ -ED-XRF). The fragments were

characterized before and after the exposition using Raman microscopy to monitor the transformation degree from yellow to red. The quantitative Raman imaging methodology was developed and validated using synthetic pellets of goethite and hematite standards. The results showed almost no transformation ($0.5\% \pm 0.4$) at 200°C . However, at 225°C some color transformation ($26.9\% \pm 2.8$) was observed. The most remarkable color change was detected at temperatures between 250°C (transformation of $46.7\% \pm 1.7$) and 275°C (transformation of $101.1\% \pm 1.2$). At this last temperature the transformation is totally completed because from 275°C to 400°C the transformation percentage remained constant.

Keywords: Yellow ochre, dehydration, Raman imaging, color transformation, quantitative analysis

Introduction

In year 79 AD Pompeii suffered one of the most violent natural disasters in history. More than 2000 people died instantly or were buried alive under an ash cloak coming from the eruption of Mount Vesuvius. However, the consequences of the impact of Vesuvius emissions went beyond the human deaths. The thick layer of ash and pumices, as high as 6-9 meters, kept the ancient city hidden and forgotten for almost seventeen centuries. Therefore, thanks to this event, Pompeii has preserved during the burial almost all of the buildings, sculptures, wall paintings and other archaeological records in a good conservation state.

Some of the most impressive remains that are still visible in Pompeii are the wall paintings. Nowadays, the Archaeological Park attracts more than 3 million visitors per year to enjoy the ancient city and its artworks [1]. However, some of the wall paintings of the houses that were excavated more than 100 years ago show different deterioration processes due to the exposure to the open modern atmosphere. In this sense, some works evidenced the deterioration of the Pompeian walls and wall paintings due to the formation of efflorescences [2,3] and darkening processes of red areas [4-6]. Although most of the detected pathologies took place after the recovery of the wall paintings, the acid gases and volcanic material at high temperatures emitted during the eruption of Mount Vesuvius may have an influence on the conservation state of Pompeian wall paintings. An example of this last pathology is the transformation of yellow painted areas of the wall paintings into red [7]. Nowadays, there are around 246 walls perceived as red and 57 as yellow. Nevertheless, the number of walls painted in red color could have been lower before the Mount Vesuvius eruption [8]. It is supposed that the impact of the hot fumaroles and pyroclastic flows was the responsible of this change of color [7], but to date, there are not experimental works that confirmed this thermal transformation hypothesis dealing with real Pompeian wall painting fragments.

The yellow color pigment that suffered this transformation is yellow ochre or goethite, an hydrated iron oxide [α -FeO(OH)] obtained from local iron-rich earths [9]. When goethite is thermally impacted at high enough temperatures, a dehydration reaction takes place. This loss of water leads to the anhydrous compound, α -Fe₂O₃, which is known as hematite. This mineral is the main component of the red ochre

pigments [10]. The dehydration reaction of goethite is the responsible of the color change from yellow to red. The composition of Pompeian pigments palette is well known, since these types of ochres and other pigments have been widely studied in the literature [9-13]. Both types of ochres (yellow and red) were used in Pompeii [9,10,13], thus we need to have a method to discriminate between wall paintings decorated nowadays with original red and red coming from the dehydration of goethite. By the moment, it could not be discriminated both red colored paintings from a molecular point of view. However, a previous work [7] demonstrated that the elemental composition can be used in order to discriminate original red ochres from yellow ochres transformed into red, since the first one presents arsenic while the transformed one does not.

Regarding the thermal impact that suffered Pompeii during the eruption of Mount Vesuvius, a previous work [14] dealing with lava clasts determined that most of the pyroclastic flow reached Pompeii at temperatures between 240-340°C. On the other hand, it is well known at which temperature goethite can be dehydrated. In the literature there are many works dealing with the study of the dehydration of goethite raw pigment into hematite in this range of temperatures [15-19]. All these studies are not focused in the transformation of real goethite pigments from Pompeii and there is not experimental data about the quantitative transformation degree depending on the temperature to explain the dehydration process that took place in the yellow wall paintings from Pompeii. Moreover, the transformation degree of original yellow ochre in Pompeian paintings is different depending on the position and orientation inside the Archaeological Park. The evaluation of the percentage of goethite transformed into

hematite as a function of temperature could help to construct an analytical model to determine at which temperature was impacted each wall. In this sense, the yellow painted walls transformed into red can act as witness of the 79 AD Mount Vesuvius eruption and impact in Pompeii. In this work we propose the development of a quantitative Raman imaging methodology to achieve the mentioned objective.

To develop this methodology, nine wall painting fragments showing intact yellow ochre pictorial layer recovered from the excavations performed in the House of Marcus Lucretius (Regio IX, Insula 3, 5-24) were considered. These fragments were subjected to different thermal ageing treatments in order to simulate the thermal impact occurred in year 79 AD. First of all, elemental and molecular images of all the fragments were acquired using micro energy dispersive X-ray fluorescence (μ -ED-XRF) spectrometry and micro-Raman spectroscopy respectively. After that, different thermal ageings at increasing temperatures (between 200-400°C every 25°C) were conducted, trying to faithfully simulate the real thermal impact that took place at year 79 AD. In this way, the goethite transformation degree depending on the temperature was quantitatively determined using Raman imaging, measuring the original fragments before and after the thermal exposition. The quantification procedure was previously validated using synthetic pellets of goethite and hematite pigments standards mixed at different percentages.

Material and methods

Samples. For the thermal ageing experiments, two detached yellow wall painting pieces recovered from the excavations done by the *Expediitio Pompeiana Universitatis*

Helsingiensis group [20] in the House of Marcus Lucretius (Reg IX, Ins 3, 5-24) from Pompeii were considered. These samples did not show goethite transformation evidences and they had not been exposed to the atmosphere since the recovery moment. The first piece was divided in three fragments (A, B and C) and the second one in six fragments (D, E, F, G, H and I).

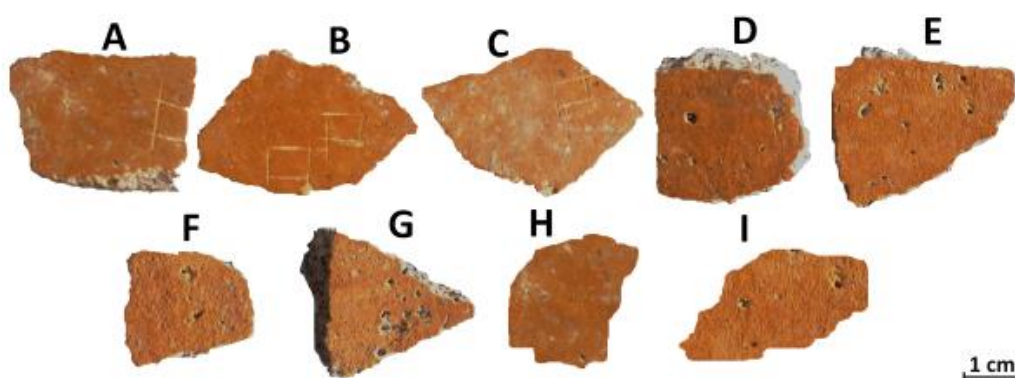


Fig. 1. Wall painting fragments recovered from the House of Marcus Lucretius showing goethite pictorial layer.

Pigments Standards. Goethite (Y-464 series, Nubiola, Spain) and hematite (99.99% metal basis, Alfa Aesar, MA, USA) standards were used to prepare the synthetic mixture used to validate the Raman imaging-based quantitative methodology.

On the other hand, for the fitting of the Raman spectra acquired on the painting fragments, the spectrum of a real Pompeian yellow ochre pigment (ref. number 112257) preserved in the Naples National Archaeological Museum was used.

Analytical Methodology. The elemental analysis was conducted before the thermal ageing using the dual M4 TORNADO (Bruker Nano GmbH, Berlin, Germany) energy

dispersive X-ray fluorescence spectrometer (ED-XRF) which allows to measure at 1 mm and down to 25 μm of lateral resolutions. In this work 25 μm of lateral resolution was selected. This low spatial resolution is achieved by poly-capillary lens. The used Rh X-ray tube operates up to 50 kV and at a maximum current of 600 μA , which were the conditions considered for the maps acquisitions. Hypermaps (distributions of the detected elements) of the nine fragments were acquired. The XRF images were acquired at 5 ms, 5 scans and a step size of 20 μm . To construct the elemental images a previous deconvolution of the signals in the sum spectrum representing the whole mapped area was conducted. After that, the distribution map of each element was represented as a function of the intensity of each detected element K_{α} line, except for Pb, using in this case the L_{β} line (12.6 keV). The spectra acquisition and treatment was performed using the M4 TORNADO software.

The polychromy of each painting fragment was characterized before and after thermal ageing by means of micro-Raman spectroscopy, using an inVia confocal Raman spectrometer (Renishaw, Gloucestershire, UK) coupled to a DMLM Leica microscope using 5, 20 and 50 \times lenses. Excitation laser of 785 nm with a nominal laser power of 350 mW was used. In order to avoid thermal decomposition of the pigment, the laser power was set at not more than 1 mW since it was tested with goethite standard that this power does not affect its decomposition. Data acquisition was carried out using the Wire 4.2 software package (Renishaw). To check the precision and accuracy of the quantitative Raman results on real yellow ochre fragments, three synthetic pellets with different compositions (25/75%, 50/50% and 75/25%; hematite/goethite) were used.

With the quantitative results obtained before and after the thermal exposure, the percentage of goethite transformation was established.

For the thermal ageing, a Hobersal HD series muffle was used. The thermal impact and its duration was the same for all the fragments, trying to simulate faithfully the real impact of the pyroclastic flow into the wall painting: an initial impact kept during 2 hours (Fragment A: 200°C, Fragment B: 225°C, Fragment C: 250°C, Fragment D: 275°C, Fragment E: 300°C, Fragment F: 325°C, Fragment G: 350°C, Fragment H: 375°C, and Fragment I: 400°C). After that, as it is expected that it started cooling down slowly, the fragments were kept in the muffle cooling down with a speed of 1 °C/min.

The grain size and distribution of both goethite and hematite pigments was analyzed by means of a JEOL JSM-7000-F (JEOL, Tokyo, Japan) scanning electron microscope coupled to an energy dispersive elemental spectrometer (SEM-EDS) (Oxford instruments INCA, Energy 350, Oxfordshire, UK). In order to improve the conductivity of the samples for the image acquisition, they were metalized by depositing ≈20 nm of a carbon layer.

Results and discussion

Elemental characterization of the fragments before thermal ageing by means of μ -ED-XRF imaging. μ -ED-XRF spectrometry by means of an imaging strategy was applied to observe mainly the distribution of iron in the surface of the fragments (see Figure 2). This allowed us to identify the best areas for the subsequent Raman imaging analysis, since areas showing the highest signal of Fe were selected in order to monitor properly the transformation. Moreover, those areas showing lines, grooves or marks which favor

the elimination of the pictorial layer were avoided, in order to minimize the inclusion heterogeneities in the areas under study.

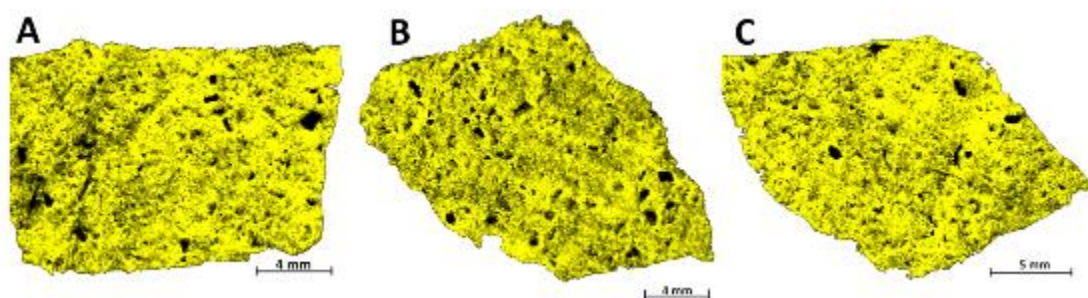


Fig. 2. Iron distribution XRF maps (in yellow) in A, B and C fragments.

As shown in Figure 2, Fe is quite homogeneously distributed along the fragments as it was expected, because the pictorial layer covered completely the surface of the wall painting fragments. However, at the microscopic scale, some areas did not show high Fe signal while some others showed higher intensity. In this way, as the goethite content was higher in those areas, the transformation into hematite could be better monitored. Therefore, those zones were selected and marked as squares (sizes of around 4x4 mm) with a scalpel (see Figure 1A-C).

Apart from Fe, other elements such as Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, As, Sr and Pb were also detected (see Figure 3). Besides, a diffraction peak at 10.1 keV (marked with an asterisk in Figure 3E) appeared because of the use of the poly-capillary lens of the instrument.

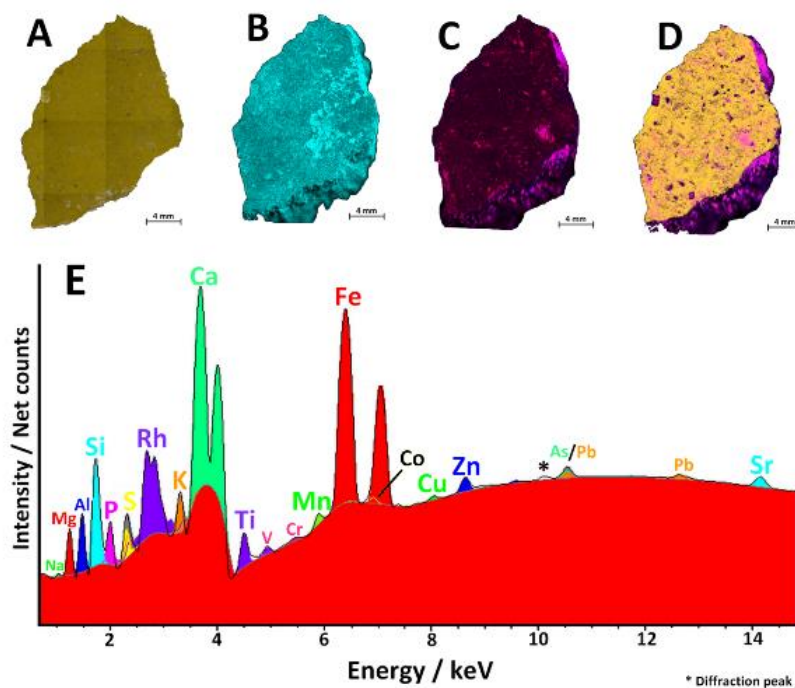


Fig. 3. A) Optical image of Fragment B collected as mosaic under the video-camera of the instrument and elemental distribution maps of B) phosphorus (blue), C) potassium + silicon (blue + red = purple), D) iron (yellow), silicon (red) and aluminum (blue) and E) sum XRF spectrum of the analyzed area. * Diffraction peak.

The obtained XRF map of fragment B (see sum spectrum of the analyzed area in Figure 3E) was representative for all the considered samples, since the same elements were detected in the nine mapped fragments. Thanks to these elemental analyses, some heterogeneities in the fragments under study were observed. In this sense, as shown in Figure 3B the elemental distribution of P showed some hotspots in which this element was distributed in a higher extend. The presence of P could be related with phosphate deposition coming from the soil of the burial in contact with the fragments for thousands of years. In this way, some areas could be enriched in certain elements such as P, Na or K. Moreover, as shown in Figure 3C-D, in the fragment specific areas rich in Al, Si and K were also observed. This could be due to the presence of some potassium alumino-silicates like feldspars (e.g. KAlSi_3O_8) coming from the burial, which

might be stuck to the fragment. Besides, some Si-rich hotspots (Figure 3D) matched with the presence of quartz in the surface of the analyzed fragment. These detected areas with contributions of the soils and volcanic materials from the burial were avoided for the Raman imaging monitoring, in order to prevent from contaminations of the yellow ochre pictorial layer.

Molecular characterization of the fragments before thermal ageing by means of Raman Imaging. To obtain goethite (α -FeOOH) distribution maps before the thermal ageing, Raman image acquisitions were performed in different areas of the fragment, selected according μ -ED-XRF results. The maps were acquired in the 100-1300 cm^{-1} spectral region, in which the bands of goethite appear. To obtain the molecular distribution images, the spectral dataset was represented according to the signal-to-baseline of the main band of goethite centered at 397 cm^{-1} , and the main band of calcite at 1086 cm^{-1} (see Figure 4).

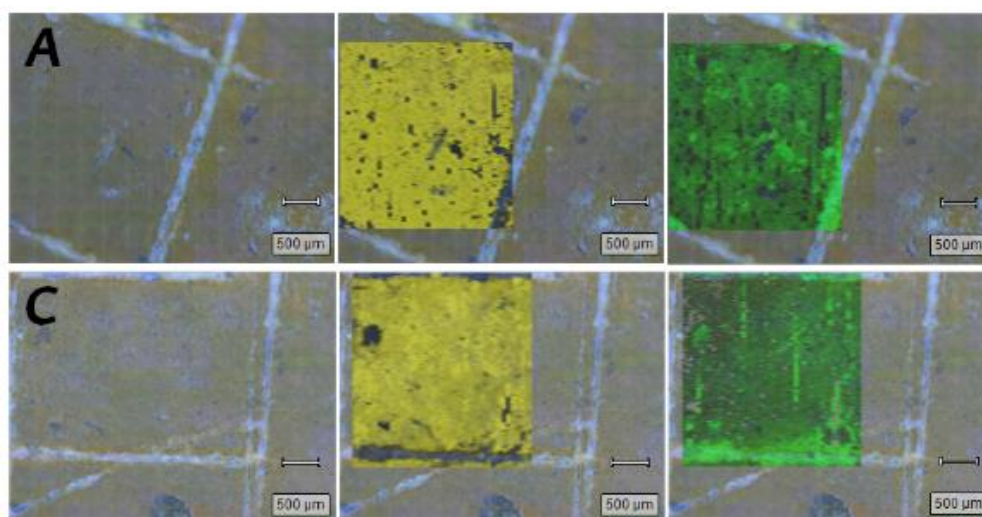


Fig. 4. Optical image of the analyzed area (x20, left), distribution maps of goethite (yellow, middle) and calcite (green, right) acquired by Raman microscopy in fragments A and C.

The goethite and calcite distribution images acquired in fragments A and C are shown in Figure 4 as representative images of all the acquired Raman mappings. As it can be seen in this last figure, goethite is homogeneously distributed in the selected areas, except in the lines marked with the scalpel where the goethite pigment was removed. In these lines the calcite belonging to the render mortar (*intonaco*) was observed. In the yellow pigment area calcite was also detected in specific points. This calcium carbonate can be related with the calcite deposits used in the *intonachino*, to join the pigment grains applied on the wall.

On the other hand, in the measured areas hematite ($\alpha\text{-Fe}_2\text{O}_3$) was not detected, discarding its presence in the studied pictorial layer. In addition, quartz ($\alpha\text{-SiO}_2$) was also identified in some spots of the surface of the fragments, which came in agreement with the acquired elemental distribution maps showed in Figure 3.

Raman imaging quantification of goethite transformation degree as a function of thermal impact. Notable color changes were observed at the naked eye in the fragments under study after all the considered thermal ageing experiments, from 200°C to 400°C, every 25°C (see Figure 5).

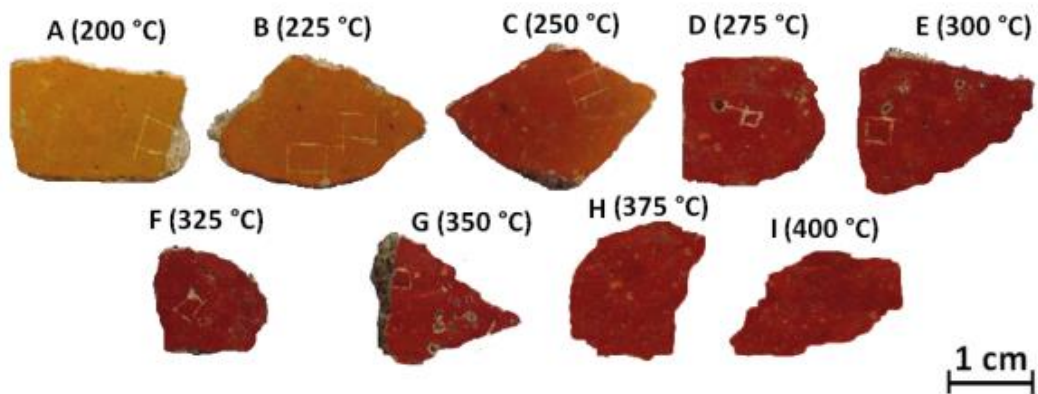


Fig. 5. Yellow goethite fragments transformed into red after the different thermal ageing experiments.

As shown in Figure 5, a clear and progressive transformation of goethite into hematite can be observed at the naked eye mainly from 200 to 275 °C. From this last temperature up to 400 °C no changes were visually observed.

Different areas of the transformed fragments were analyzed by means of Raman microscopy following an imaging strategy. Thanks to this study, the quantitative transformation of goethite into hematite was determined at each exposed temperature. The used conditions were the same in all cases: 0.5 s and 1 accumulation acquired in 100-1350 cm^{-1} spectral region. Spectra were acquired every 20 μm in both directions of the image. After the Raman image was acquired, baseline correction, smoothing and cosmic ray removal were applied to all the set of spectra in order to avoid problems arising from the background of the spectra, which in this case showed some fluorescence.

The Raman quantitative analysis was performed by means of Direct Classical Least Squares (DCLS) algorithm. It is based on the comparison of each spectrum acquired in the map with the spectrum of goethite and hematite standards acquired in the same

conditions. The scaling factor is automatically selected to fit as best as possible with the spectra of the Raman map. For that, four different images were acquired before and after the thermal exposure in different areas in order to obtain the average value with its 95% confidence interval. To validate the quantitative methodology, synthetic pellets using different amounts of hematite and goethite standards (50/50%, 25/75% and 75/25% w/w, hematite/goethite) were prepared. The accuracy and precision of the quantitative results based on Raman imaging and using different magnification lenses are shown in Table 1.

Table 1. Quantitative results (average concentration together with the 95% confidence interval in weight percentage unit) obtained for the hematite/goethite synthetic standards employing the Raman imaging quantitative method.

Real Hematite/Goethite concentrations (w/w %)	Hematite/Goethite quantitative Raman estimates (w/w %) 50x objective lens	Hematite/Goethite quantitative Raman estimates (w/w %) 20x objective lens	Hematite/Goethite quantitative Raman estimates (w/w %) 5x objective lens
25/75	23.5 ± 2.2 / 76.5 ± 7.3	23.8 ± 0.3 / 76.2 ± 1.0	23.4 ± 0.1 / 76.6 ± 0.4
50/50	48.8 ± 5.2 / 51.2 ± 5.5	49.8 ± 1.1 / 50.2 ± 1.1	48.9 ± 0.8 / 51.1 ± 0.9
75/25	77.8 ± 10.3 / 22.2 ± 2.9	77.3 ± 1.7 / 22.7 ± 0.5	77.1 ± 1.5 / 22.9 ± 0.4

Notice that the 95% confidence interval connected to the estimated concentrations using the objective lens of 50x magnification was high (up to 10.3%). This increase of the error using the highest magnification objective lens must be related with the heterogeneity in the surface of the pellets at the lateral resolution achieved with this objective lens (around 20 μm). In Figure S1 from Supporting Information a microscopic image acquired using the 50x objective lens is presented to show that the grains of goethite and hematite mixed to prepare this pellets are heterogeneously distributed at

the scale of 20 μm . A homogeneous distribution of the compounds was not achieved since the goethite and hematite used to perform these pellets were mixed manually by grinding both compounds. This heterogeneity includes a higher variability in the obtained quantitative result and therefore an increase in the associated error. On the contrary, the distribution of both hematite and goethite obtained using the 5x objective lens (120 μm spot size or lateral resolution) can be considered homogeneous, minimizing the uncertainty due to sampling (effective diameter spot), and reducing the error associated to the estimated result (see Table 1).

Considering that the heterogeneous distribution of the compounds in the synthetic pellet led to the major contribution of the error comparing with the contribution of the instrumental or methodological error itself, the selection of the objective lens for the monitoring of the thermal transformation degree quantitatively by Raman imaging will be crucial. Before this selection, it will be mandatory to verify the grain size of goethite and hematite in the fragments under study.

Unlike the synthetic pellets, the pictorial layer in the fragments seems homogeneous observed under the 50x objective lens (see Figure S2 in the Supporting Information). In Figure S3, two SEM-EDS images showing the distribution of Fe in two selected fragments are presented. Although those areas free of marks were selected for the study it is necessary to consider that the goethite pigment grains are bound by calcite (CaCO_3) deposits in the pictorial layer (fresco painting). Calcium carbonate deposits are represented as black holes in the EDS maps and Fe coming from goethite as white spots in Figure S3. Considering that the size of calcium carbonate deposits acting as binder of the pigment grains cover areas lower than 20 microns, the pictorial layers in

the fragments under study can be considered heterogeneous at lateral resolutions down to the mentioned value. Additionally, the grain size of goethite in the fragments under study was set between 3-10 μm (see Figure S3). Taking this into account, it was decided to use the 50x lens to acquire the Raman maps before and after the thermal impact in all the fragments. In this case, the spot size is around 20 μm (larger than the size of the individual grains of pigment), which ensures to minimize the error associated to the estimated concentration.

The molecular distribution of hematite in the exposed fragments was determined using its main band at 411 cm^{-1} . As shown in Figure S4 in the Supporting Information, quite homogeneous Raman images of hematite were obtained for all fragments, with except of some points inside the measured areas in which there is not pictorial layer, and therefore hematite was not present. For example, the spot in the upper-left side of fragment E where there was not hematite corresponds to a spot in which there was not any color (see Figure S4), and thus, calcite was detected in the Raman image. These areas showing calcite were avoided for the goethite/hematite concentration calculations. In this sense, areas where the presence of calcite was the minimum one, or even negligible, were selected in order to not distort the quantitative results. Four different frames of 1 mm x 1mm were analyzed and considered for the quantitative calculations. The obtained transformation percentages of goethite into hematite at different temperatures are presented in Figure 6, showing the corresponding uncertainties.

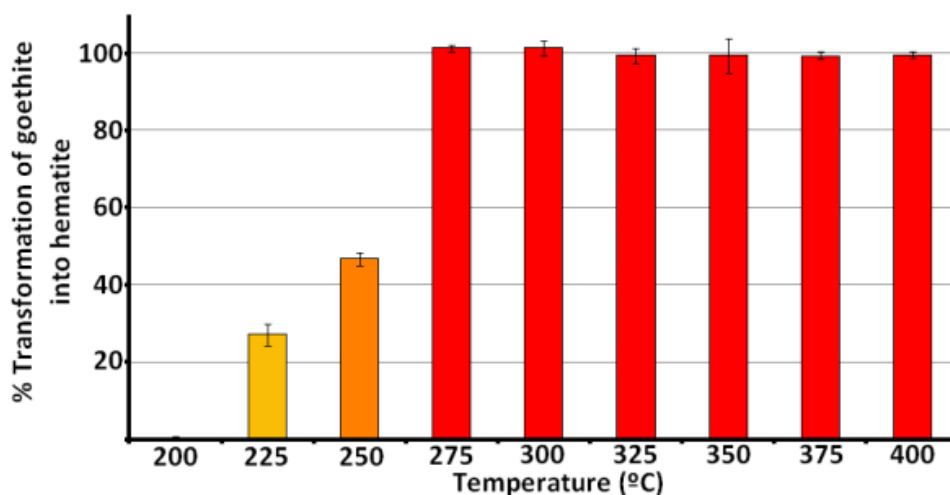


Fig. 6. Transformation of goethite into hematite degree (w/w %) at increasing temperatures with the standard deviation of the different measurements.

As shown in Figure 6, the transformation of goethite into hematite seems to start at temperatures around 200°C. At this temperature, a very small transformation of goethite into hematite ($0.5 \pm 0.4\%$) was observed. To check if the exposure time has some influence in the transformation process, further thermal ageings were conducted at longer exposition times (3, 4, 5, 6 and 7 hours) at 200 °C in order to observe if a longer time of exposition at this temperature promotes higher transformations. In this case, additional transformation was not observed. Therefore, it can be assumed that the key factor to promote the transformation of goethite into hematite is the temperature and not the exposure time during the thermal impact.

At the ageing temperature of 225°C some reddish hues were observed at the naked eye (see Figure 5), and a transformation into hematite of $26.9 \pm 2.8\%$ was determined by the quantitative Raman imaging methodology (see Figure 6). After the transformation had started in the interval of 200-225°C, the highest increase takes place at temperatures between 225-275°C maintaining stable from 275 until 400 °C.

These results suggest that the thermal transformation is completed at 275°C because from this temperature up to 400°C, the obtained transformation values did not show any significant variation ($46.7 \pm 1.7\%$ at 250°C; $101.1 \pm 1.2\%$ at 275°C; $101.2 \pm 1.9\%$ at 300°C; $99.2 \pm 1.9\%$ at 325°C; $99.3 \pm 4.4\%$ at 350°C; $99.4 \pm 0.6\%$ at 375°C; $99.6 \pm 0.8\%$ at 400°C).

The fitting of the Raman spectra acquired during the Raman imaging quantitative studies, and therefore those data used to extract the transformation percentages of goethite into hematite in the fragments was performed using the spectrum of a real Pompeian raw goethite pigment recovered from the burial (see experimental section). The spectrum of hematite used for the fitting was obtained by ageing the used Pompeian goethite pigment at 350 °C and therefore obtaining a hematite as similar as possible as the one present in the pictorial layer of the aged fragments under study. In order to see up to what extent the quantitative results, and therefore the calculated transformation percentages can change using different Raman spectra as standards for the fitting of the Raman spectra in the imaging study, pure goethite and hematite commercial pigment standards were also used with this purpose. The quantitative results obtained using both ways were similar for the fragments aged up to 250°C. However, the transformation percentages of the fragments aged from 275°C to 400°C obtained by using the spectra acquired from the commercial pigments were of around 70%. On the other hand, as shown in Figure 6, by using the real Pompeian goethite pigment, the transformation degree reached the 100% being a more realistic result. The high difference in the obtained quantitative transformation degree could be related with the presence of additional molecular phases at minor levels in the pictorial

layer of goethite in the Pompeian wall painting fragments. Among these possible compounds, different kind of silicates such as quartz, kaolinite and illite, all of them identified in Pompeian yellow ochre pigments [9], can be mentioned. Considering that the composition of goethite and hematite commercial standards is almost 100% of goethite or hematite, the differences in the predicted quantitative transformation degrees can be related with the different molecular composition between Pompeian ochre pigments and commercial ones.

Conclusions

The aim of this work was to study the transformation of goethite into hematite in wall painting fragments from Pompeii caused by the thermal impact of the pyroclastic flow coming from the 79AD Mount Vesuvius eruption. This is the first time in which this kind of research has been performed on real Pompeian wall painting fragments instead of using goethite pigment powders or mock ups. Moreover, this is also the first time that a quantitative percentage of transformation depending on the specific temperature impact has been obtained.

The thermal ageing steps were successfully performed in the yellow fragments under study and the transformation of goethite into hematite was determined both at the naked eye and in an analytical way by means of Raman imaging. The temperature that marks the start of the transformation progress seems to be 200 °C, because at this temperature a transformation of 0.5% was determined, while at 225 °C a transformation of 26.9% was registered. Nevertheless, the most notable transformation variation was observed in the transit from 225 to 275 °C in which all the

goethite was transformed at this last temperature. Thus, taking into account the results obtained in this work the temperature of 250 °C can be assumed as the inflection temperature for the dehydration process of goethite, and 275 °C as the temperature at which the transformation is completed.

Moreover, it has been proven that the most important factor that promotes the thermal transformation is the temperature and not the exposure time, since the fragment aged at 200 °C did not show any additional transformation when the ageing time increased up to 7 hours.

To obtain faithful transformation values, the adequateness of the standard to be used for the quantification method had to be evaluated. It was corroborated that for this case, it was better to use a thermally aged Pompeian goethite standard than pure hematite standard because more accurate and realistic results were obtained since its composition is more similar to the pictorial layer in real wall painting fragment.

The proposed methodology is valid to identify in a very easy way the temperatures of the pyroclastic flow that reached Pompeii without the necessity of performing more complex geochemical analyses described in the literature, such as the analysis of a high number of samples (about 200) of lava clasts by thermal remnant magnetization (TRM) [14]. Therefore, thanks to this work, yellow painted walls transformed into red can be used as a witness of the thermal impact of 79 AD Mount Vesuvius eruption, and a map of temperatures depending on the area and the orientation could be constructed.

Finally, although this work has been developed using a benchtop instrument, considering that in the last years new developments and possibilities in the in situ Raman mapping field using portable instruments will take place [21], it is feasible to

think that in the near future quantitative Raman imaging methodologies will be applicable on site. Thus, this last instrumental development will permit to this methodology be transferable to a totally non-destructive perspective which will allow determining, without extracting any painting fragment, the temperature at which each goethite painted wall was impacted according to its position and orientation in the Archeological Park of Pompeii and additional archaeological sites which suffered the impact of 79 AD eruption such as Herculaneum.

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Compliance with ethical standards.

This research does not involve any human participants or animals.

Conflict of interests: The authors declare that they have no conflict of interest.

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