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Elucidation of the Chemical Role of the Pyroclastic Materials on the State of Conservation of Mural Paintings from Pompeii

Silvia Pérez-Diez,^[a] Luis Javier Fernández-Menéndez,^[b] Héctor Morillas,^{[a][c]} Alberta Martellone,^[d] Bruno De Nigris,^[d] Massimo Osanna,^[e] Nerea Bordel,^[b] Juan Manuel Madariaga^[a] and Maite Maguregui^[f]

^[a] 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

*Email: silvia.perezd@ehu.eus

^[b] Department of Physics, Faculty of Sciences, University of Oviedo, Asturias, Spain

^[c] Department of Didactics of Mathematics and Experimental Sciences, Faculty of Education and Sport, University of the Basque Country (UPV/EHU), Vitoria-Gasteiz, Basque Country, Spain

^[d] Applied Research Laboratory of the Archaeological Park of Pompeii, via Plinio 4, Pompeii, Italy

^[e] Former General Director of the Archaeological Park of Pompeii, via Plinio 4, Pompeii, Italy

^[f] Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country (UPV/EHU), P.O. Box 450, 01080 Vitoria-Gasteiz, Basque Country, Spain

*Email: maite.maguregui@ehu.eus

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Abstract: Pyroclastic strata have always been thought to protect the archaeological remains of the Vesuvian area (Italy), hence allowing their conservation throughout the centuries. In this work, we demonstrate that they constitute a potential threat for the conservation state of the mural paintings of Pompeii. The ions that could be leached from them, together with the influence of the groundwater rich in ions coming from the volcanic soil/rocks, may contribute to the crystallisation of salts. Thermodynamic modelling not only allowed to predict which salts can precipitate from these leaching events, but also assisted the identification of additional sources of mainly sulfates and alkali metals, to explain the formation of the sulfates identified in efflorescences from the mural paintings of Pompeii. For the future, fluorine, only related to a volcanic origin, can be proposed as a marker to monitor in situ the extension of the impact in the mural paintings of Pompeii.

Introduction

The ancient city of Pompeii was buried under ash and pumice in 79 AD as a consequence of the volcanic eruption of Mount Vesuvius, as described by Pliny the Younger.[1] This fateful event enabled the incomparable preservation of the archaeological remains of the Vesuvian area (namely, architectural structures, mural paintings, mosaics and varied artefacts). The pyroclastic materials ejected sealed Pompeii, acting as a protective shield against the external deterioration sources. The possible risks associated to such pyroclastic deposits have not been studied in depth. However, some recent results suggest that they may also represent a risk that endangers the state of conservation of the wall paintings. Concretely, acting as nutrient for the proliferation of microorganisms.[2][3]

Apart from biocolonisation, the formation of soluble salts in the wall paintings of Pompeii is a well-known pathology, which could lead to the detachment of the pictorial layers. In this sense, most of the works presented until now proposed water capillarity rise, rainfall and previous restoration/consolidation works as sources of ions that can promote salt crystallisations.[4–6] Still, none of them studied the origin of those ions that can migrate to the walls by capillarity. In this sense, groundwater can be enriched by ions leachable from the minerals of volcanic origin of the area. Moreover, over a period of almost 2000 years, the pyroclastic deposits in the burial could release different ions that can be mobilised to the buried archaeological records. This has not been proved yet in the context of the Archaeological Park of Pompeii.

Acid gases, such as H_2S , SO_2 , HCl and HF are usually emitted during a volcanic eruption.[7] Thus, the possible contribution of sulfates, chlorides and fluorides from pyroclastic materials is expected. Moreover, the erosion/weathering of the volcanic soils/minerals of the Vesuvian area can also increase the concentration of these ions in the groundwater of the area.[8]

In the mural paintings of Pompeii, sulfates and chlorides can be formed as a consequence of the influence of additional sources (atmospheric SO_2 , sulfates coming from the mortars used in past consolidations of the paintings, chloride coming from marine aerosol of the Bay of Naples or biocides used in past interventions, etc.).

Apart from the physicochemical damage caused by soluble salts on mural paintings, additional pathologies can be induced by their presence. As some authors pointed out,[9–13] chlorides assist the degradation of specific pigments, such as the blackening process of the cinnabar (α - HgS) pigment, which was used in some of the magnificent panels from Pompeii (e.g. Villa dei Misteri). The influence of other halides, such as fluoride, in this transformation process therefore deserves to be investigated. Hence, the identification of the sources of halides and the magnitude of its impact becomes essential for the preventive conservation of certain pigments, such as the red cinnabar.

In most of the soluble salts crystallised on mural paintings of Pompeii, sulfates and nitrates have been previously detected.[5,6] Less efforts have been done in the detection of halides. Since fluoride is most likely related to the pyroclastic deposits or volcanic soils/minerals of the area, its identification in the soluble salts formed on the archaeological records of the Vesuvian area affected by the eruption of the 79 AD might act as an indicator of their influence on their degradation.

Bearing in mind that the sampling procedure is quite restricted at the Archaeological Park of Pompeii, non-invasive methodologies using portable instrumentation should be an appropriate analysis alternative to conventional laboratory studies. Fluorine is not easily detectable by

portable analytical techniques due to its low atomic number. Nonetheless, in recent years, Laser Induced Breakdown Spectroscopy (LIBS) has become an emerging technique for the detection of halogens. Still, it is a challenging task because the most intense emission lines of these atoms are located in the vacuum ultraviolet (VUV) spectral region, whose acquisition requires complex experimental set-ups. Other procedures use the near infrared (NIR) lines, which are less intense and yield poor limits of detection (LOD). On the contrary, the acquisition of molecular spectra from LIBS plasmas is very useful for the detection of halogens.[14–17] Molecular emission bands from CaF and CaCl radicals have been attiring great attention within the LIBS community since their first application by Gaft et al.[18] Although specific applications have been developed for reinforced concrete,[15] none has been presented for materials of cultural significance.

Taking into account that fluorine can only be related to a volcanic origin, the same has been selected to trace the influence of pyroclastic deposits in the formation of soluble salts on the wall paintings of Pompeii. To this aim, pyroclastic deposits (ash, lapilli and their mixtures) from the Archaeological Park of Pompeii, which have been (and in some cases still are) in contact with mural paintings, have been considered. Special attention was paid to the identification of possible mineral phases rich in halides through X-Ray Diffraction (XRD) and Raman microspectroscopy. LIBS was also implemented in the analytical methodology not only as laboratory technique, but also as a portable instrument (p-LIBS), to detect directly the presence of halides (Cl⁻ and F⁻) in the volcanic materials from the Archaeological Park. The ability of a commercial p-LIBS system for the detection of both halides was also validated thanks to the benchtop LIBS observations. Finally, the transfer of the ions that can be leached from the pyroclastic materials to the mural paintings, assisted by rainwater and groundwater, was modelled through a leaching experiment and a subsequent quantification of the dissolved ions. The obtained values were subjected to geochemical modelling to thermodynamically evaluate the salts that may precipitate from the leachates. To obtain experimental evidences of the fluoride present – among others – in the salts crystallised on the wall paintings, efflorescence samples from two Pompeian wall paintings located in two different houses were analysed by XRD, Raman microspectroscopy and p-LIBS.

Results and Discussion

Mineralogical characterisation of the pyroclastic deposits

In this work, a series of pyroclastic materials taken at the Archaeological Park of Pompeii have been studied (see Figure 1 and Table S1). Four stratigraphies, representing the emission events that took place in the 79 AD eruption, were sampled inside the Archaeological Park of Pompeii at the Necropoli di Porta Nola (VN), Porta di Stabia (PS), Insula dei Casti Amanti (CA) and Porta Marina (PM). In all cases, the higher the number of the stratum (e.g. 7), the more internal the sampling was accomplished. Additionally, ash (ASH) and lapilli (LAP) materials out of archaeological context and lapilli from the basement of the House of Ariadne (ARI) were also included in the investigations.

Table S2 reports a summary of all the mineralogical phases detected in each pyroclastic stratum by XRD. Neither F- nor Cl-minerals were detected by this technique, probably because they are part of the amorphous material or because their presence is below the LOD (around 1-3%)[19] of the technique. Nonetheless, the OH⁻ group of certain micas, such as biotite, can be substituted by F⁻. Hence, a further optical microscopy study of certain volcanic samples (PS 1, PS 3, PS 7, VN 4, CA 1, ARI) was carried out in order to assess the presence of F-rich micas. This revealed the

abundance of brown micas in PS 1, PS 7, VN 4 and ARI, whereas CA 1 contained white mica crystals. Micas were less abundant in PS 3.

Mica crystals were selected in the aforementioned samples and subjected to single crystal XRD[20] to verify if the crystallographic parameters agreed with the presence of fluorine in these minerals. It is relevant to recall that the c unit cell parameters differ between biotite (F = 1.1%, c = 10.23 Å) and fluorphlogopite (F = 8.7%, c = 10.14 Å) and that the shortest c unit cell parameter, the higher OH⁻ → F⁻ and/or OH⁻ → O²⁻ substitution.

The pyroclastic deposits offered the following c unit cell parameters: PS 1, c = 10.25 Å; PS 3, c = 10.28 Å; PS 7, c = 10.24 Å; ARI, c = 10.18 Å; VN 4, c = 20.28 Å, being thus closer to the c unit cell of biotite. However, fluorine may be also present in other crystalline minerals, as well as in non-vitreous amorphous phases. Thus, further studies were accomplished to verify the presence of fluorine and chlorine in the pyroclastic materials and to assess the availability of these halides in the leaching process, which could point out to their accumulation in amorphous species.

Even if simple halides, such as NaCl, are not detectable by Raman spectroscopy, there are other F- and Cl-bearing minerals, common in volcanic environments, which present a valuable Raman signature (e.g., fluorite, phlogopite, humite, chondrodite, vesuvianite, chlorocalcite, eriochalcite or paratacamite).[21] However, after an exhaustive analysis of the pyroclastic strata through micro-Raman spectroscopy, it was impossible to detect any F- or Cl-mineral phase among the identified compounds (see Supporting Information for further details).

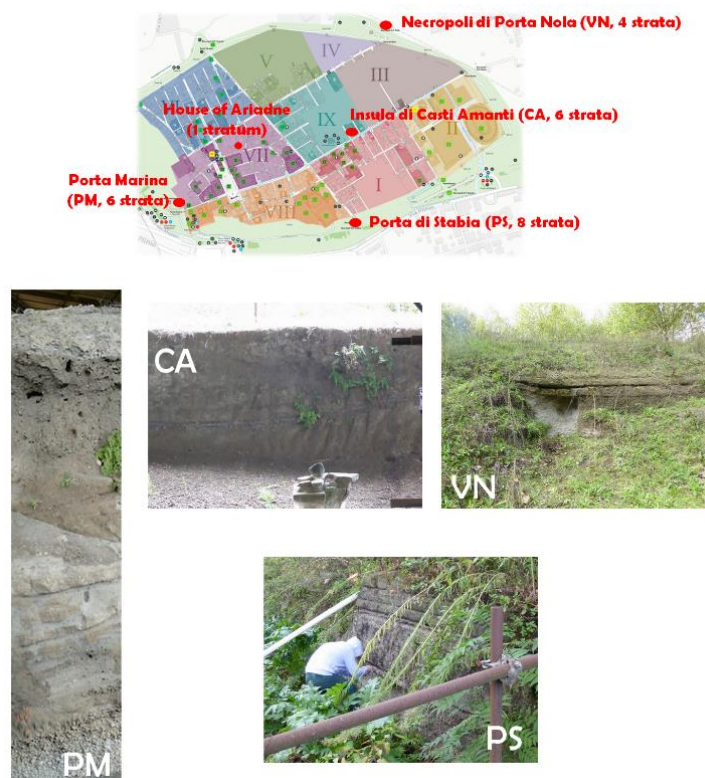


Figure 1. Localisation of the volcanic strata sampled for the characterisation inside the Archaeological Park of Pompeii and details of some of the stratigraphies. The map of the Archaeological Park of Pompeii was modified after the original version available at <https://pompeisites.org>.

Halides detection in the pyroclastic strata using portable and benchtop LIBS

Pyroclastic materials of the Vesuvian area contain F- and Cl-compounds,[20,22,23] albeit not at a high enough content or as crystalline phases identifiable by XRD. Since neither the XRD nor the Raman analyses offered conclusive information about the presence of fluorine and/or chlorine in the analysed samples, LIBS measurements were conducted with the portable commercial instrument (p-LIBS) to evaluate its ability for the in situ detection of the molecular bands of the aforementioned halides. Afterwards, the benchtop equipment was incorporated into the analytical methodology to confirm the adequacy of the performance of p-LIBS for the identification of these halides.

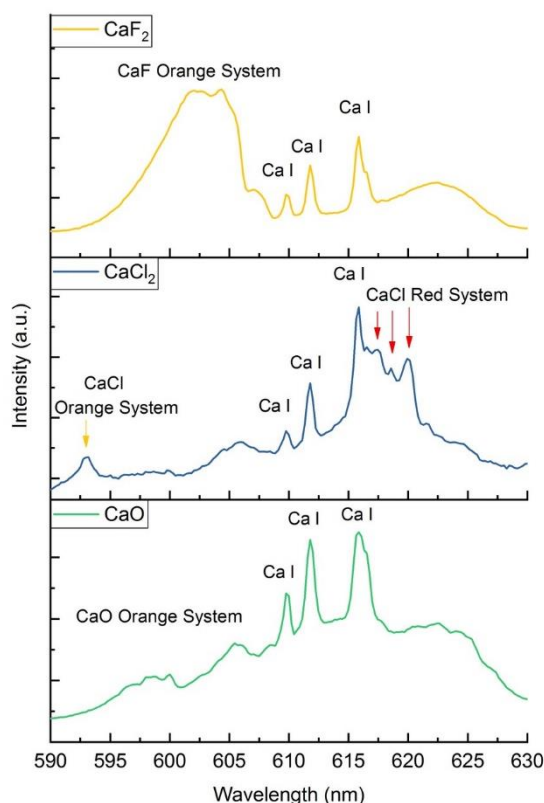


Figure 2. LIBS spectra of CaF, CaCl and CaO molecular bands between 590 and 630 nm, acquired with the portable LIBS instrument on pressed pellets of pure compounds.

To begin with, pressed pellets of pure compounds (CaF₂, CaCl₂ and CaO) were analysed with p-LIBS in order to have the consequent comparison spectra. Figure 2 presents the molecular bands of interest to be found in the studied spectral range (590-630 nm): orange systems of CaF and CaCl (the red system of CaCl is often completely interfered by the CaO orange system).

Thereafter, the pyroclastic strata were measured using p-LIBS. The integrated values for the CaF and CaCl molecular systems, measured with p-LIBS for all stratigraphies are provided in Tables S3 to S7. The samples gave rise to spectra where the orange systems of CaF, CaCl and CaO (see Figure 3A) are present. The CaF and CaCl orange systems are only recognisable in all strata after the subtraction of the CaO reference spectrum (see Figure 3B).

Regarding the orange system of CaCl (see Figure S1), it was detected via the portable instrument in PS 3-4, 6-8; CA 2-5 and 7; PM 1 and 7 and VN 3, as well as in the lapilli sampled in the basement of the House of Ariadne. On the other hand, the CaCl head at 593.40 nm was less noticeable or

barely distinguishable from the background in the ash and lapilli sampled in 2011, PS 1-2, 5; CA 1, 3-4; PM 2-5 and VN 2, 4-5.

Afterwards, the complete stratigraphy of Porta Marina was analysed using the benchtop LIBS equipment to verify if p-LIBS had yielded satisfactory results, especially regarding chlorine. The integrated values for the CaF and CaCl molecular systems, measured with the benchtop LIBS for the stratigraphy of Porta Marina, are provided in Table S8. Although the molecular bands were less intense in PM 2 and 3, the CaF molecular emission was identified in the spectra of all strata, thus confirming the presence of fluorine in both samples, as already assessed by p-LIBS. The head at 593.40 nm attributable to CaCl (orange system) was identified in all strata, being particularly intense in PM 1, PM 5-7 and weaker in PM 2-4.

The p-LIBS equipment had only been able to detect CaCl in PM 1 and PM 7 of this stratigraphy (two of the samples where the molecular band was found to be more intense using the benchtop instrument) and not in PM 2-5. This confirms that the portable equipment has a slightly lower sensitivity for CaCl. A comparison between the benchtop and the p-LIBS spectra of PM 2 is reported in Figure S2.

Considering that the emission of CaCl is less intense, and still interfered by the orange system of CaO, and taking into account the lower sensitivity of the p-LIBS compared to the benchtop instrument, it is possible that the commercial p-LIBS would not be able to detect chlorine in situ below a certain concentration.

Leaching test of pyroclastic deposits and quantification of solubilised ions by Ion Chromatography (IC)

The pyroclastic materials were subjected to leaching experiments (see more details in Supporting Information) without a previous grinding process. In this sense, the direct leaching of the pyroclastic deposits in the burial has been simulated. In Tables S9-S16 (see Supporting Information), the concentrations of five cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) and seven anions (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) detected by Ion Chromatography in the leachate of each sample are shown. The values of soluble ions in the pyroclastic materials are related to the water-soluble compounds adhered to the surface of the particles, since there might be non- or scarcely leachable Cl- or F-bearing minerals in the samples (e.g., if they are tightly bounded in the atomic structure). In addition, fluorine bounded to certain amorphous phases, such as allophane or imogolite, is only leached with oxalic acid (a microbial metabolite),[24] but not with water. These experiments were useful to evaluate the hypothesis of the migration of these ions to the walls, but not to perform a complete quantification of both leachable and non-leachable forms. Nitrates, nitrites and phosphates can be related to organic material present in the volcanic soils and samples. Finally, sulfates can come from groundwater that periodically saturate the Roman paleosol,[25] volcanic emissions, atmospheric pollutants or the marine aerosol.

It is necessary to remark that the pyroclastic deposits analysed in this work are related to stratigraphies eroded with the passage of time and due to their exposure to the surrounding environment in the opened excavation area. Therefore, the leachable ions that can be quantified in this experiment are related to those remaining after the mentioned events.

Regarding the stratigraphy of Insula dei Casti Amanti, CA 7 is constituted by lapilli and showed high concentrations of leachable chloride (30 ± 4 mg/L), nitrate (27 ± 4 mg/L), potassium (21 ± 3 mg/L) and calcium (20.6 ± 0.8 mg/L). These values corroborate the results from the LIBS

spectrum, which presented the most intense CaCl band of the whole stratigraphy. The leachate of stratum CA 5 is also enriched in potassium (23.5 ± 0.4 mg/L) and sodium (11.0 ± 0.4 mg/L). On the other hand, the highest values of leachable fluoride were found in stratum CA 1 (1.3 ± 0.2 mg/L) and CA 3 (1.0 ± 0.3 mg/L).

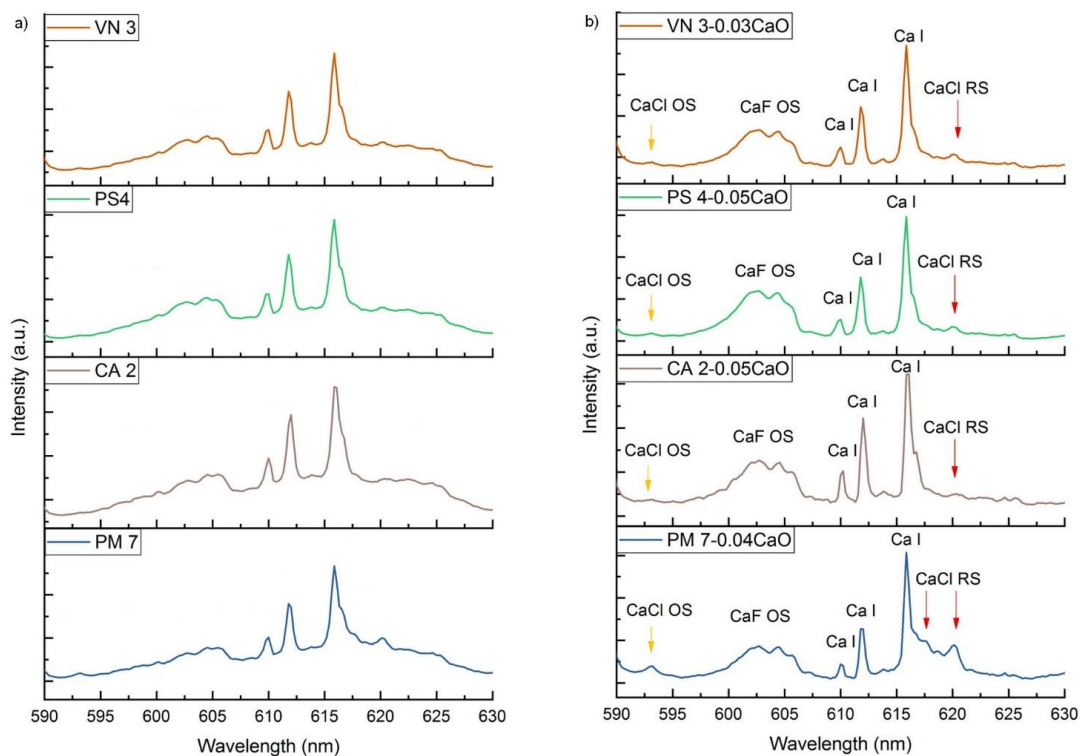


Figure 3: A) Raw LIBS spectra of Pompeian pyroclastic materials between 590 and 630 nm. B) LIBS spectra of Pompeian pyroclastic materials after subtracting the reference spectrum of CaO acquired in the same measurement conditions. OS stands for Orange System and RS for Red System.

Concerning the stratigraphy of Necropoli di Porta Nola, the highest leachable fluoride content was detected in stratum VN 4 (1.9 ± 0.2 mg/L) and VN 5 (1.2 ± 0.4 mg/L). Stratum VN 4 was also the richest in leachable chloride (8.1 ± 0.4 mg/L), sodium (16 ± 1 mg/L) and potassium (43 ± 2 mg/L). Considering that the most intense CaF and CaCl emission bands were found in the spectrum of VN 3, this result supports the different origins of these halides in the stratigraphy, being Cl⁻ and F⁻ in this stratum not as easily leachable as in VN 4 and VN 5.

Strata PS 1, PS 3 and PS 7 of the stratigraphy of Porta di Stabia stood out for the high fluoride (3.6 ± 0.7 , 2 ± 1 and 3.3 ± 0.4 mg/L, respectively) and chloride (23 ± 9 , 140 ± 100 and 239 ± 10 mg/L respectively) concentrations in their leachates, as expected according to the LIBS analyses. The leachable chloride content of stratum PS 6 was also significant: 40 ± 3 mg/L. The more efficient leaching of stratum PS 7 (also evident in terms of sodium (72 ± 4 mg/L), potassium (114 ± 2 mg/L) and calcium (60 ± 20 mg/L) concentrations) might be justifiable by the finer morphology of its grains.

The de-contextualised lapilli sample showed the lowest levels of leachable fluoride (0.14 ± 0.04 mg/L) and chloride (0.5 ± 0.1 mg/L). Leachable fluoride levels were modest as well as in the de-contextualised ash sample and in the lapilli of the House of Ariadne (0.57 ± 0.04 and 0.79 ± 0.02

mg/L, respectively). Nonetheless, this does not imply that these samples have the lowest total fluoride or chloride concentrations, since they might be in non-leachable forms. On the other hand, the lapilli sampled at the basement of the House of Ariadne presented high concentrations of leachable chloride (89 ± 8 mg/L), nitrate (230 ± 20 mg/L) and sulfate (110 ± 20 mg/L).

Sulfates may correspond to volcanic emissions adsorbed onto the surface of the lapilli, be the consequence of the enrichment of the sample with groundwater,[25] as it was taken from the soil of the basement, or relate to the atmospheric pollutant SO_x . Sulfates are generated in water-saturated soils by oxidation of organic sulfur or inorganic sulfide.[25] This leachate showed moderate to high contents of potassium (29.6 ± 0.5 mg/L), magnesium (21 ± 1 mg/L) and, specially, calcium (120 ± 10 mg/L).

The quantitative IC data of the pyroclastic materials were also subjected to a chemometric study to evaluate the correlation among the ions. The Pearson correlation coefficients exhibited the correlation in the leachable content of Na^+ , K^+ , F^- and Cl^- (Na^+F^- : 0.818, Na^+Cl^- : 0.77, K^+F^- : 0.771, K^+Cl^- : 0.893); SO_4^{2-} and Cl^- (0.806) and Ca^{2+} , Mg^{2+} , NO_3^- and SO_4^{2-} ($\text{Ca}^{2+}\text{NO}_3^-$: 0.884, $\text{Ca}^{2+}\text{SO}_4^{2-}$: 0.892, $\text{Mg}^{2+}\text{NO}_3^-$: 0.918, $\text{Mg}^{2+}\text{SO}_4^{2-}$: 0.881), as summarised in Table S17 of Supporting Information.

Thanks to the previous single crystal XRD analyses of the volcanic samples, it was already known that fluoride could also relate to other cations (e.g., Mg^{2+} or Fe^{2+}) in non-soluble mineral forms. The good correlation between Na^+ and F^- and K^+ and F^- possibly indicates the presence of water-soluble NaF, hexafluorides or tetraborofluorides on the surface of the particles.

Calcite was also identified by XRD in almost all volcanic samples. However, since calcite is non-leachable, the correlation established in our test links calcium cations to nitrates and sulfates. However, Vogel and Märker[25] also mentioned the transformation of CaCO_3 in water-soluble $\text{Ca}(\text{HCO}_3)_2$ in soils with a pH between 6.5 and 8.[25] Since carbonates were not included in the ion chromatography analyses, this hypothesis could not be tested in this case. Besides that, although sulfur-compounds are also emitted in volcanic eruptions,[26,27] SO_4^{2-} ions are only correlated with leachable chlorides (0.806) and not fluorides, suggesting an additional input (e.g., the marine aerosol of the bay of Naples or groundwater affecting the Roman paleosol).[25]

Thermodynamic modelling to predict the precipitation of salts from the leachates

Using the concentration values of the ions in each leachate, and after measuring the pH value of the aqueous extracts, saturation indices were calculated with the PHREEQC software at 25 and 10 °C, the latter useful to simulate winter climatic conditions of the area. [28]

Among the calculations for each stratum, the results obtained for strata PS 7, PS 8 and ARI are here presented (see Table 1, which also shows the measured pH of each leachate). As can be noticed, the leachate of PS 7 is almost saturated with respect to fluorite (CaF_2) and PS 8 and ARI are supersaturated at 25 °C. This proves the possible precipitation of this halide, after the migration of the solubilised ions from the pyroclastic deposits to the mural paintings and other buried archaeological records via rainwater or groundwater leaching and subsequent precipitation due to the evaporation of the water that acts as carrier. In addition, the leachate from the basement of the House of Ariadne (ARI) showed the supersaturation of the solution with respect to anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and görgeyite ($\text{K}_2\text{Ca}_5(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$) at 25 and 10 °C, too. Finally, at a temperature of 10 °C, fluorite (CaF_2) would have already precipitated in all three strata, whereas anhydrite and gypsum would be very close to do so in PS 8.

Table 1. Saturation indices (SI) obtained using PHREEQC software for the leaching solutions of strata PS 7, PS 8 and ARI. In this table, only those positive SI or the ones closer to 0 are included.

Stratum	pH	SI at 25 °C	SI at 10 °C	SI at 10 °C, 100x Na ⁺ , K ⁺ , Cl ⁻ and SO ₄ ²⁻ concentrations
PS 7	7.78 ± 0.01	Anhydrite (-1.92)	Anhydrite (-1.92)	Anhydrite (-1.12)
		Fluorite (-0.11)	Fluorite (0.10)	Arcanite (-1.42)
		Gypsum (-1.70)	Gypsum (-1.67)	Fluorite (-0.76)
				Görgeyite (-1.18)
				Gypsum (-0.89)
PS 8	8.21 ± 0.01	Anhydrite (-0.77)	Anhydrite (-0.76)	Anhydrite (0.12)
		Fluorite (1.76)	Fluorite (1.99)	Arcanite (-0.12)
		Gypsum (-0.55)	Gypsum (-0.50)	Fluorite (1.12)
				Görgeyite (6.29)
				Gypsum (0.34)
ARI	7.75 ± 0.01	Anhydrite (0.75)	Anhydrite (0.78)	Anhydrite (3.63)
		Fluorite (2.02)	Fluorite (2.29)	Aphthitalite (1.21)
		Görgeyite (6.03)	Görgeyite (6.34)	Arcanite (1.32)
		Gypsum (0.96)	Gypsum (1.02)	Epsomite (-0.62)
				Fluorite (1.21)
				Görgeyite (25.12)
				Gypsum (3.47)
				Halite (-0.40)
				Mirabilite (-0.94)
				Niter (-0.29)
		Polyhalite (9.85)		
		Sylvite (0.36)		
		Syngenite (4.43)		
		Thenardite (-0.56)		

In-situ experimental evidences and thermodynamic modelling to reveal the nature of the main soluble salts in efflorescences from Pompeian mural paintings

Two samples of Pompeian efflorescences were analysed by XRD, Raman spectroscopy and p-LIBS to identify the nature of the main salts that can be formed on the mural paintings of Pompeii.

Regarding the efflorescence sampled in the wall painting from the west wall of the triclinium of the House of Marcus Lucretius (sample S1), the XRD measurements allowed the determination of apthitalite ($\text{NaK}_3(\text{SO}_4)_2$), arcanite (K_2SO_4) and niter (KNO_3). The presence of apthitalite (Raman bands at 453, 620, 993 and 1204 cm^{-1}), arcanite (Raman bands at 453, 984, 1095, 1110 and 1146 cm^{-1}) and niter (Raman bands at 716 and 1051 cm^{-1}) was also confirmed by Raman analysis (see Figure 4A).

Apart from sulfates, in the p-LIBS spectrum of this efflorescence the CaF orange molecular system was detected (see Figure 4B), representing the first fluorine detection in an efflorescence of Pompeii, a relevant conclusion that confirms the influence of the pyroclastic materials or groundwater in the Pompeian mural paintings. Moreover, the high intensity of unresolved Na I emission lines in this efflorescence may be linked to the presence of apthitalite.

Efflorescence S2 was sampled at a low/middle height of the west wall of the exedra from the House of Ariadne (Room 22). The Raman analyses on it allowed the identification of syngenite ($\text{K}_2\text{Ca}(\text{SO}_4)_2$) thanks to its bands at 982 and 1006 cm^{-1} (see Figure 4A), while the CaCl orange system was clearly identified in the p-LIBS spectra (see Figure 4B). Considering that, according to the concentration of the ions obtained from the leaching experiments of the pyroclastic deposits, it was not possible to thermodynamically predict the formation of chlorides; three situations should be considered to explain the possible precipitation of chloride salts in the efflorescences of the exedra of the House of Ariadne. Either i) a continuous leaching and migration of chlorides from pyroclastic deposits during thousands of years in the burial, ii) a high concentration of chlorides in the groundwater incorporated in the mural through capillarity or iii) an increment of chlorides coming from the diffuse influence of marine aerosol.

In this same S2 efflorescence, it was not possible to identify the presence of fluorine, which could suggest that the concentration of this halide is set below the sensitivity of the p-LIBS detector or that there has been low or non-existent volcanic origin contribution in this wall.

The situation of the underground basement of the House of Ariadne, where pyroclastic material ARI was sampled, is quite different. In a previous work, anhydrite, gypsum and nitratine (NaNO_3) were identified in the efflorescences of this area.[29] Although the precipitation of anhydrite and gypsum was expected in the ARI leachate according to the PHREEQC simulation, even at $25\text{ }^\circ\text{C}$, it was not possible to predict the precipitation of nitratine by the thermodynamic modelling due to the lack of this compound in the PHREEQC databases. Despite the fact that the ARI leachate is the most concentrated in nitrates, which are prone to come from groundwater, since it is an underground basement, the strikingly high water-solubility ($91.2\text{ g}/100\text{ g water at }25\text{ }^\circ\text{C}$)[30] of this salt precludes the supersaturation of the solutions in which it is dissolved, except from extremely dry areas. Hence, in a future work, a seasonal monitoring should be conducted in this basement to evaluate the precipitation of nitrates depending on the climatic conditions.

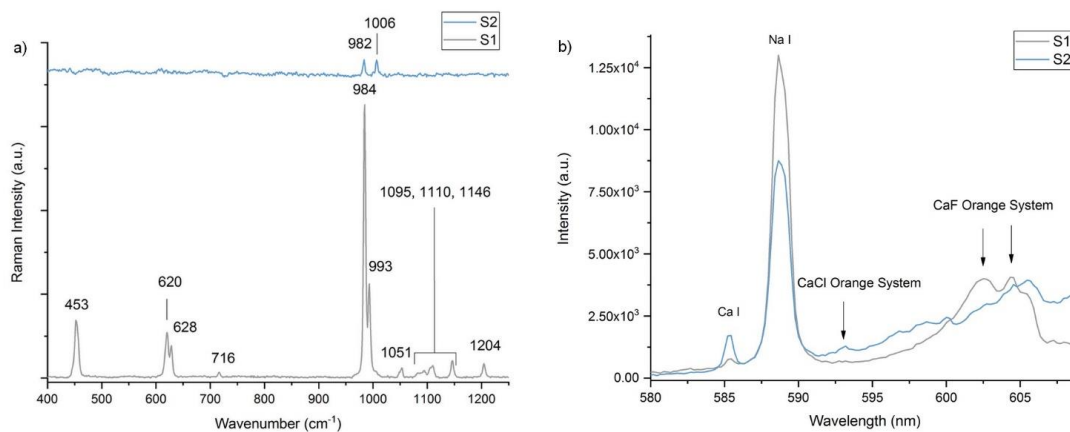


Figure 4. A) Raman spectrum of efflorescence S1, showing the Raman bands of apthitalite (453, 620, 993 and 1204 cm^{-1}), arcanite (453, 984, 1095, 1110 and 1146 cm^{-1}) and niter (716, 1051 cm^{-1}). Raman spectrum of efflorescence S2, showing the Raman bands of syngenite (982 and 1006 cm^{-1}). B) LIBS spectra of samples S1 and S2 showing the emission of the CaF and CaCl orange systems, respectively.

Apthitalite, a sodium-potassium sulfate, has been experimentally detected in sample S1, although this was not thermodynamically predicted only considering the volcanic influence. Bearing in mind that the leachates of pyroclastic deposits are more concentrated in potassium than in sodium (with the exception of two samples, PS 1 and PS 3, see Table S13), an additional non-volcanic source could be suggested as the responsible of the sodium increase in in the triclinium of the House of Marcus Lucretius (S1). Moreover, in this case, other potassium sulfate and nitrate salts were also identified, suggesting an additional input of potassium, sulfates and nitrates in this room of the House of Marcus Lucretius. The same is valid for efflorescence S2 of the exedra of the House of Ariadne, where an unknown chloride and syngenite were detected, indicating the occurrence of other sources of potassium, chlorides and sulfates.

To predict the influence of an additional input of Na^+ , K^+ , Cl^- and SO_4^{2-} , increments of them have been added to the ions concentrations obtained from the leachates of the pyroclastic deposits, to thermodynamically simulate the formation of the aforementioned salts.

To evaluate which salts can precipitate depending on the increments of Na^+ , K^+ , Cl^- and SO_4^{2-} , additional thermodynamic modellings were run. Figure 5A shows the increment in the saturation indices of various sulfates and chlorides when the concentrations of the previously mentioned four ions are increased 25, 50, 75 and 100 times. These increments can also be reached in the real scenario when part of the water of the solution evaporates.

Depending on the pyroclastic deposit, the thermodynamic modelling with the increments does not predict the crystallisation of additional salts (see the case of PS 7 in Table 1 with the maximum increment of 100). However, in specific pyroclastic strata (see PS 8 and ARI in Table 1) the thermodynamic modelling with the maximum increment of 100 times predicts the precipitation of certain sulfates: apthitalite, arcanite, syngenite, etc. In addition, the ARI leachate solution is almost saturated as well with respect to niter (KNO_3), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), halite (NaCl), thenardite (Na_2SO_4) and mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$).

Some of these salts were identified in the efflorescences from the mural paintings considered in this work and in further in situ analyses at the Archaeological Park of Pompeii,[5,31] and are

known to create significant problems in stones and other building materials such as mortars. [32–34]

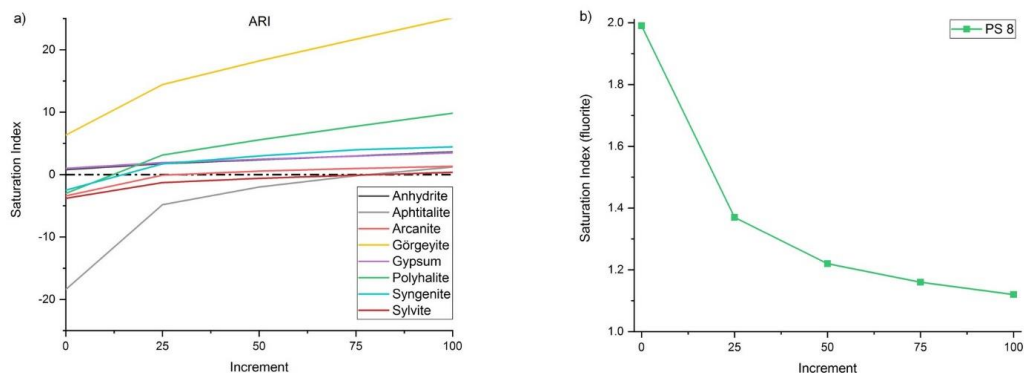


Figure 5. A) Evolution of the saturation indices of various sulfates and halides predicted by the PHREEQC software in the ARI leachate when the Na^+ , K^+ , SO_4^{2-} and Cl^- concentrations are increased 25, 50, 75 and 100 times. B) Decrease of the fluorite saturation index in the PS 8 leachate modelled by the PHREEQC software when the Na^+ , K^+ , SO_4^{2-} and Cl^- concentrations are increased 25, 50, 75 and 100 times.

Special attention should be paid to the formation of sylvite (KCl) in the ARI leachate, which suggests a preferential formation of this alkali metal chloride due to the higher concentration of both ions in the modelling. Moreover, the concentration needed for the supersaturation is more than 75 times higher than the one of the leachate. This could mean that additional inputs of chlorine, such as marine aerosol could play an important role in the crystallisation of chloride salts in the mural paintings of Pompeii.

Regarding the precipitation of fluorite, the increment in the mentioned ions promotes a decrease in its saturation index while the concentrations of Na^+ , K^+ , SO_4^{2-} and Cl^- are increased (see the example of PS 8 in Figure 5B). This might be due to the greater solubility of the combination of fluoride with these cations or to a possible formation of a soluble complex.

Conclusion

Thanks to the analytical methodology developed in this work, it has been demonstrated that fluorine and chlorine can be detected in the pyroclastic materials through the identification of CaF and CaCl molecular bands by p-LIBS. Therefore, in the future, this technique could also be applied as a rapid tool to in situ identify the remains of pyroclastic materials on mural paintings, sometimes difficult to see properly at the naked eye and that should be removed for the proper conservation of the mural paintings.

Bearing in mind that the considered samples are not pristine pyroclastic materials and have already been subjected to natural weathering (almost 2000 years) and leaching processes (exposed strata), the quantitative values here presented do not reflect the maximum water-leachable contents of the non-exposed pyroclastic materials that still remain in the burial. However, the experimental evidences here presented confirm that chlorides and fluorides, among other ions, can migrate from the pyroclastic materials onto the surface of wall paintings and other archaeological records during and after the burial, if remains of pyroclastic materials are not completely removed from the surface of the mentioned items. Therefore, these materials shall be regarded as a possible source of ions, which could take part in different

deterioration process, such as the precipitation of soluble salts, and contribute to the blackening of the red cinnabar from Pompeii in the case of halides.

In the future, the role of groundwater rich in ions coming from the erosion/weathering of the volcanic soils/minerals of the area should be monitored as a parallel source of ions of volcanic origin that can be incorporated in the mural paintings of Pompeii through capillarity. The precipitation of salts assessed thanks to the thermodynamic model and the detection of fluorine and chlorine in the efflorescences of two different mural paintings of two Pompeian houses confirm the real influence of the pyroclastic materials in the walls of Pompeii, which represent a threat for the conservation of mural paintings and probably other archaeological records (e.g. mosaics).

According to the thermodynamic models, an additional input of chlorides is usually required to explain the formation of halides (sylvite) in the mural paintings of Pompeii. The most probable source can be the marine aerosol. In this sense, it cannot be rejected that, in specific cases, halite could be formed in the mural paintings. However, due to its high solubility, this salt is not the favoured one to be explained through water geochemical calculations.

The same trend has been observed for the sulfate salts formation, since to explain the formation of specific ones (e.g. apthitalite and syngenite) an increase in the sulfate ions concentration is needed. Therefore, since these salts were experimentally detected, additional sources of sulfates must have impacted the mural paintings of Pompeii (e.g. anthropogenic SO₂, use of consolidation mortars rich in sulfates in past restorations, etc.).

Moreover, although the Na⁺ concentration was also incremented in the thermodynamic calculations to explain the formation of some salts experimentally detected, the lack of supersaturation of mirabilite and thenardite in most of the cases suggests that a much higher concentration of this alkali metal should be present for the precipitation of these salts. Since mirabilite/thenardite have been widely identified in the murals of Pompeii,[5,31] and considering that sodium is not the most concentrated alkali metal of volcanic origin, an additional source should be identified for the formation of these kind of sulfates (e.g. consolidation mortars rich in alkali metals used in past restorations).

All these evidences lead us to conclude that, from a conservation point of view, the concentration and distribution of both mentioned halides and sulfates should be monitored in a larger scale using p-LIBS and Raman spectroscopy, in order to extract conclusions about the sources of impact, including the influence of pyroclastic materials.

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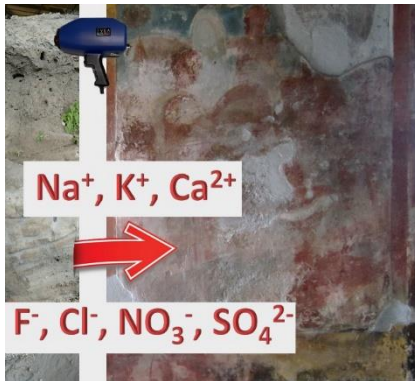
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Pyroclastic materials buried and protected ancient Pompeii throughout the centuries. However, we demonstrate that they could represent a threat for the conservation state of the mural paintings, since rainwater and groundwater cause the leaching and transfer of ions to the mural paintings, promoting cycles of crystallisation of soluble salts. In the case of Pompeii, the latter are one of the main causes of the detachment of the pictorial layers.