



Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Chemometrics and elemental mapping by portable LIBS to identify the impact of volcanogenic and non-volcanogenic degradation sources on the mural paintings of Pompeii



Silvia Pérez-Diez ^{a,*}, Luis Javier Fernández-Menéndez ^b, Marco Veneranda ^{a,c}, Héctor Morillas ^{a,d}, Nagore Prieto-Taboada ^{a,e}, Silvia Fdez-Ortiz de Vallejuelo ^a, Nerea Bordel ^b, Alberta Martellone ^f, Bruno De Nigris ^f, Massimo Osanna ^g, Juan Manuel Madariaga ^{a,h}, Maite Maguregui ^{i,**}

^a Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Bilbao, Spain

^b Department of Physics, Faculty of Sciences, University of Oviedo, Oviedo, Spain

^c Department of Condensed Matter Physics, Crystallography and Mineralogy, University of Valladolid, Valladolid, Spain

^d Department of Didactic of Mathematics and Experimental Sciences, Faculty of Education and Sport, University of the Basque Country UPV/EHU, Vitoria-Gasteiz, Spain

^e Department of Applied Chemistry, Faculty of Chemistry, University of the Basque Country UPV/EHU, Donostia, Spain

^f Applied Research Laboratory of Archaeological Park of Pompeii, Via Plinio 4, Pompeii, Italy

^g General Director of Archaeological Park of Pompeii, Via Plinio 4, Pompeii, Italy

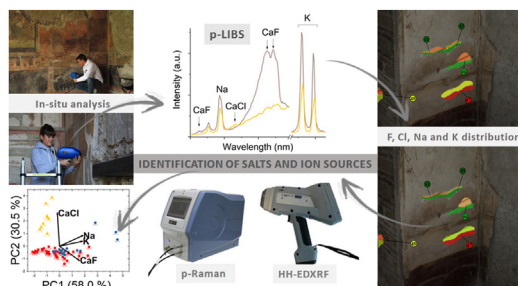
^h UNESCO Chair of Cultural Landscapes and Heritage, University of the Basque Country UPV/EHU, Vitoria-Gasteiz, Spain

ⁱ Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, Vitoria-Gasteiz, Spain

HIGHLIGHTS

- Mapping of Na, K, F and Cl on Pompeian mural paintings by p-LIBS.
- Creation of a scale of impact by salt crystallization on mural paintings.
- Discrimination among ion sources by chemometrics applied to p-LIBS.
- Influence of pyroclastic materials, groundwater and marine aerosol.
- Role of restoration mortars as reservoirs of sulfate salts.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 February 2021

Received in revised form

31 March 2021

Accepted 20 April 2021

Available online 3 May 2021

Keywords:

Mural paintings

Halides

ABSTRACT

Crystallization of soluble salts is a common degradation phenomenon that threatens the mural paintings of Pompeii. There are many elements that contribute to the crystallization of salts on the walls of this archaeological site. Notably, the leachates of the pyroclastic materials ejected in 79 AD by Mount Vesuvius and local groundwater, rich in ions from the erosion of volcanic rocks. Both sources could contribute to increase the concentration of halides (fluorides and chlorides) and other salts in these walls. The distribution of volcanogenic salts and their impact on the conservation of Pompeian mural paintings have however not yet been fully disclosed. In this work, an analytical methodology useful to determine the impact of the main sources of degradation affecting the mural paintings of Pompeii is presented. This methodology combines the creation of qualitative distribution maps of the halogens (CaF

* Corresponding author.

** Corresponding author.

E-mail addresses: silvia.perezdz@ehu.es (S. Pérez-Diez), maite.maguregui@ehu.es (M. Maguregui).

Salt crystallization
Portable LIBS
Chemometrics

and CaCl) and related alkali metals (Na and K) by portable Laser Induced Breakdown Spectroscopy (LIBS) and a subsequent Principal Component Analysis of these data. Such maps, together with the in-situ identification of sulfate salts by portable Raman spectroscopy, provided information about the migration and distribution of volcanogenic halides and the influence of ions coming from additional sources (marine aerosol and modern consolidation mortars). Additionally, the thermodynamic modeling developed using the experimentally determined ionic content of Pompeian rain- and groundwater allowed to determine their specific role in the formation of soluble salts in the mural paintings of Pompeii.

© 2021 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

In recent years, significant efforts have been undertaken to improve the preservation of the Archaeological Park of Pompeii. Thanks to The Great Pompeii Project [1], the requalification of the site of Pompeii was achieved in December 2015. In parallel, the IBeA research group of the University of the Basque Country (UPV/EHU) has been carrying out in-situ analysis campaigns since 2010 within the APUV project (*Analytica Pompeiana Universitatis Vasconicae*).

One of the primary goals of this project was to diagnose the conservation problems related to mural paintings of Pompeii [2–5]. For this purpose, several portable analytical techniques, such as portable Raman spectroscopy, handheld energy dispersive X-ray fluorescence spectrometry (HH-EDXRF), portable Infrared Spectroscopy in Diffuse Reflectance mode (DRIFTS) and portable Laser Induced Breakdown Spectroscopy (LIBS), have been employed, since sampling from this site is highly restricted [2–7].

One of the main preventive conservation issues in Pompeii is related to the crystallization of soluble salts on mural paintings. Usually, groundwater is one of the main carriers of ions that can migrate to mural paintings promoting salts formation [8,9]. In volcanic areas, the enrichment of groundwater in ions due to erosion/leaching of volcanic minerals is expected. Additionally, the leachates of pyroclastic material ejected in 79 AD by Mount Vesuvius are a major source of ions (Na^+ , K^+ , SO_4^{2-} , Cl^- , F^-) that may cause new formation of salts on walls and mural paintings [10].

To date, all of the in-situ [4,11] and laboratory [12,13] studies conducted in mural paintings from Pompeii allowed the identification of mainly sulfate and nitrate salts. In a recent work, however, chlorides and fluorides have been identified in efflorescences [10]. Seawater and the diffuse influence of the marine aerosol can be considered another Cl^- source. In Pompeii, and due to its closeness to the bay of Naples, aquifers could be enriched in this halide and other ions – such as Na^+ – coming from seawater [14]. Nevertheless, this observation should be experimentally confirmed. On the other hand, since no other relevant F^- sources can be found in Pompeii, this halide can be used to track the influence of volcanogenic ion sources [15,16].

The in-situ identification of both Cl and F in salt crystallizations or on the pictorial layer of mural paintings represents a challenge. In general terms, Raman spectroscopy cannot be considered an adequate technique due to the absent or low Raman scattering of halide salts [10,17]. Moreover, at present, the accessibility to portable X-Ray Diffractometers is relatively difficult. In addition, the content of these halides in the painting substrate could be below the Limit of Detection (LOD) of this last technique (around 1% wt.). However, in recent years, LIBS has been successfully employed for the detection of halogens by means of emission bands, coming from diatomic molecules formed by the recombination of a halogen and an alkaline earth element [10,18–20], improving their LOD compared with the detection of their atomic emission lines.

The main goal of this work is to identify the influence of volcanogenic and non-volcanogenic degradation sources causing salt crystallization on the mural paintings of Pompeii. To this end, herein are presented, for the first time, qualitative maps of distribution of halogens (CaF and CaCl) and related alkali metals (Na and K) through the application of LIBS. HH-EDXRF was also used to support the Cl detection. The obtained experimental evidences were used to track the migration of the specified halogens and alkali metals coming from volcanogenic and non-volcanogenic sources. Raman spectroscopy was also applied to identify additional salts in the formed efflorescences.

A thermodynamic modeling of the local rain- and groundwater ionic content was also carried out to evaluate the role of both sources in the salt crystallization process. Finally, chemometrics applied to LIBS data was implemented in the methodology to identify the influence of the main degradation sources causing the crystallization of salts based on the specific area in the Pompeian mural paintings.

2. Experimental section

2.1. Mural paintings and samples under study

Selected mural paintings of the House of the Golden Cupids (Regio VI 16, 7: Rooms G, I and Q) and the House of Ariadne (Regio VII 4, 31/51: basement and Room 17) have been considered for this study. All mural paintings are protected by roofs and only the rear of the east and north walls of Room G, the north wall of Room I (House of the Golden Cupids) and the south and west walls of Room 17 (House of Ariadne) are non-protected against rainfall (see Fig. S1). However, considering that the prevalent wind directions in Pompeii are east-northeast and south-southwest [21], a slight impact of rainfall on their rear is only expected for the east wall of Room G in case of south-southwest wind and for the west wall of Room 17 in case of north-northeast wind (see Fig. S1).

Details of the mapped mural paintings (showing the possible presence of efflorescences) are reported in the Results section and in Table S1 and S2 and Fig. S3 to S9. The total number of points analyzed by portable LIBS, HH-EDXRF and portable Raman was 62 in the House of Ariadne and 163 in the House of the Golden Cupids (see Tables S1 and S2 and Fig. S3–S9).

To evaluate the direct influence of the pyroclastic deposits on the mural paintings, apart from the in-situ studies, 4 micro-samples were extracted from the mural painting of the basement of the House of Ariadne (Fig. S2 and Table S1) [22]. Sample M0 was taken from the lower part of the mural, which shows pyroclastic residues not correctly removed during the course of the excavations [22]. Samples M1 and M3 were extracted from areas of the same mural with an apparent absence of these deposits. Sample M2 was obtained from white drips/crusts observable in the upper part of the same mural painting (see Fig. S2).

Additionally, samples of rainwater and groundwater were collected and analyzed. To collect rainwater, a 250 mL beaker was placed at the House of the Golden Cupids during several days throughout an in-situ analysis campaign in order to obtain a composite sample. The sample of groundwater was collected from a well that dates back to the 2nd century BC and belongs to an underground basement [23], located under the peristyle of the House of N. Popidius Priscus (Regio VII, 2, 20). The well is 27.8 m deep and the water level is around 1.5 m [24]. To the authors' knowledge, this is the only ancient well of Pompeii accessible today at the Archaeological Park, thus it was not possible to obtain additional samples from other wells. Both samples of water were stored frozen in 50 mL polypropylene vials before the analysis.

2.2. Instrumentation

For the in-situ LIBS measurements, the EasyLIBS IVEA (model Easy 2C) device was used. This instrument employs a pulsed Nd:YAG laser, whose operating wavelength is 1064 nm. The spectrum from the induced plasma is acquired by two spectrometers, covering the ranges from 196 to 419 nm and from 580 to 1000 nm, respectively. All measurements were acquired with a gate width of 1 ms and a delay time of 3 μ s.

For the mural paintings screening, several laser pulses (5–30) were applied to each point. To improve the signal-to-noise ratio, all reliable spectra measured of each point have been added using the AnaLIBS 6.3 software to obtain a representative LIBS spectrum, which was normalized against the number of valid laser pulses. If the first and external pulse/pulses offered different information comparing with the subsequent ones applied on the point (between 5 and 30), the external pulse/pulses was/were attributed to dirt/dust and therefore removed from the calculations. The software MATLAB 2019a was employed to integrate the signals of interest in the added spectra.

In this work, the detection of CaF and CaCl molecular emissions was possible since Ca is a major element in the mortar matrix. However, considering the strong interference caused by the CaO emission, for the integration of the CaF and CaCl molecular systems, a reference spectrum of a pressed pellet of CaO has been measured in the same experimental conditions and adjusted to all added spectra in order to subtract the contribution of the CaO orange system. Afterwards, the CaF orange system was integrated between 600.5 and 603.4 nm and the CaCl orange system was integrated between 592.4 and 594.4 nm. The atomic emission lines of Na I (589.13 nm) and K I (766.52 nm) were also integrated after the subtraction of the baseline between 587.3 and 590.5, and 756.1 and 773.3 nm, respectively.

MATLAB 2019a was also used to perform Principal Component Analysis (PCA) and to calculate the Pearson correlation coefficients using the obtained LIBS datasets.

To draw the qualitative distribution images of each element under study in each mural painting, Adobe Photoshop 6.0 was used. To this aim, the intensities (net areas) of all analytical signals in every point were sorted and a color scale was established to represent the relative variations within each wall. To improve the visualization of the distribution images, the color outline of the analyzed points was increased. Moreover, when two points under study were closely located, the outline was interpolated through linear or bilinear interpolation to present the average signals distribution integrated in the areas under study:

Additional information related to the rest of the instrumentation (a HH-EDXRF spectrometer, a portable Raman spectrometer, SEM-EDS, OCT and an ion chromatograph) and software employed to perform the thermodynamic modeling are presented in Supplementary Material.

3. Results and Discussion

3.1. Halogens and alkali metals detection by portable LIBS on Pompeian mural paintings

Since 5 to 30 laser pulses were performed on each point of the Pompeian mural paintings, a fresco mock-up was prepared to evaluate the penetration depth replicating the number of pulses in the same measuring conditions. Afterwards, the craters dimensions were studied by Optical Coherence Tomography (see Supplementary Material) [25,26], varying between 70 and 300 μ m (see Fig. S10). Hence, the results here presented refer only to the pictorial layer of the stratigraphy (usually less than 100 μ m in Pompeii) [27] and superficial *intonaco*.

In the LIBS measurements acquired on the Pompeian mural paintings, it was possible to detect the molecular emission bands of CaF and CaCl, but not the atomic emission lines of the halogens. As an example of CaF molecular emission detection, the spectrum obtained through the analysis of the point 32 in the lower part of the mural painting of the basement of the House of Ariadne is presented in Fig. S11. Fig. S12 illustrates how a proper spectral treatment revealed low CaF signals. Finally, CaCl molecular emission bands have also been in situ identified in efflorescences via LIBS (see Fig. S13).

Apart from CaF and CaCl, the presence of Na and K in the mural paintings under study was also remarkable. According to previous works, Na and K are present in the leachates of halide salts in pyroclastic materials [10] and restoration mortars, too.

3.2. Halogens and alkali metals distribution on the mural painting of the basement of the House of Ariadne

The mural painting of the basement of the House of Ariadne (see Fig. S2 and S3) is partially covered by pyroclastic residues. The identification of F, a halide of volcanic origin, in M0 sample confirms this assumption (see Fig. S14). This halide has been used in this work as marker to track the presence of volcanic residues [10] or volcanogenic salts crystallizations. Thus, in this case, the highest intensities of CaF were expected to be found in the lower left part (see Fig. 1A, where the most relevant analysis points, which will be discussed in this section, have been distinguished with an ellipse). However, although many of the analyzed points showed a clear presence of CaF, others did not yield any molecular emission. This could be due to an inhomogeneous distribution of the pyroclastic deposit remains/salts on the wall or to the presence of a bio-colonization [22], especially evident in points ARI_B:23, 24.

In the white drips/crusts on the garland decoration (upper part), related to solubilization/recrystallization cycles of the wall painting binder [5], remarkable CaF intensities were recorded. SEM-EDS analyses on sample M2, extracted from this area, offered the highest F content (close to 4% wt.). Therefore, during the recrystallization of calcite as crusts, a possible enrichment of F coming from the leaching of the pyroclastic materials or from groundwater may occur.

Moreover, samples M1 and M3, taken from a pictorial layer of mural (see Fig. S2 and Table S1) and free of macroscopic pyroclastic deposits, presented 1–2% wt. of F, demonstrating the migration of this halogen to the surface of the painting and its possible crystallization. In addition, points ARI_B:1, 5, 18–21 are also related to the pictorial layer and yielded noticeable CaF intensities (see Fig. 1A).

Besides that, Na and K were highly accumulated in those areas showing more intense CaF emission, with the exceptions of ARI_B:25, 26 (see Fig. 1B and C), in which the Na signal was strikingly more intense than that attributed to K, pointing to a



Fig. 1. Qualitative LIBS distribution images of A) CaF, B) Na, C) K in the basement of the House of Ariadne. Red areas correspond to the points with higher relative net intensities, while green areas correspond to lower relative net intensities. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

recrystallized crust rich in sodium sulfates.

CaCl molecular bands were not detected by LIBS nor by HH-EDXRF spectrometry in this mural painting.

3.3. Halogens and alkali metals distribution on the mural paintings of the House of the Golden Cupids

In this section, the results of Room G and Room Q of the House of the Golden Cupids are hereunder presented.

Room G was especially rich in efflorescences on the lower parts of the wall, as Room 17 of the House of Ariadne (points ARI_17:1–17, see Fig. S4), which has been subjected to restoration processes in the last decade. The murals of both houses showed a similar trend: CaF mainly accumulated in the lower areas related to efflorescences and CaCl concentrated in the upper parts (see Fig. 2B). This observation is corroborated by the HH-EDXRF results (see the example of Room 17 of the House of Ariadne in Fig. S15).

Special attention should be paid to the Cl accumulation in the *predella* of the south wall of the House of the Golden Cupids (see Fig. 2B and Table S3 to compare the integrated values in the *predella* and in the central panel), which was painted with cinnabar and now nearly completely blackened (the same applies for ARI_17B-7 in Room 17, as shown in Fig. S15). Some studies related to cinnabar in wall and easel paintings point out that chlorides may play a crucial role in this pigment degradation process [28].

In Fig. S16 and S17, the qualitative distribution maps of Na and K in Room G of the House of the Golden Cupids are displayed. In the *predella* of the south wall, no remarkable signals of these elements were found.

Signals from both alkali metals are also less intense in the central panel of the eastern wall of the House of the Golden Cupids than in the lower parts of the northern and southern walls (see Fig. S16 and S17), where efflorescences are concentrated and the highest CaF intensities were detected.

Regarding the Raman spectra of the efflorescences of Room G,

gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was detected in the three walls, whilst thenardite (Na_2SO_4) was identified in the southern wall (bands at 452, 466, 621, 634, 647, 994, 1103, 1132 and 1153 cm^{-1}), and apthitalite ($(\text{K,Na})_3(\text{SO}_4)_2$) bands at 452, 621, 993, 1083 and 1204 cm^{-1}) in the northern wall.

In addition, the walls from Room Q of the House of the Golden Cupids constitute a very interesting case study, since this room has been subjected to past interventions [4], introducing restoration mortars (see the northern wall on the left of the open door and the southern wall on the right in Fig. 3A and S18). Hence, measurements were conducted close to the new materials, where efflorescences are concentrated.

No signals ascribable to the presence of Cl were detected. The normalized intensities of CaF, Na and K in the sum spectrum of each measured area are shown in Fig. 3B and the integrated values of CaF, Na and K are presented in Table S4.

Some efflorescences (GC_Q:37, 39–41, 44–46, 48) presented high to medium Na and K intensities and low to zero CaF intensities (see Table S4). The corresponding Raman spectra showed the presence of apthitalite and gypsum. The occurrence of apthitalite could explain the detection of both intense Na and K signals. On the other hand, additional efflorescences (GC_Q:42, 43, 47) showed high to medium CaF intensities and a rather weak contribution of Na and K. This suggests the occurrence of two different ion sources to the salt crystallizations, which will be thoroughly discussed in section 3.5.

3.4. Evaluation of the role of local rainwater and groundwater in the salt crystallization process

As can be observed in Table S5, the concentrations of Na^+ , K^+ , F^- and Cl^- in local rainwater are lower than the values in groundwater. However, F^- concentration exceeds the average $50\text{ }\mu\text{g L}^{-1}$ reported for rainwater of industrial urban areas [16], thus being related to current volcanic activity.



Fig. 2. Qualitative LIBS distribution image of A) CaF and B) CaCl of Room G of the House of the Golden Cupids. Vertical wide lines mark the separation of the north, eastern and south walls. Red areas correspond to the points with higher relative net intensities, while green areas correspond to lower relative net intensities. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

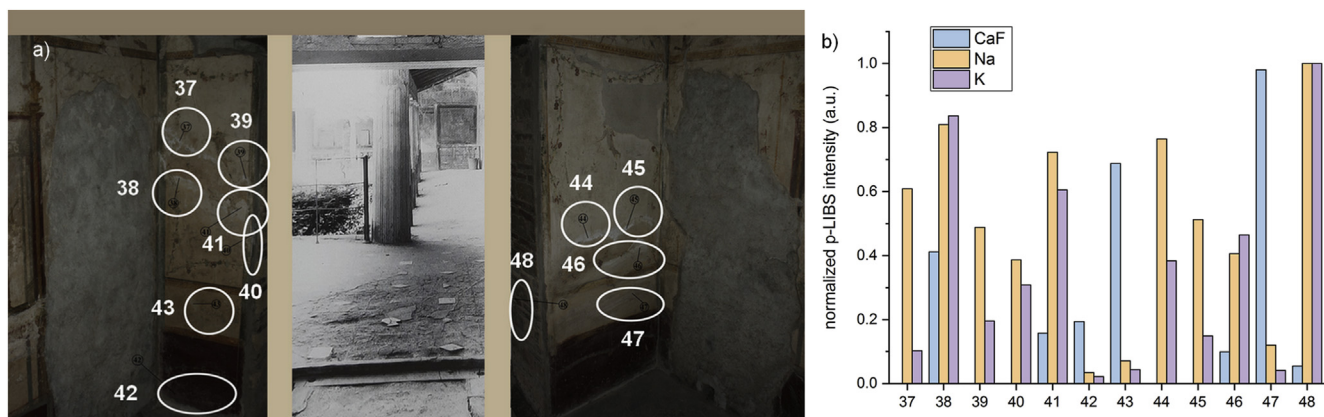


Fig. 3. A) Analyzed efflorescences in Room Q of the House of the Golden Cupids (points GC_Q:37–48). B) CaF, Na and K LIBS relative intensities to the maximum of emission for each element in the marked efflorescences. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

As regards to groundwater, the concentration of K^+ is twice the one of Na^+ , as was the case of the leachates of pyroclastic deposits analyzed in a previous study [10]. Moreover, Na^+ and Cl^- concentrations are not so high compared with the more elevated values registered in Phlegraean Fields groundwater [29], which suffers from the infiltration of seawater. Concretely, the concentrations of Na^+ and Cl^- in these aquifers are 9 and 56 times higher than the ones of the Pompeian groundwater. Therefore, although the latter can still be considered an important source of Na^+ and Cl^- , salt-water intrusions do not seem to play as predominant a role as in other Campanian aquifers.

The concentration of F^- , an ion of volcanic origin, in Pompeian groundwater ($3.0 \pm 0.2 \text{ mg L}^{-1}$) is in accordance with the average expected for shallow wells (down to 15 m depth) in the Phlegraean Fields ($3 \pm 2 \text{ mg L}^{-1}$) [29]. The concentration of this ion in leachates from non-pristine pyroclastic materials [10] is close to the groundwater value, thus the contribution of both sources to the crystallization of F^- salts should be considered.

Taking into account the ion concentrations of both water samples, aqueous geochemical calculations were conducted using the PHREEQC software. The range of pH studied was between 5 and 10, to compare the typical more acidic pH of rainwater [30] with that expected for subterranean water. The thermodynamic modeling was conducted at 10 and 25 °C, the former to simulate the average winter climatic conditions in Campania [31]. In the case of rainwater, the models did not predict the precipitation of any salt through the mentioned pH range, confirming the low contribution of ions from this source to the sample paintings studied. However, in the case of groundwater, the precipitation of fluorite (CaF_2) is expected at 10 °C, being its saturation index lower when acidity is increased (0.08–0.09 between pH = 5 and pH = 10). Fluorite precipitation was also modeled in the case of the leachates coming from pyroclastic materials of Pompeii [10].

3.5. Identification of the main degradation sources causing the crystallization of salts on Pompeian mural paintings

To discriminate the different ion sources that contribute to halide salts and alkali metals-bearing salt crystallizations in the considered mural paintings, a classification according to the relative LIBS intensities of halogens and alkali metals is proposed in Table 1, based on the results of the previous section together with a publication concerning the analysis of pyroclastic materials [10].

To confirm or reject if LIBS data could be used to determine the influence of these sources, the net areas of Na, K, CaF and CaCl

obtained in all measured points of each mural painting by portable LIBS were subjected to PCA. Table 2 shows the ranges of variation for the variables used in each one of the PCA carried out in this study. As can be seen in this table, there are differences between the scale of the CaCl values and those of the rest of variables. More specifically, the maximum values of CaCl are one or two orders of magnitude lower than that of the rest of the variables.

Since the range of variation of the CaCl signals is much smaller than the range of variation of the rest of the variables, a previous Z-score normalization of the dataset was necessary prior to PCA determination. The PCA was conducted by diagonalizing the covariance matrix.

The score and loading plots obtained from the LIBS dataset of the House of Ariadne are shown in Fig. 4 and the Pearson correlation coefficients are presented in Table S6. Three different groups are clearly distinguished: elevated CaCl intensities (yellow group in Fig. 4, see the location of points ARL_17B:1–9 in Fig. S4 and S15), high Na and K intensities (blue points ARL_17:1–4 in Fig. 4, see the location of the points in Fig. S4) and variable CaF, Na and K contribution together with CaCl absence (red and blue points in Fig. 4, see location in Fig. S3 and S4).

The HH-EDXRF measurements confirmed the use of cinnabar as pigment in the upper west wall of Room 17, corresponding to the yellow group in Fig. 4. Marine aerosol is likely the Cl^- source, since the low Na intensities could be explained due to the formation of mercury-chlorine compounds (Cl correlated to Hg), typical degradation products of red cinnabar pigment.

Concerning the lower part of the southern wall of the same room, whose points are related to high Na and K (ARL_17:1–4, Fig. 4), both a restoration mortar and the marine aerosol may be contributing factors impacting this area.

Finally, the correlation of CaF with both alkali metals in the basement and the south wall of Room 17 of the House of Ariadne

Table 1

Classification of ion impact sources according to the intensity of halogens and alkali metals expected by LIBS.

Ion source	Expected LIBS intensities			
	Na	K	CaF	CaCl
Marine aerosol	High	Medium	Very low	Very high
Groundwater	Medium-low	High	High	Medium-high
Rainwater	Low	Low	Low-medium	Low-medium
Restoration mortars	High	High	Low	Low
Volcanic contribution	Medium	High	High	Medium

Table 2
Ranges of variation (minimum and maximum) for each one of the variables used in the PCA analysis.

Variable	House of Ariadne		House of the Golden Cupids (before outliers removal)		House of the Golden Cupids (after outliers removal)	
	Min. (a.u.)	Max. (a.u.)	Min. (a.u.)	Max. (a.u.)	Min. (a.u.)	Max. (a.u.)
CaF	0	1420	0	1390	0	980
CaCl	0	24	0	32	0	32
Na	2	340	18	972	18	410
K	2	1224	20	4640	20	4640

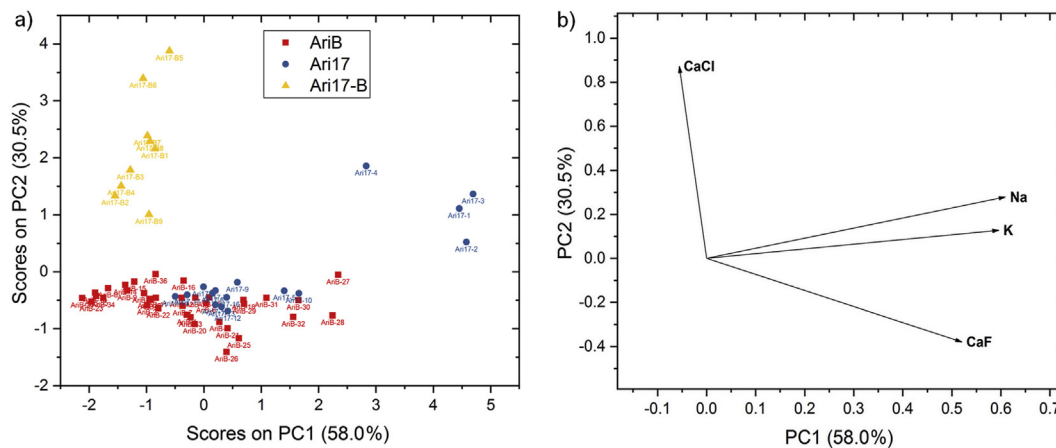


Fig. 4. Principal Component Analysis for the LIBS dataset (CaF, CaCl, Na and K) of the House of Ariadne: A) score and B) loading plots for PC1 and PC2 (ARI-B: basement, ARI-17: south wall, Room 17; ARI-17B: west wall, Room 17).

(see Table S6) would be in accordance with the presence of pyroclastic deposits (especially evident in the basement, see points ARI_B:27–32 in Fig. S3 and Fig. 1), their leaching and/or the infiltration of groundwater. The interaction with further ion sources that do not enrich the surface in F^- , but in other ions such as SO_4^{2-} and alkali metals, can cause the incomplete correlation between the mentioned variables (CaF, Na and K). In addition, CaCl has not been detected in this basement (points in red in Fig. 4), suggesting that the penetration of marine aerosol is very restricted in this underground room and it should not be considered as a major ion source.

In Fig. 5, two PCA studies of the LIBS dataset of the House of the Golden Cupids are shown. Pearson correlation coefficients are also presented in Tables S7 and S8. In the first PCA (Fig. 5A and B), only one group was discernible (elevated Na and K intensities). The points pertaining to this group correspond to efflorescences formed in the vicinity of restoration plasters, very likely acting as sacrificial mortars: GC-Q (yellow points in Fig. 5A, see their location in Fig. 3), GC-G (red points in Fig. 5A, see location of GC-G: 63, 65, 67, 72, 75 and 81 in Fig. S6 and S8) and GC_I-40 (blue point in Fig. 5A, see location in Fig. S9).

To overcome the strong influence of modern restoration mortars, a new PCA was conducted (see Fig. 5C and D) excluding the aforementioned points. In this case, two new groups can be observed: elevated CaCl and variable Na, K and CaF contribution, respectively.

A large number of points of Room G and certain points of Room I (red and blue points in Fig. 5C, see location in Fig. S5 to S9) are affected by a relevant Cl contribution, probably coming from the marine aerosol. More specifically, points GC_G:82–85, 89 were acquired on the red-cinnabar *predella* of Room G (see Fig. S5 and S8), now completely blackened. The low Na contribution, contrary to that expected for marine aerosol, is readily explained thanks to the identification of calomel (Hg_2Cl_2) by Raman.

Whereas conversely, the rest of the points of Rooms G, Q and I (red, blue and yellow points in Fig. 5C, see location in Fig. 3 and S5 to S9) shows a correlation between Na, K and CaF, already visually observed in Fig. 2, S6 and S17.

Even if Na–K salts were identified in Room I (GC_I:36, 41, 42), where syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$), mirabilite ($Na_2SO_4 \cdot 10H_2O$) and apthitalite were detected by Raman (see Fig. S19), F^- -bearing species (e.g. CaF_2) remained unnoticed. LIBS chemometric data treatment facilitates the determination of occurrences of this halide next to alkali metals sulfates on efflorescences and on the surface of mural paintings. These evidences confirm that groundwater and pyroclastic materials are relevant degradation sources.

According to Table 1, Na and K should be inversely correlated to infer the influence of Vesuvian groundwater. Nevertheless, none of the mentioned ion sources acts separately. Hence, the joint contribution of groundwater and pyroclastic materials is evidenced by high CaF intensities, whereas the medium-high intensities of Na and K in volcanic emissions mask the medium-low Na values expected for groundwater.

4. Conclusions

In-situ qualitative screening by LIBS has proven to be a suitable strategy for the detection and evaluation of the distribution of halogens (CaF and CaCl) and alkali metals (K and Na) on the mural paintings of the Archaeological Park of Pompeii. The qualitative distribution maps could help to identify high impact areas when making decisions regarding their conservation. These data will be extremely relevant to assist conservation protocols of the mural paintings of this archaeological site, as well as others that suffer the impact of ion sources. Moreover, the approach here developed about the in-situ LIBS detection and mapping of halides could be conveniently extended to other scientific disciplines such as building materials science, geochemistry, and so on.

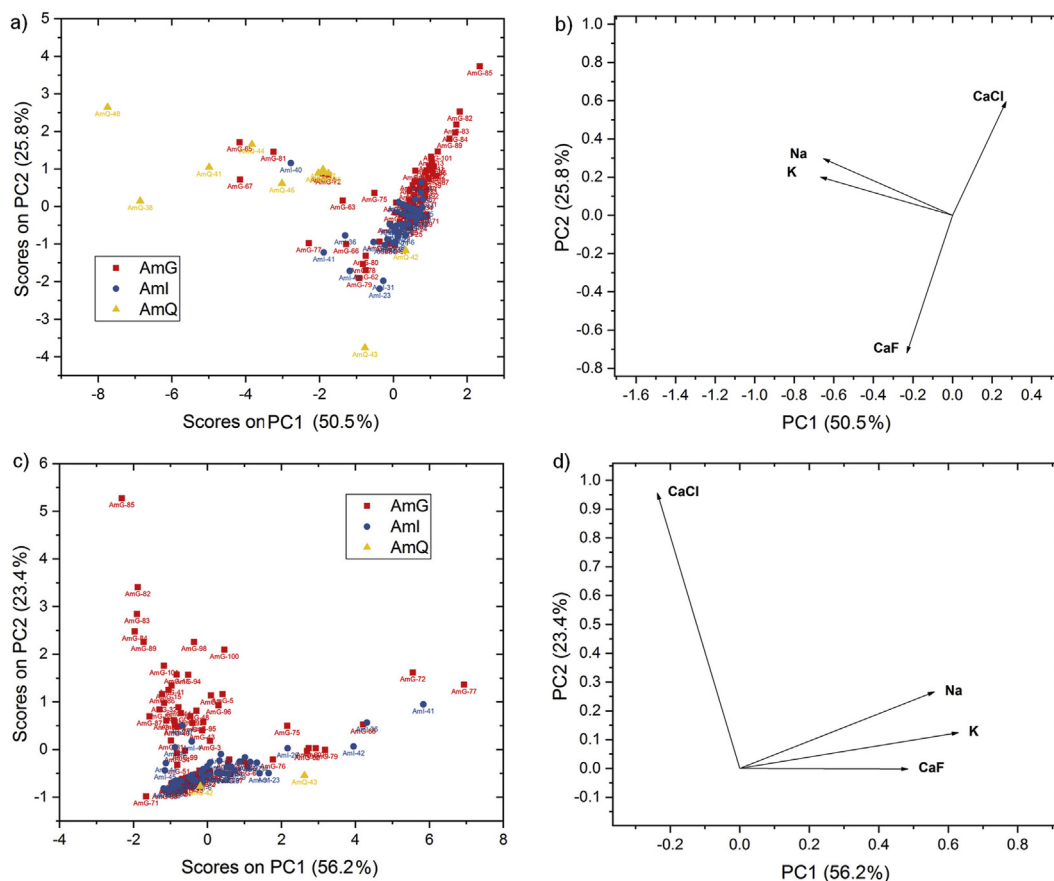


Fig. 5. Principal Component Analysis for the LIBS dataset (CaF, CaCl, Na and K) of the House of the Golden Cupids: A) score and B) loading plots for PC1 and PC2 (GC-G: Room G, GC-Q: Room Q, GC-I: Room I). C) Score and D) loading plots for PC1 and PC2 of the same LIBS dataset after excluding the strong influence of the points associated to restoration mortars. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

In this work, the tracking of fluorine distribution to detect the impact of volcanogenic ion sources has been demonstrated to be essential. In fact, this is the first time that this last halide has been detected in situ on archaeological mural paintings.

Fluorine has mainly accumulated in the lower part of the studied sample paintings, in areas especially related to efflorescences. Concretely, in the basement of the House of Ariadne, this halide is detected both in areas with superficial deposits of pyroclastic materials and in apparently cleaned areas. In this last case, fluorine could be present as non-visible micrometric size pyroclastic deposits or either as salts formed by pyroclastic materials leaching or groundwater capillary infiltrations.

Of special interest is the presence of whitish crusts on the mural paintings, since the evaluation of the fluorine presence can mark the influence of volcanogenic sources. Additionally, if those patinas undergo solubilization processes, soluble ions (F^- among others) could be mobilized to other areas, promoting the crystallization of new F-salts and therefore a subsequent deterioration process.

In the present work, it has also been demonstrated that the groundwater of Pompeii is enriched in Na^+ , K^+ , F^- , Cl^- , SO_4^{2-} and NO_3^- . According to thermodynamic modeling, the precipitation of CaF_2 can occur. However, to explain the formation of specific sulfates such as apthitalite, experimentally detected, much higher concentrations of SO_4^{2-} , Na^+ and K^+ than those provided by groundwater or pyroclastic materials are needed [10]. Its identification in the areas close to the restoration mortar in Room Q of the House of the Golden Cupids confirms that these restoration materials could act as reservoir of SO_4^{2-} , Na^+ and K^+ , necessary to explain

its precipitation. However, the direct impact of the pyroclastic density currents of the 79 AD eruption should not be discarded as a source of sulfates in Room G or Room I, where the role of the restoration mortars is not clear.

The two PCA models conducted with the LIBS data matrices of the mural paintings of both houses offered identical conclusions. Therefore, this coincident PCA result is proposed as a reference to determine the influence of the main impact sources causing salt crystallization in roof-protected – and not directly impacted by rainfall – Pompeian mural paintings.

In the future, additional PCA should be conducted with LIBS data obtained from rainfall-exposed mural paintings to ascertain the impact of this ion source after years of exposure. Additional rainwater samples should be collected at least four times over the span of a year in order to detect seasonal high ion concentrations that may turn rainwater into a sporadic efflorescences source. Finally, to evaluate the inclusion of F originating from the water used to prepare the mortars, additional analyses on *arriccio* and *intonaco* of mural paintings should be conducted. Moreover, a possible F contribution coming from the original composition of the pigments should also be explored.

CRediT authorship contribution statement

Silvia Pérez-Diez: Conceptualization, Methodology, Investigation, Writing – original draft, Visualization. **Luis Javier Fernández-Menéndez:** Methodology, Software, Formal analysis, Data curation, Writing – review & editing. **Marco Veneranda:** Investigation,

Writing – review & editing. **Héctor Morillas**: Investigation, Writing – review & editing. **Nagore Prieto-Taboada**: Investigation, Writing – review & editing. **Silvia Fdez-Ortiz de Vallejuelo**: Investigation, Writing – review & editing. **Nerea Bordel**: Methodology, Formal analysis, Writing – review & editing. **Alberta Martellone**: Resources. **Bruno De Nigris**: Resources. **Massimo Osanna**: Resources. **Juan Manuel Madariaga**: Investigation, Writing – review & editing. **Maite Maguregui**: Conceptualization, Methodology, Investigation, Supervision, Project administration, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The research leading to these results has received funding from “la Caixa” Foundation (Silvia Pérez-Diez, ID 100010434, Fellowship code LCF/BQ/ES18/11670017). This work has been supported by the Spanish Agency for Research AEI (MINECO- FEDER /UE) through the projects MADyLIN (BIA2017-87063-P) and MINECO-17-CTQ2016-77887-C2-1-R, and the Government of the Principality of Asturias (GRUPIN IDI/2018/000186). The authors thank for technical and human support provided by the laboratory Raman-LASPEA of SGiker (UPV/EHU/ ERDF, EU). Eusebio Real and Adolfo Cobo (University of Cantabria) are kindly thanked for the OCT measurements and Arturo Sánchez-Palacio for his suggestions on the PCA. Francesco Caruso (SIK-ISEA) is greatly acknowledged for the revision of the manuscript and Slawka Grabowska for the language revision and editing of the text. Florian Seiler and Peter Grunwald, (German Archaeological Institute, DAI), are also acknowledged for their permission to reproduce herein the reconstructions of the rooms of the House of the Golden Cupids, included in the book *Häuser in Pompeji, 10 Bde, Bd.5, Casa degli Amorini Dorati (VI 16, 7.38)*.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.aca.2021.338565>.

References

- [1] The Great Pompeii project, Pompeii sites. <http://pompeisites.org/en/the-great-pompeii-project/> accessed July 31, 2020.
- [2] M. Maguregui, U. Knuutinen, I. Martínez-Arkarazo, A. Giakoumaki, K. Castro, J.M. Madariaga, Field Raman analysis to diagnose the conservation state of excavated walls and wall paintings in the archaeological site of Pompeii (Italy). *J. Raman Spectrosc.* 43 (2012) 1747–1753, <https://doi.org/10.1002/jrs.4109>.
- [3] J.M. Madariaga, M. Maguregui, K. Castro, U. Knuutinen, I. Martínez-Arkarazo, Portable Raman, DRIFTS, and XRF analysis to diagnose the conservation state of two wall painting panels from Pompeii deposited in the Naples national archaeological museum (Italy). *Appl. Spectrosc.* 70 (2016) 137–146, <https://doi.org/10.1177/0003702815616589>.
- [4] N. Prieto-Taboada, S. Fdez-Ortiz De Vallejuelo, M. Veneranda, I. Marcaida, H. Morillas, M. Maguregui, K. Castro, E. De Carolis, M. Osanna, J.M. Madariaga, Study of the soluble salts formation in a recently restored house of Pompeii by in-situ Raman spectroscopy. *Sci. Rep.* 8 (2018), <https://doi.org/10.1038/s41598-018-19485-w>.
- [5] M. Veneranda, N. Prieto-Taboada, S. Fdez-Ortiz de Vallejuelo, M. Maguregui, H. Morillas, I. Marcaida, K. Castro, J.M. Madariaga, M. Osanna, In-situ multi-analytical approach to analyze and compare the degradation pathways jeopardizing two murals exposed to different environments (Ariadne House, Pompeii, Italy). *Spectrochim. Acta, Part A* 203 (2018), <https://doi.org/10.1016/j.saa.2018.05.115>.
- [6] I. Marcaida, M. Maguregui, S. Fdez-Ortiz de Vallejuelo, H. Morillas, N. Prieto-Taboada, M. Veneranda, K. Castro, J.M. Madariaga, 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. Bioanal. Chem.* 409 (2017) 3853–3860, <https://doi.org/10.1007/s00216-017-0329-3>.
- [7] I. Marcaida, M. Maguregui, H. Morillas, N. Prieto-Taboada, M. Veneranda, S. Fdez-Ortiz de Vallejuelo, A. Martellone, B. De Nigris, M. Osanna, J.M. Madariaga, In situ non-invasive multi-analytical methodology to characterize mosaic tesserae from the House of Gilded Cupids, Pompeii. *Herit. Sci.* 7 (2019) 3, <https://doi.org/10.1186/s40494-019-0246-1>.
- [8] G. Scherer, Stress from crystallization of salt. *Cement Concr. Res.* 34 (2004) 1613–1624, <https://doi.org/10.1016/j.cemconres.2003.12.034>.
- [9] R. Wüst, C. Schlüchter, The origin of soluble salts in rocks of the thebes mountains, Egypt: the damage potential to ancient Egyptian wall art. *J. Archaeol. Sci.* 27 (2000) 1161–1172, <https://doi.org/10.1006/jasc.1999.0550>.
- [10] S. Pérez-Diez, L.J. Fernández-Menéndez, H. Morillas, A. Martellone, B.D. Nigris, M. Osanna, N. Bordel, F. Caruso, J.M. Madariaga, M. Maguregui, Elucidation of the chemical role of the pyroclastic materials on the state of conservation of mural paintings from Pompeii. *Angew. Chem. Int. Ed.* 60 (2021) 3028–3036, <https://doi.org/10.1002/anie.202010497>.
- [11] J.M. Madariaga, M. Maguregui, S. Fdez-Ortiz de Vallejuelo, U. Knuutinen, K. Castro, I. Martínez-Arkarazo, A. Giakoumaki, A. Pitarch, 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.* 45 (2014) 1059–1067, <https://doi.org/10.1002/jrs.4611>.
- [12] I. Angelini, Y. Asscher, M. Secco, M. Parisatto, G. Artioli, The pigments of the frigidarium in the Sarno Baths, Pompeii: identification, stratigraphy and weathering. *J. Cult. Herit.* 40 (2019) 309–316, <https://doi.org/10.1016/j.culher.2019.04.021>.
- [13] N. Prieto-Taboada, S. Fdez-Ortiz de Vallejuelo, A. Santos, M. Veneranda, K. Castro, M. Maguregui, H. Morillas, G. Arana, A. Martellone, B. de Nigris, M. Osanna, J.M. Madariaga, Understanding the degradation of the blue colour in the wall paintings of Ariadne’s house (Pompeii, Italy) by non-destructive techniques. *J. Raman Spectrosc.* (2020) 1–10, <https://doi.org/10.1002/jrs.5941>.
- [14] V. Allocca, S. Coda, P. De Vita, B. Di Rienzo, L. Ferrara, A. Giarra, O. Mangoni, L. Stellato, M. Trifuoggi, M. Arienzo, Hydrogeological and hydrogeochemical study of a volcanic-sedimentary coastal aquifer in the archaeological site of Cumae (Phlegraean Fields, southern Italy). *J. Geochem. Explor.* 185 (2018) 105–115, <https://doi.org/10.1016/j.gexplo.2017.11.004>.
- [15] M. Cangemi, S. Speziale, P. Madoniu, W. D’Alessandro, D. Andronico, S. Bellomo, L. Brusca, K. Kyriakopoulos, Potentially harmful elements released by volcanic ashes: examples from the Mediterranean area. *J. Volcanol. Geoth. Res.* 337 (2017) 16–28, <https://doi.org/10.1016/j.jvolgeores.2017.03.015>.
- [16] P. Sahu, Fluoride pollution in groundwater, in: P.K. Sikdar (Ed.), *Groundwater Development and Management: Issues and Challenges in South Asia*, Springer International Publishing, Cham, 2019, pp. 329–350, https://doi.org/10.1007/978-3-319-75115-3_14.
- [17] P. López-Arce, A. Zornoza-Indart, C. Vázquez-Calvo, M. Gomez-Heras, M.A. de Buergo, R. Fort, Evaluation of portable Raman for the characterization of salt efflorescences at petra. *Jordan, Spectrosc. Lett.* 44 (2011) 505–510, <https://doi.org/10.1080/00387010.2011.610411>.
- [18] M. Gaft, L. Nagli, N. Eliezer, Y. Groisman, O. Forni, Elemental analysis of halogens using molecular emission by laser-induced breakdown spectroscopy in air. *Spectrochim. Acta, Part B* 98 (2014) 39–47, <https://doi.org/10.1016/j.sab.2014.05.011>.
- [19] C. Álvarez-Llamas, J. Pisonero, N. Bordel, Quantification of fluorite mass-content in powdered ores using a Laser-Induced Breakdown Spectroscopy method based on the detection of minor elements and CaF molecular bands. *Spectrochim. Acta, Part B* 100 (2014) 123–128, <https://doi.org/10.1016/j.sab.2014.07.024>.
- [20] T. Dietz, J. Klose, P. Kohns, G. Ankerhold, Quantitative determination of chlorides by molecular LIBS. *Spectrochim. Acta, Part B* 152 (2019) 59–67, <https://doi.org/10.1016/j.sab.2018.12.009>.
- [21] Istituto Superiore per la Protezione e la Ricerca Ambientale, Istituto Superiore per La Protezione e La Ricerca Ambientale. <https://www.isprambiente.gov.it/en>, 2021 accessed January 19, 2021.
- [22] M. Veneranda, N. Prieto-Taboada, S. Fdez-Ortiz de Vallejuelo, M. Maguregui, H. Morillas, I. Marcaida, K. Castro, J.M. Madariaga, M. Osanna, Biodeterioration of Pompeian mural paintings: fungal colonization favoured by the presence of volcanic material residues. *Environ. Sci. Pollut. R.* 24 (2017), <https://doi.org/10.1007/s11356-017-9570-8>, 19599–19608.
- [23] D. Oswald, Entwicklung und Funktionen der Mehrstöckigkeit in der frühkaiserzeitlichen Wohnarchitektur in Pompeii. <https://www.sub.uni-hamburg.de/startseite.html>, 2016 accessed July 22, 2020.
- [24] L. Pedroni, La casa di N. Popidius Priscus a Pompeii (VII, 2, 20) : contributi allo studio dell’edificio (indagini 2003–2005). *Vesuviana : Int. J. Archaeol. Hist.-Stud. Pompeii and Herculaneum* 4 (2012) 111–134.
- [25] E.A. Kaszewska, M. Sylwestrzak, J. Marczak, W. Skrzeczanowski, M. Iwanicka, E. Szmit-Naud, D. Anglos, P. Targowski, Depth-resolved multilayer pigment identification in paintings: combined use of laser-induced breakdown spectroscopy (LIBS) and optical coherence Tomography (OCT). *Appl. Spectrosc.* 67 (2013) 960–972, <https://doi.org/10.1366/12-06703>.
- [26] F. Poggialini, G. Fiocco, B. Campanella, S. Legnaioli, V. Palleschi, M. Iwanicka, P. Targowski, M. Sylwestrzak, C. Invernizzi, T. Rovetta, M. Albano, M. Malagodi, Stratigraphic analysis of historical wooden samples from ancient bowed string instruments by laser induced breakdown spectroscopy. *J. Cult.*

- Herit. 44 (2020) 275–284, <https://doi.org/10.1016/j.culher.2020.01.011>.
- [27] R. Piovesan, R. Siddall, C. Mazzoli, L. Nodari, The Temple of Venus (Pompeii): a study of the pigments and painting techniques, *J. Archaeol. Sci.* 10 (2011) 2633–2643, <https://doi.org/10.1016/j.jas.2011.05.021>.
- [28] M. Cotte, J. Susini, N. Metrich, A. Moscato, C. Gratziu, A. Bertagnini, M. Pagano, Blackening of Pompeian cinnabar paintings: X-ray microspectroscopy analysis, *Anal. Chem.* 78 (2006) 7484–7492, <https://doi.org/10.1021/ac0612224>.
- [29] D. Ducci, M. Sellerino, Natural background levels for some ions in groundwater of the Campania region (southern Italy), *Environ. Earth. Sci.* 67 (2012) 683–693, <https://doi.org/10.1007/s12665-011-1516-8>.
- [30] A.E. Charola, Acid rain effects on stone monuments, *J. Chem. Educ.* 64 (1987) 436, <https://doi.org/10.1021/ed064p436>.
- [31] P. Merello, F.-J. García-Diego, M. Zarzo, Microclimate monitoring of Ariadne's house (Pompeii, Italy) for preventive conservation of fresco paintings, *Chem. Cent. J.* 6 (2012) 145, <https://doi.org/10.1186/1752-153X-6-145>.