



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

Iker Marcaida<sup>1</sup> · Maite Maguregui<sup>2</sup> · Héctor Morillas<sup>1</sup> · Silvia Perez-Diez<sup>1</sup> · Juan Manuel Madariaga<sup>1,3</sup>

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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,  $\alpha$ -FeOOH) into red color (hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) 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 archeological site of Pompeii and which include yellow ochre pigment were subjected to thermal ageing experiments (exposition to temperatures from 200 to 400 °C every 25 °C). Before the experiments, elemental information of the fragments was obtained by micro-energy dispersive X-ray fluorescence ( $\mu$ -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 since from 275 to 400 °C the transformation percentage remained constant.

**Keywords** Yellow ochre · Dehydration · Raman imaging · Color transformation · Quantitative analysis

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✉ Iker Marcaida  
iker.marcaida@ehu.es

<sup>1</sup> Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, P. O. Box 644, 48080 Bilbao, Basque Country, Spain

<sup>2</sup> Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, P. O. Box 450, 01080 Vitoria-Gasteiz, Basque Country, Spain

<sup>3</sup> Unesco Chair of Cultural Landscapes and Heritage, University of the Basque Country UPV/EHU, P. O. Box 450, 01006 Vitoria-Gasteiz, Basque Country, Spain

## Introduction

In the 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 m, kept the ancient city hidden and forgotten for almost seven centuries. Therefore, thanks to this event, Pompeii has preserved during the burial almost all of the buildings, sculptures, wall paintings, and other archeological 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, a hydrated iron oxide [ $\alpha$ -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,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 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, both red-colored paintings could not be discriminated 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 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 ( $\mu$ -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.

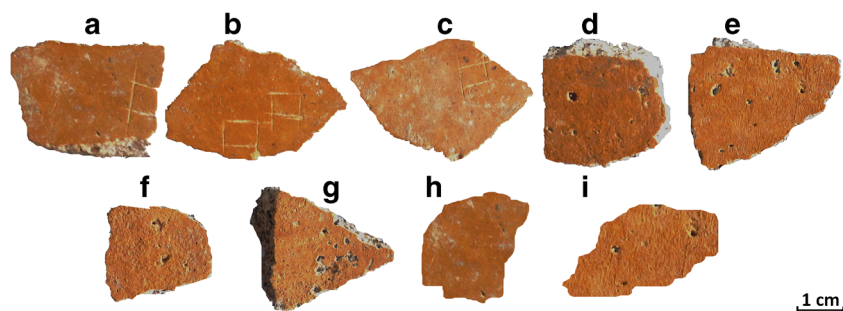
## Material and methods

**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).

**Pigment 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)

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



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 measuring at 1 mm and down to 25  $\mu\text{m}$  of lateral resolutions. In this work, 25  $\mu\text{m}$  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  $\mu\text{A}$ , 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  $\mu\text{m}$ . 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  $K_{\alpha}$  line, except for Pb, using in this case the  $L_{\beta}$  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  $\times 5$ ,  $\times 20$ , and  $\times 50$  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 h (Fragment A: 200  $^{\circ}\text{C}$ , Fragment B: 225  $^{\circ}\text{C}$ , Fragment C: 250  $^{\circ}\text{C}$ , Fragment D: 275  $^{\circ}\text{C}$ , Fragment E: 300  $^{\circ}\text{C}$ , Fragment F: 325  $^{\circ}\text{C}$ , Fragment G: 350  $^{\circ}\text{C}$ , Fragment H: 375  $^{\circ}\text{C}$ , and Fragment I: 400  $^{\circ}\text{C}$ ). 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  $^{\circ}\text{C}/\text{min}$ .

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  $\approx 20$  nm of a carbon layer.

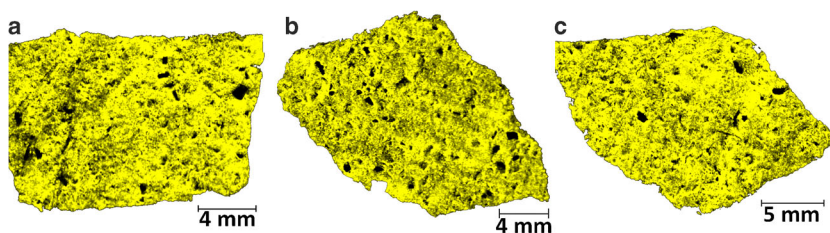
## Results and discussion

**Elemental characterization of the fragments before thermal ageing by means of  $\mu\text{-ED-XRF}$  imaging**  $\mu\text{-ED-XRF}$  spectrometry by means of an imaging strategy was applied to observe mainly the distribution of iron in the surface of the fragments (see Fig. 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.

As shown in Fig. 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  $4 \times 4$  mm) with a scalpel (see Fig. 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

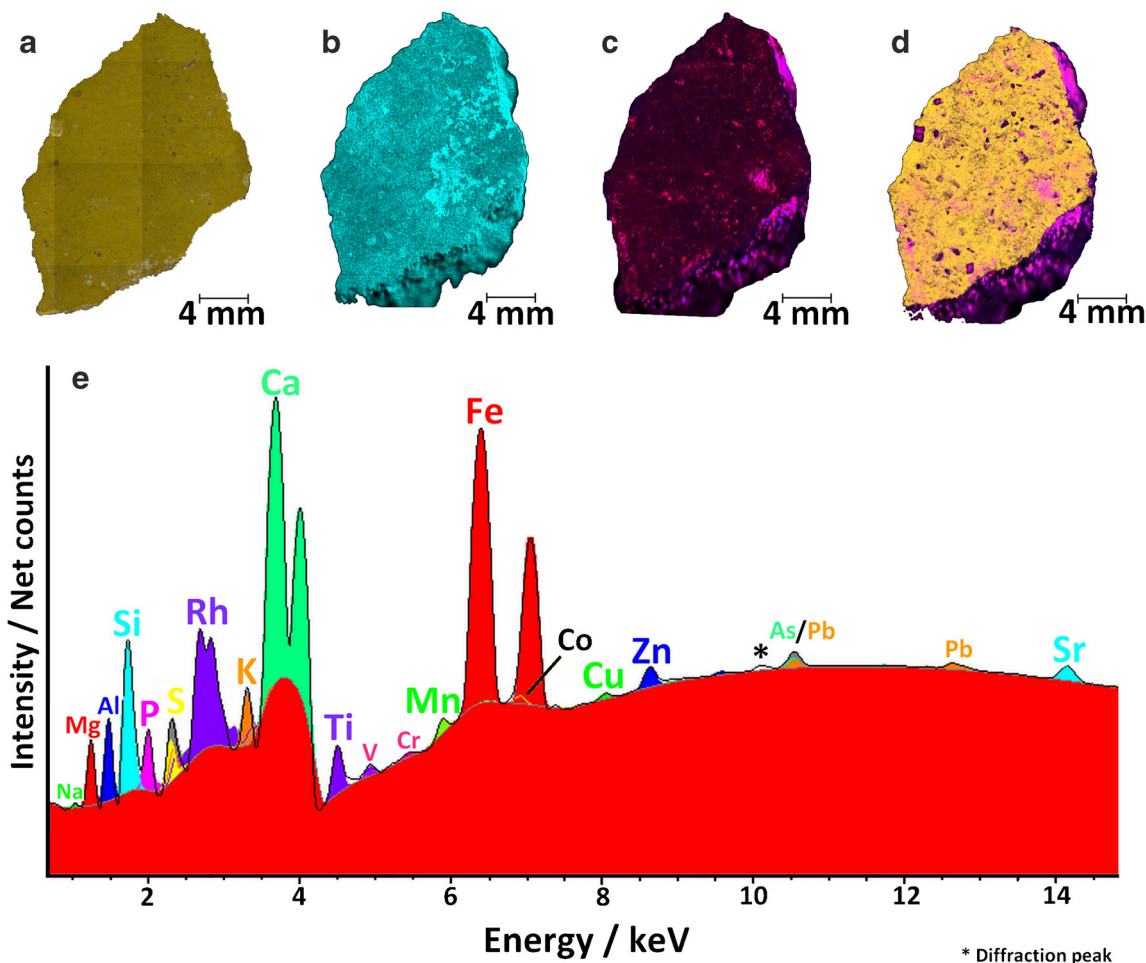
**Fig. 2** Iron distribution XRF maps (in yellow) in A, B, and C fragments



detected (see Fig. 3). Besides, a diffraction peak at 10.1 keV (marked with an asterisk in Fig. 3e) appeared because of the use of the poly-capillary lens of the instrument.

The obtained XRF map of fragment B (see sum spectrum of the analyzed area in Fig. 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 Fig. 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 Fig. 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.,  $\text{KAlSi}_3\text{O}_8$ ) coming from the burial, which might be stuck to the fragment. Besides, some Si-rich hotspots (Fig. 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



**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. Asterisk means diffraction peak

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 ( $\alpha$ -FeOOH) distribution maps before the thermal ageing, Raman image acquisitions were performed in different areas of the fragment, selected according  $\mu$ -ED-XRF results. The maps were acquired in the 100–1300  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ , and the main band of calcite at 1086  $\text{cm}^{-1}$  (see Fig. 4).

The goethite and calcite distribution images acquired in fragments A and C are shown in Fig. 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.

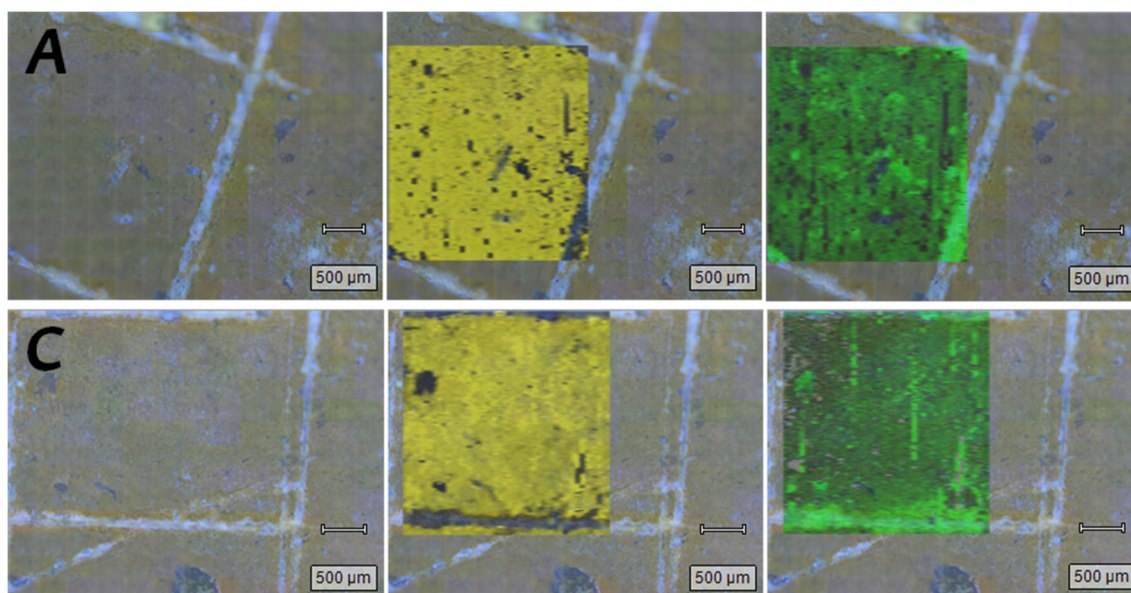
On the other hand, in the measured areas, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) was not detected, discarding its presence in the studied pictorial layer. In addition, quartz ( $\alpha$ -SiO<sub>2</sub>) was also identified in some spots of the surface of the fragments, which came in agreement with the acquired elemental distribution maps showed in Fig. 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 to 400 °C, every 25 °C (see Fig. 5).

As shown in Fig. 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.

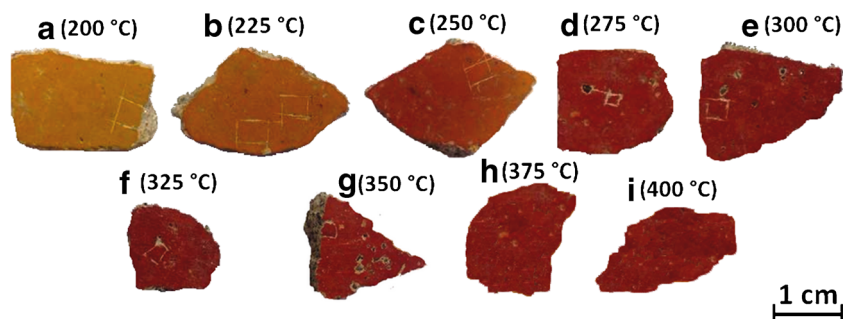
Different areas of the transformed fragments were analyzed by means of Raman microscopy following an imaging strategy. Thanks to this study, the quantitative transformation of goethite into hematite was determined at each exposed temperature. The used conditions were the same in all cases: 0.5 s and 1 accumulation acquired in 100–1350  $\text{cm}^{-1}$  spectral region. Spectra were acquired every 20  $\mu\text{m}$  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



**Fig. 4** Optical image of the analyzed area ( $\times 20$ , left), distribution maps of goethite (yellow, middle) and calcite (green, right) acquired by Raman microscopy in fragments A and C

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



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.

Notice that the 95% confidence interval connected to the estimated concentrations using the objective lens of  $\times 50$  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  $\mu\text{m}$ ). In Fig. S1 from Electronic Supplementary Material (ESM), a microscopic image acquired using the  $\times 50$  objective lens is presented to show that the grains of goethite and hematite mixed to prepare these pellets are heterogeneously distributed at the scale of 20  $\mu\text{m}$ . 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  $\times 5$  objective lens (120  $\mu\text{m}$  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 homogenous observed under the  $\times 50$  objective lens (see Fig. S2 in the ESM). In that ESM Fig. 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 ( $\text{CaCO}_3$ ) deposits in the pictorial layer (it is a fresco painting). Calcium carbonate deposits are represented as black holes in the EDS maps and Fe coming from goethite as white spots in ESM Fig. 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  $\mu\text{m}$  (see ESM Fig. S3). Taking this into account, it was decided to use the  $\times 50$  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  $\mu\text{m}$  (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  $411\text{ cm}^{-1}$ . As shown in Fig. S4 in the ESM, 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

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

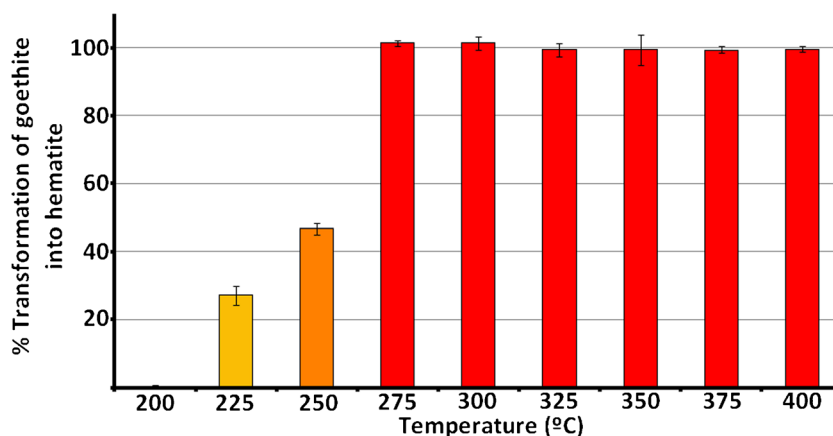
there was not hematite corresponds to a spot in which there was not any color (see ESM Fig. S4), and thus, calcite was detected in the Raman image. These areas showing calcite were avoided for the goethite/hematite concentration calculations. In this sense, areas where the presence of calcite was the minimum one, or even negligible, were selected in order to not distort the quantitative results. Four different frames of 1 mm × 1 mm were analyzed and considered for the quantitative calculations. The obtained transformation percentages of goethite into hematite at different temperatures are presented in Fig. 6, showing the corresponding uncertainties.

As shown in Fig. 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 h) 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 Fig. 5), and a transformation into hematite of  $26.9 \pm 2.8\%$  was determined by the quantitative Raman imaging methodology (see Fig. 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 to 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 to 400 °C obtained by using the spectra acquired from the commercial pigments were of around 70%. On the other hand, as shown in Fig. 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 kinds 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 compositions between Pompeian ochre pigments and commercial ones.

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



**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 79 AD 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, demonstrating in this way the real pathway that promoted the transformation of yellow ochre into red in Pompeian wall paintings. 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 h.

To obtain faithful transformation values, the adequateness of the standard to be used for the quantification method must 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 archeological 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 interest** The authors declare that they have no conflict of interest.

## References

1. <http://pompeiiisites.org/en/archaeological-park-of-pompeii/visitor-data/> (last accessed August 2019)
2. Madariaga JM, Maguregui M, Fdez-Ortiz De Vallejuelo S, Knuutinen U, Castro K, Martínez-Arkarazo I, et al. In situ analysis with portable Raman and ED-XRF spectrometers for the diagnosis of the formation of efflorescence on walls and wall paintings of the Insula IX 3 (Pompeii, Italy). *J Raman Spectrosc.* 2014;45:1059–67.
3. Merello P, García-Diego FJ, Zarzo M. Evaluation of corrective measures implemented for the preventive conservation of fresco paintings in Ariadne’s house (Pompeii, Italy). *Che Cent J.* 2013;7: 87–98.
4. Maguregui M, Knuutinen U, Martínez-Arkarazo I, Castro K, Madariaga JM. Thermodynamic and spectroscopic speciation to explain the blackening process of hematite formed by atmospheric SO<sub>2</sub> impact: the case of Marcus Lucretius House (Pompeii). *Anal Chem.* 2011;83:3319–26.
5. Maguregui M, Castro K, Morillas H, Trebolazabala J, Knuutinen U, Wiesinger R, et al. Multianalytical approach to explain the darkening process of hematite pigment in paintings from ancient Pompeii after accelerated weathering experiments. *Anal Methods.* 2014;6: 372–8.
6. Cotte M, Susini J, Metrich N, Moscato A, Gratzu C, Bertagnini A, et al. Blackening of Pompeian Cinnabar Paintings: X-ray Microspectroscopy Analysis. *Anal Chem.* 2006;78:7484–92.
7. Marcaida I, Maguregui M, Fdez-Ortiz de Vallejuelo S, Morillas H, Prieto-Taboada N, Veneranda M, et al. In situ X-ray fluorescence-based method to differentiate among red ochre pigments and yellow ochre pigments thermally transformed to red pigments of wall paintings from Pompeii. *Anal Bional Chem.* 2017;409:3853–60.



8. Higgings C. Pompeii shows its true colors. <https://www.theguardian.com/science/2011/sep/22/pompeii-red-yellow>. 2011. The Guardian.
9. Marcaida I, Maguregui M, Morillas H, Veneranda M, Prieto-Taboada N, Fdez-Ortiz de Vallejuelo S, et al. Raman microscopy as a tool to discriminate mineral phases of volcanic origin and contaminations on red and yellow ochre raw pigments from Pompeii. *J Raman Spectrosc*. 2019;50:143–9.
10. Marcaida I, Maguregui M, Morillas H, Fdez-Ortiz de Vallejuelo S, Prieto-Taboada N, Veneranda M, et al. In situ non-invasive characterization of the composition of Pompeian pigments preserved in their original bowls. *Microchem J*. 2018;139:458–66.
11. Aliatis I, Bersani D, Campani E, Casoli A, Lottici PP, Mantovan S, et al. Green pigments of the Pompeian artists' palette. *Spectrochim Acta A*. 2009;73:532–8.
12. Marcaida I, Maguregui M, Morillas H, García-Florentino C, Knuutinen U, Carrero JA, et al. Multispectroscopic and isotopic ratio analysis to characterize the inorganic binder used on Pompeian Pink and Purple Lake pigments. *Anal Chem*. 2016;88:6395–402.
13. Aliatis I, Bersani D, Campani E, Casoli A, Lottici PP, Mantovan S, et al. Pigments used in Roman wall paintings in the Vesuvian area. *J Raman Spectrosc*. 2010;41:1537–42.
14. Cioni R, Gurioli L, Lanza R, Zanella EJ. Temperatures of the AD 79 pyroclastic density current deposits (Vesuvius, Italy). *Geophys Res*. 2004;109:B02207.
15. Ruan HD, Frost RL, Kloprogge JT, Duong L. Infrared spectroscopy of goethite dehydroxylation: III. FT-IR microscopy of in situ study of the thermal transformation of goethite to hematite. *Spectrochim Acta A*. 2002;58:967–81.
16. Romero P, González JC, Bustamante A, Ruiz Conde A, Sánchez-Soto PJ. Study of the in-situ thermal transformations of Limonite used as pigment coming from Peru. *Bol Soc Esp Ceram Vidr*. 2013;52:127–31.
17. Pomies MP, Menu M, Vignaud CJ. TEM observations of goethite dehydration: application to archaeological samples. *Eur Ceram Soc*. 1999;19:1605–14.
18. Prasad PSR, Prasad KS, Chaitanya VK, Babu EVSSK, Sreedhar B, Murthy SRJ. In situ FTIR study on the dehydration of natural goethite. *Asian Earth Sci*. 2006;27:503–11.
19. De Faria DLA, Lopes FN. Heated goethite and natural hematite: can Raman spectroscopy be used to differentiate them? *Vib Spectrosc*. 2007;45:117–21.
20. <https://blogs.helsinki.fi/pompeii-project/> (last accessed August 2019)
21. Lauwers D, Brondeel P, Moens L, Vandenabeele P. In situ Raman mapping of art objects. *Phil Trans R Soc A*. 2016;374:20160039.

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