CONSERVAR PATRIMÓNIO

International Symposium Archaeology of Colour
Simpósio Internacional Arqueologia da Cor
ARTICLE / ARTIGO

Pigments from Pasargadae and Persepolis in the Metropolitan Museum of Art (NY): recent scientific investigations on four paper squeezes

Pigmentos de Pasárgada e Persépolis no Metropolitan Museum of Art (NY): investigações científicas recentes em quatro moldes em papel

ATEFEH SHEKOFTEH [1*]
ALEXANDER NAGEL [2]
OMID OUDBASHI [3]

1. Department of Scientific Research, Metropolitan Museum of Art, 1000 Fifth Ave, NY 10028, USA
2. Department of Art History, State University of New York, FIT, 227 West 27th Street, NY 10001, USA
3. Department of Conservation, University of Gothenburg, Medicinaregatan 7 B, 41390, Sweden

**shekofte.as@gmail.com*

Abstract

Paper squeezes from architectural features and fragments from Pasargadae and Persepolis in the Metropolitan Museum of Art (MMA) in New York City were examined using microscopic investigation, imaging techniques, and chemical and molecular analyses. The study focused on pigments from (1) an anthropomorphic ear from a relief fragment in Palace P, (2) a fragment of a rosette from the crown of a Lamassu from Gate R ("Gate House"), both in Pasargadae; (3) a stone axe from a delegation depicted on the north façade of the Apadana, and (4) a stone block with a Hebrew inscription from one of the standing door or window jambs of the Tachara at Persepolis. Analyses confirmed red pigments identified in previous studies and revealed new evidence of lazurite as a blue pigment and magnetite as black. The findings can help us construct further aspects of specific ancient polychromatic contexts at Pasargadae and Persepolis.

KEYWORDS
Pasargadae
Persepolis
Pigments
Lazurite
Hematite
Goethite

Resumo

Os moldes em papel retirados de fragmentos arquitetónicos de Pasárgada e Persépolis do Metropolitan Museum of Art (MMA) de Nova Iorque foram caracterizados através de investigação microscópica, técnicas de imagem e análises químicas e moleculares. O estudo centrou-se nos pigmentos de (1) um relevo de uma orelha antropomórfica de um fragmento do Palácio P, (2) um fragmento de uma roseta da coroa de um Lamassu da Porta R ("Casa da Porta"), ambos em Pasárgada; (3) um machado de pedra de uma delegação representada na fachada norte da Apadana, e (4) um bloco de pedra com uma inscrição hebraica de uma das molduras de porta ou janela do Tachara, Persépolis. As análises confirmaram pigmentos vermelhos já identificados em estudos anteriores e revelaram novas evidências de lazurite como pigmento azul e magnetite como pigmento negro. Os resultados podem ajudar a construir outros aspetos de contextos específicos de policromia antiga em Pasárgada e Persépolis.

PALAVRAS-CHAVE
Pasárgada
Persépolis
Pigmentos
Lazurite
Hematite
Goetite

Introduction paper squeezes as evidence for monumental painting in ancient Iran

Carved between the sixth and fourth centuries BCE, the surfaces of the limestone facades of the monuments built under the Achaemenid rulers in Pasargadae and Persepolis in Fars, Iran – both UNESCO world heritage sites today (Figure 1), were originally covered with abundant paints [1]. Work has been done to analyze some of the pigments in the twentieth century. Recent investigations have summarized the potential for new work on reconstructing aspects of the original polychromies, the painting process, and the people involved [2].

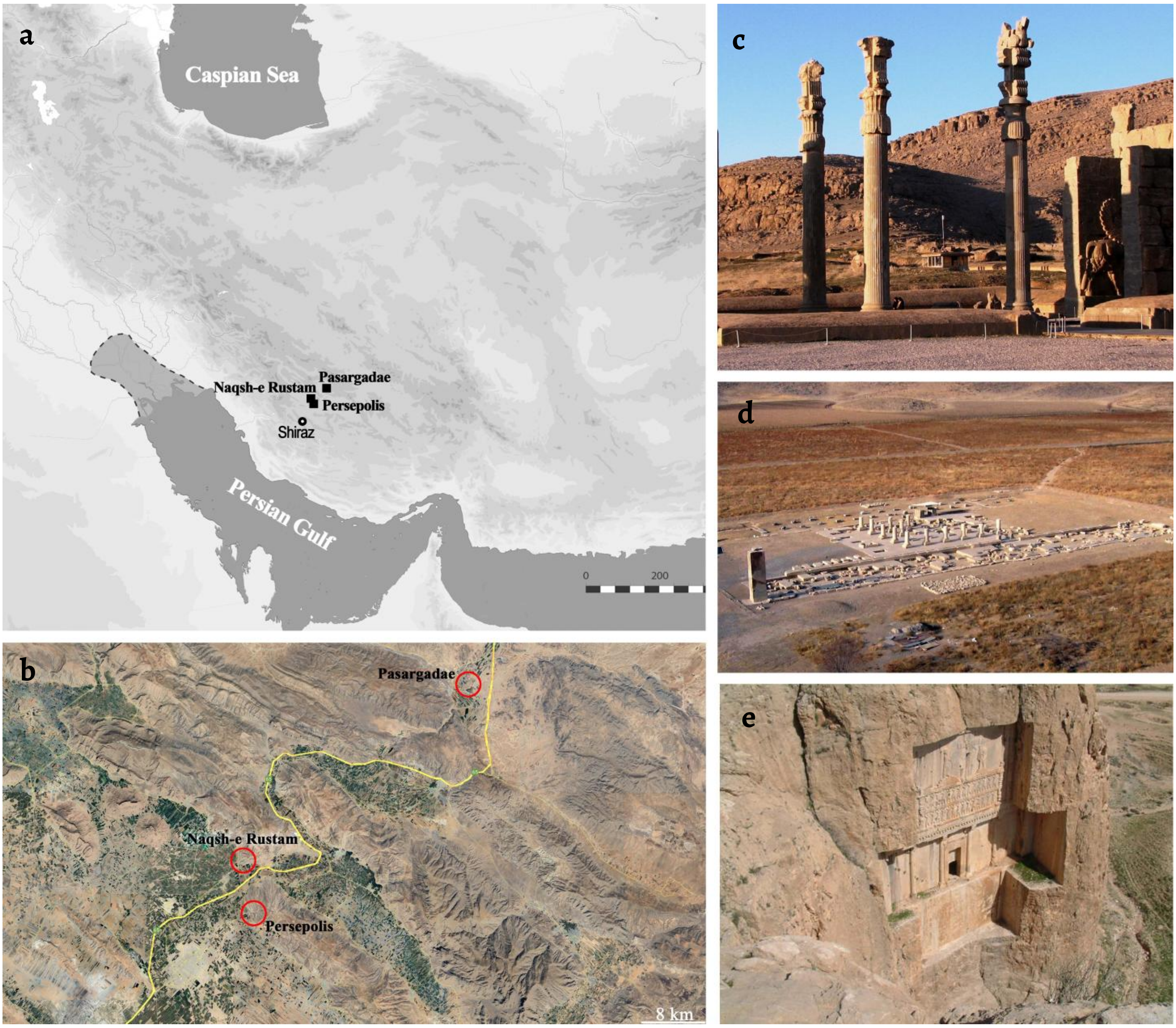

Figure 1. UNESCO world heritage sites: *a)* the sites of Pasargadae, Persepolis and Naqsh-e Rustam in Iran; *b)* satellite map of heritage sites in Fars province (photograph: Google Earth); *c)* Persepolis, Gate of All Nations; *d)* Pasargadae, Palace P (photograph: Archive of the Pasargadae WHS); *e)* Naqsh-e Rustam.

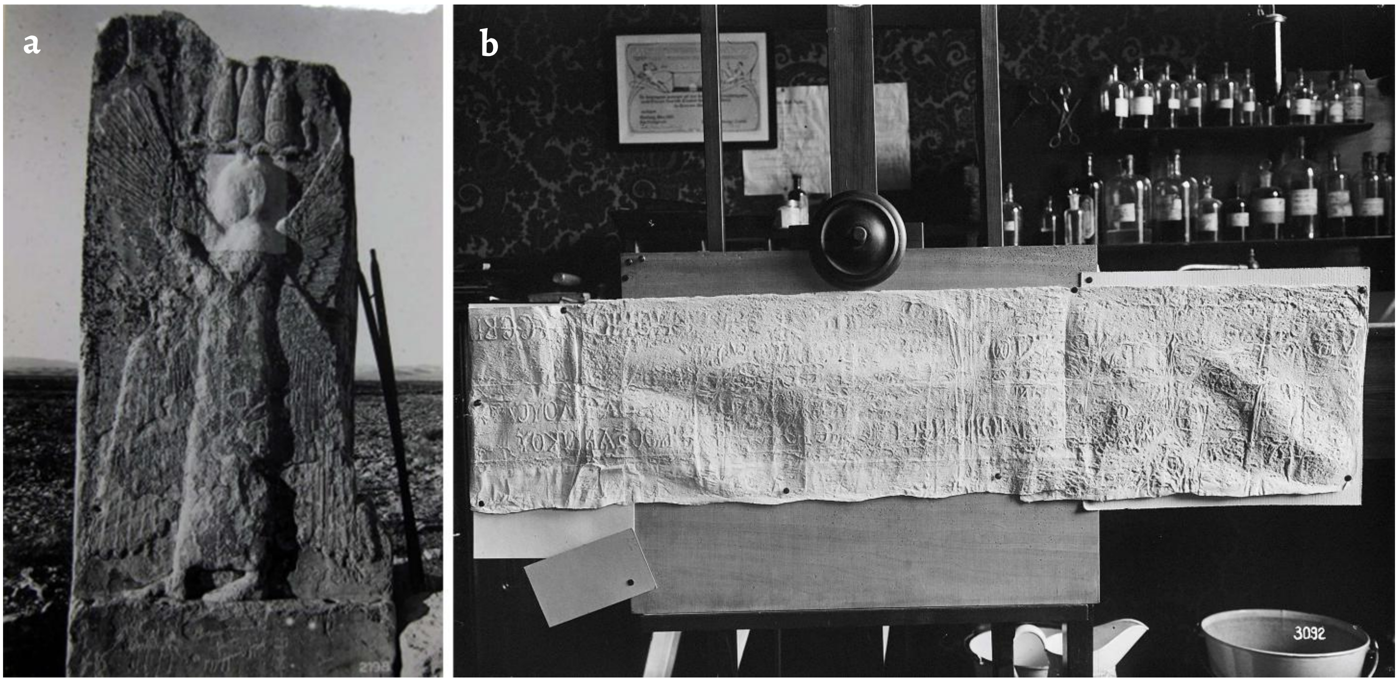

Figure 2. Paper squeezes applied: *a)* excavation of Pasargadae, Gate R (Gate House, Palace with the Relief): view of Winged figure with paper squeeze applied on the face, c. 1923 (photograph: E. Herzfeld [3, photo 2198]); *b)* Palmyra (Syria): view of a paper squeeze with a Greek inscription (photography: E. Herzfeld, [3, photo 3092]).

During archaeological fieldwork and early modern interventions on monuments and buildings on both sites in the early twentieth century, Ernst Herzfeld (1879–1948) and his team took paper squeezes of free-standing monuments and excavated objects to document epigraphical and iconographic features of interest. In diaries and notebooks, we found information about the process of squeeze-making, and how Herzfeld would read these squeezes later. During a longer visit to Persepolis in 1923, Herzfeld notes that "… the entire day, Djawad and Djuml made molds of the great terrace inscription. I read them in the tent in the evening" (December 19, 1923, trans. A. Nagel) [4]. In a letter to his father, photographer Hans-Wichart von Busse (1903–1962), who assisted Herzfeld during an excavation season in 1933 describes: "…one takes large sheets of thin cigarette paper, that was carefully hammered on [the surface of the stone] with a hard brush, while damp. When it was well molded to the form, new layers were added … Once dry, one could lift off the paper layer … and had an exact reproduction of the original" (September 23, 1933, trans. A. Nagel) [4]. In essence, these paper squeezes are cast impressions from (often inscribed) surfaces of ancient monuments. There is no documentation that the stone facades would have been cleaned before the papers were attached and wetted though we can assume that some light brushing happened to remove any dust or dirt (Figure 2).

After Herzfeld's permanent relocation to the Institute of Advanced Studies at Princeton in America in 1936, he sold some of the paper squeezes to the Metropolitan Museum of Art (MMA) in New York City in 1944, while he donated others to the Smithsonian Institution's Freer Gallery of Art, today's National Museum of Asian Art in Washington, D.C. (NMAA) [2, 5]. In recent years, the research potential of such paper squeezes has been recognized [2, 6-9]. In 2023, four of Herzfeld's paper squeezes housed in the MMA's Department of Ancient Near Eastern Art were investigated for possible traces of ancient paint residues (Figure 3). It is important to reconstruct the archaeological context of the paper squeezes first since it will help us evaluate the new evidence. Some of the structures introduced were hitherto never examined for evidence of painting.

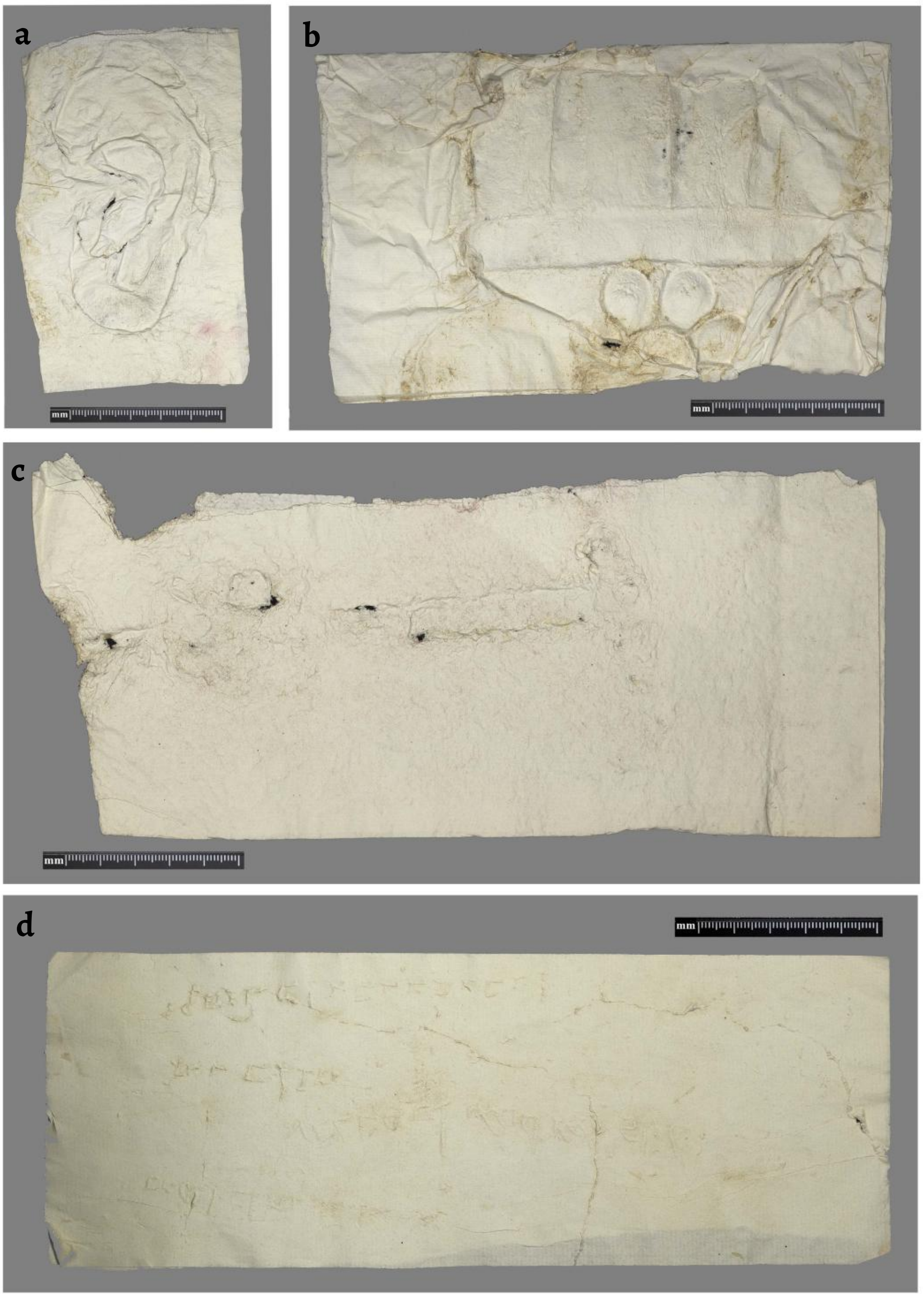

Figure 3. Four paper squeezes from carved limestone facades at Pasargadae and Persepolis, MMA: *a)* ear from Palace P in Pasargadae; *b)* rosette from a lamassu crown fragment at Pasargadae's Gate R; *c)* axe from the North façade of the Apadana in Persepolis; *d)* limestone block with a Hebrew Inscription from the Tachara at Persepolis.

The archaeological contexts of the paper squeezes

A paper squeeze from Palace P in Pasargadae (A)

According to a notebook entry written while excavating and opening a trench in Palace P on the site of Pasargadae on April 26, 1928, Herzfeld, his assistant Friedrich Krefter (1898-1995) and their team discovered a white limestone fragment with a human ear, slightly larger than life-size by the east door, deep in the foundations. As a note next to a sketch of the ear in the find notebook indicates, a paper squeeze (*Abklatsch*) was made immediately (Figure 4).

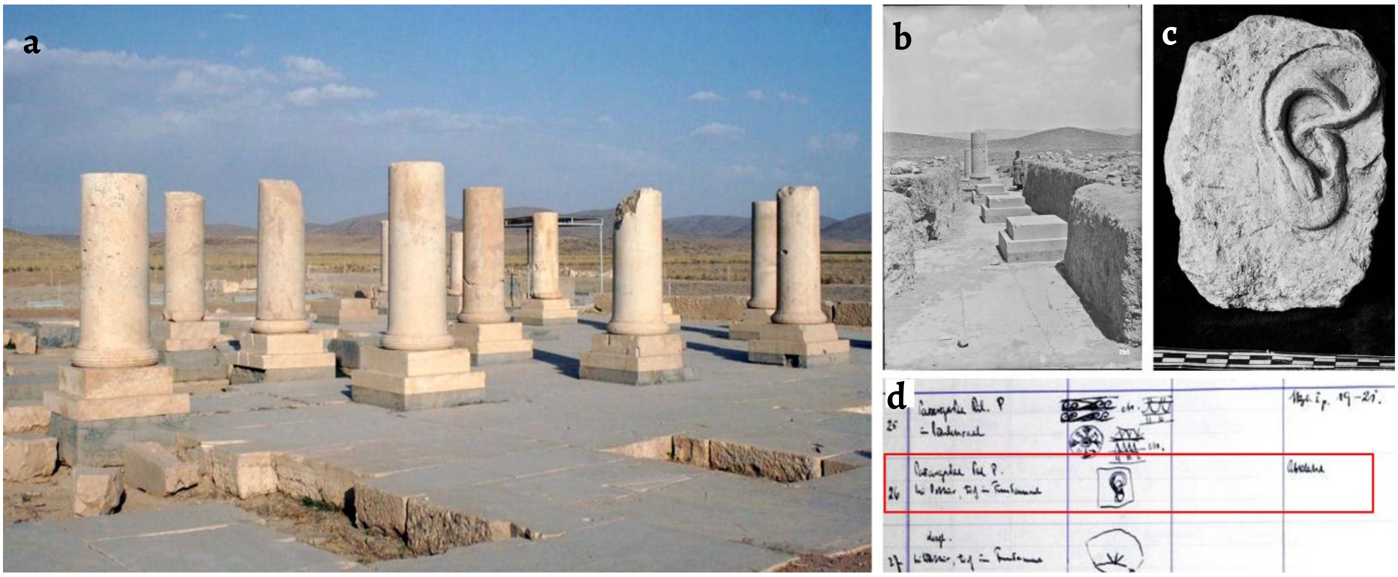

Figure 4. Pasargadae, Palace P: *a)* in 2018; *b)* during excavations in April 1928 [3, photo FSA A.6 04.GN.0295]; *c)* limestone fragment [3, photo FSA A.6 04.GN.0455] *d)* Herzfeld's Find Notebook from Pasargadae (N-92) with a sketch of the limestone fragment with the carved ear. Note the reference to the paper squeeze ("Abklatsch") [3, photo FS-FSA_A.6_03.92.05, 10].

It is unknown how and where the objects from the Spring 1928 excavation season were first deposited, and it is also unknown how and when Herzfeld was able to transport them out of Persia. Visiting Pasargadae in 1905, 1923, and 1928, and later, Herzfeld documented and collected materials at Pasargadae during all his visits. Today, materials from Pasargadae are in museums in Berlin, Washington, D.C., Jerusalem, and Chicago. A photograph of the limestone fragment of the ear was likely taken in the field shortly after excavations. It is unknown to us where this limestone fragment with the ear is today. In Herzfeld's publications on his fieldwork at Pasargadae, objects excavated were dealt with only summarily if they were mentioned at all [11]. The ear was not mentioned in any of Herzfeld's publications or subsequent publications on fieldwork on the site [10, 12-13]. In a caption to the photograph added (in English) at some unknown time later it is described as a "Sculptor's model of an ear".

Palace P, in which the ear was excavated, consisted of a central columned hall with doorways on four sides. The building had two porticoes, one facing a large green garden area. Recently analyzed fragments of painted plaster found in the debris of the same palace, housed in Washington, D.C., indicate that the upper portions of the columns of Palace P were made of plaster-covered wood rather than stone [14]. There is currently no consensus about the exact chronology of Palace P. Since the ear was excavated deep in the foundations, we conclude that it likely stems from one of the early phases of the building, maybe under the time of Cyrus the Great (c. 590-530 BCE). Later excavator David Stronach [12] suggested, "Palace P was begun during the reign of Cyrus, its construction was halted, probably at the time of Cyrus' sudden death, and that the structure was only completed, with certain evident economies, by Darius". Only the lower parts of the doorway reliefs from Palace P are preserved depicting a king dressed in a long-pleated robe originally adorned with gold inlays, followed by an attendant. According to Stronach, "inscriptions on the pleats of the robe identify the depicted monarch as Cyrus but the style of the pleats can be associated with the reign of Darius" [13]. Herzfeld had noted traces of paint on the robe. Judith Lerner was allowed to remove traces of paint from a stone relief in Palace P, and she gave them to Harvard University where they were analyzed by a scientific team [1]. Their results indicated that parts of the surface of the stones were decorated with red ocher – a naturally occurring mixture of iron oxides (hematite). Traces of cinnabar were also identified on Palace P surface carvings. Our first question was whether our previously unpublished paper squeeze of the limestone ear of Palace P would provide additional information on the polychromy of the monument.

A paper squeeze of a Lamassu crown rosette fragment at Pasargadae (B)

The original stone fragment from which this paper squeeze was taken was excavated by Herzfeld at Gate R, referred to as the "Gate House" or "Palace with the Relief" in 1928. It was photographed shortly after (Figure 5). A handwritten note on a blueprint of the photo (in English) reads "Pasargadae, R. Frgm. of a crown of Lamassu". A sketchbook preserves a hand-made drawing of the fragment, where it is described as *Kronenrand* (crown rim) and a note that a *Abklatsch* (paper squeeze) was made. All sculptural fragments excavated at this Gate House at Pasargadae were only briefly mentioned by Herzfeld but never published [11-12]. Again, the current location of the crown fragment is unknown. There is significance in the fact that Herzfeld's documentation including the paper squeeze is currently our only important evidence for the colossal winged lamassu which once flanked the outer portal of the monumental Gate. During later excavations on the same structure, Ali Sami and David Stronach discovered more fragments of winged beasts [12, 44n. 7, Pls. 47c-d]. The much better-preserved crowns of the lamassus flanking the Gate of Xerxes at Persepolis provide an idea of the original layout of the animals at Pasargadae, now almost completely lost (Figure 5c).

Only four petals of a rosette and parts of the feathers of the crown are visible in the Pasargadae Gate R paper squeeze preserved at the MMA. Rosettes with twelve petals were featured on multiple stone animals excavated on the site of Persepolis. Sketches in Herzfeld's find notebooks preserved at the University of Chicago refer to pigments still visible on the surface of these rosettes at Persepolis: according to Herzfeld, the petals and background of the framed rosettes on one of such animals as excavated in March 1932 near "the great Gate" preserved red paint, while the carpel or interior of the rosette was blue [2, p. 95 fig. 3.3]. Much like in Palace P at Pasargadae, the excavated limestone fragments of the Gate R structure indicate that the stone facades were originally painted. Of his sketchbooks from 1923 and his 1928 season at Pasargadae (SK, IV, IX, X, and XI) in the NMAA, one (IV, p. 8) contains references to pigments he observed at Gate R's standing remains ("Pasargadae, palace with the Genius … traces of red color on fringes and wings") [15]. No reference to samples or paint on Gate R was made in Stodulski's study of paint materials from Pasargadae and Persepolis [1].

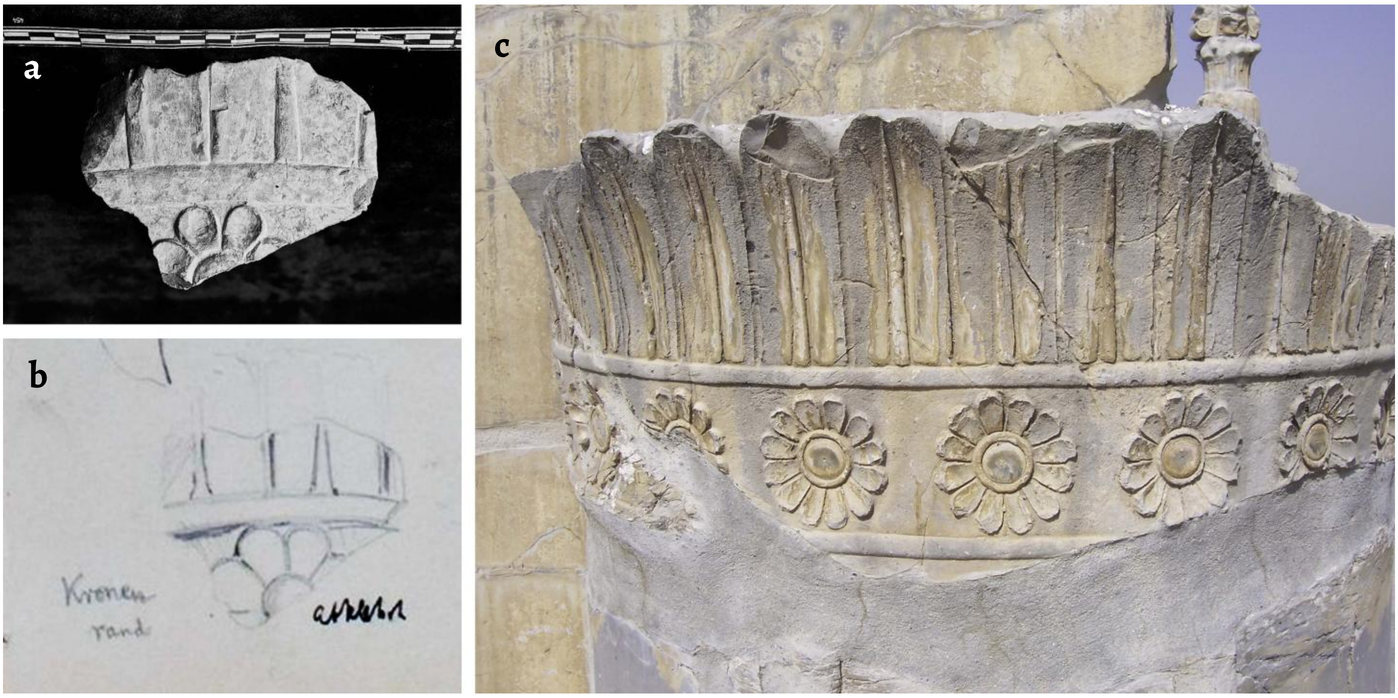

Figure 5. Original limestone fragment excavated by Herzfeld in Gate R, Pasargadae in 1928 [3, photo FSA A.6 04.GN.0454] *(a)*. Herzfeld's sketch of the fragment in a sketchbook (SK IX "Pasargadae I", p. 28) [3, photo FS-FSA_A.6_02.02.09.027] *(b)*. Close up to the Crown of one of the Lamassus at the Gate of Xerxes at Persepolis (photograph: A. Nagel) *(c)*.

A paper squeeze of a stone axe from the north façade of the Apadana in Persepolis (C)

While the Pasargadae paper squeezes themselves were not written upon, two paper squeezes from Persepolis in the MMA were labeled by Herzfeld. On one paper squeeze, we read the label "Tributzug II i 3". Connecting the label to drawings made by Herzfeld in his sketchbooks, notebooks, and other circumstances, the paper squeeze likely corresponds with a stone axe depicted on delegation XVII ("Sogdians") on the west wing of the north façade of the Apadana at Persepolis [16, pl. 43; 17, p. 49 No. 9; 18, pp. 93-94, pl. 24; 19, p. 335, fig. 8d (east façade)] (Figure 6).

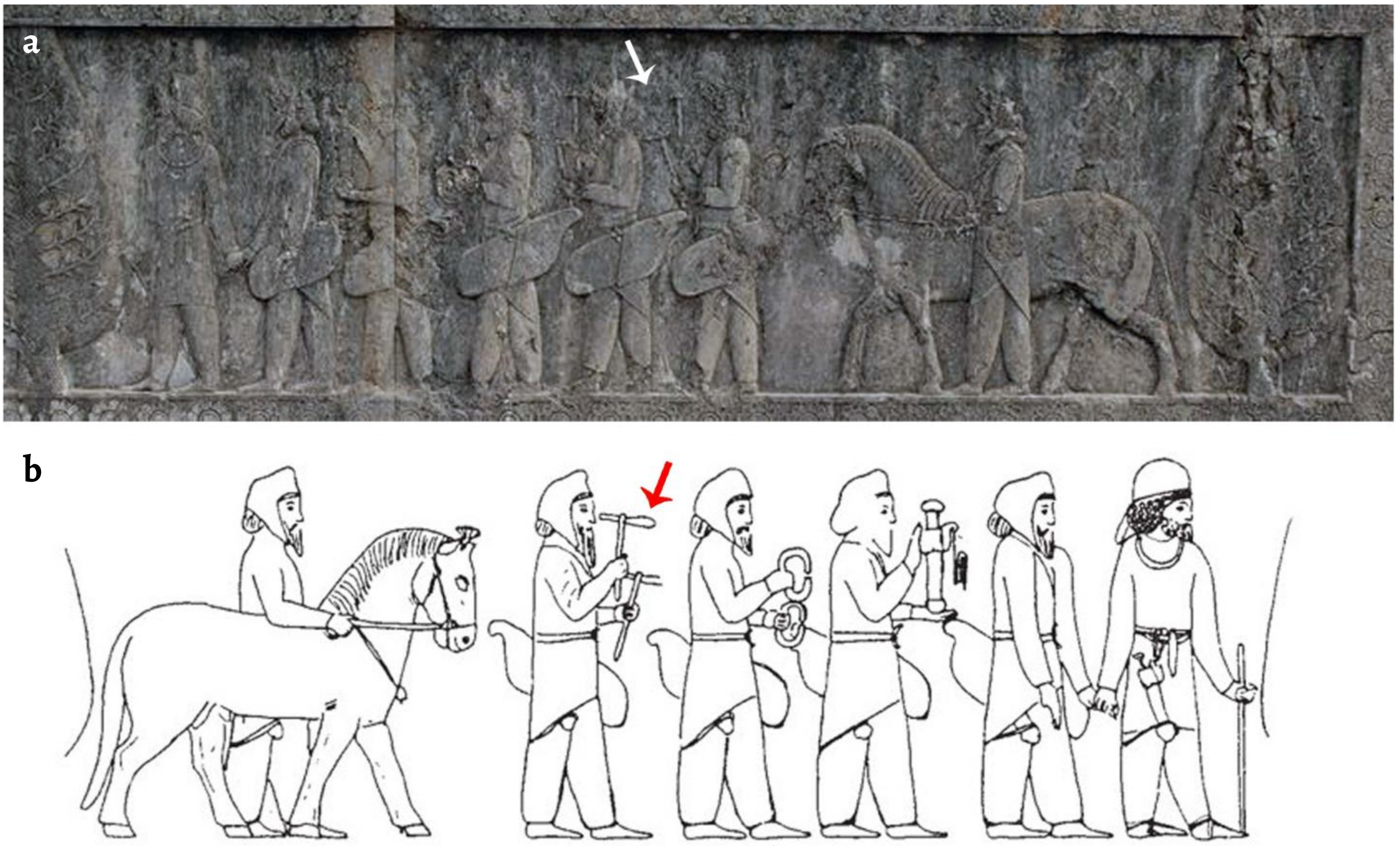

Figure 6. Stone axes carried by the Sogdian delegation, north façade, Apadana, Persepolis (photography: J. Lenderling [20]) *(a)*. Stone axes in the same delegation on the better-preserved east façade of the Apadana [21, p. 335 fig. 8d] *(b)*.

Construction of the Apadana began shortly after 520 BCE. Construction of the north façade was finished under Xerxes I between c. 486 and 465 BCE. The facades on the north side of the Apadana were exposed to weathering conditions and molding by multiple expeditions in modern times thereby destroying much of the evidence of original paint. British and French explorers molded standing stone sculptures throughout the nineteenth century. At the same time, fragments were hacked off; accumulated debris with fragments was cleared and the stone items were transported to museums in London and elsewhere. The largest set of molds was made by Lorenzo Giuntini (1843-1920) on behalf of a delegation from the British Museum in London in 1892 and 1893. In 1899 and 1900, Friedrich Sarre (1865-1945) took an additional set of molds from the north façade. Finally, following a complaint by Herzfeld that there is no complete cast of the tribute bearers depicted on the north façade, Herzfeld was the latest in a series of Westerners who made molds and paper squeezes of individual parts of the north façade [16, 18, 22].

While testimonies of early modern visitors commenting on the remains of the standing stone columns are preserved, the facades on the east side of the Apadana were completely buried by debris until 1932 when Herzfeld and his team of workmen financially supported by the University of Chicago began excavations. During his fieldwork, Herzfeld noted traces of paint preserved on the lower parts of the east façade. Ceramic bowls with pigments deposited in front of the monument provide evidence of the painter's activities decorating the facades [2, pp. 101-104]. Describing what was depicted on these facades, especially after Herzfeld had fully excavated the better-preserved east facade in 1932, became a lifelong endeavor that was only fulfilled by Gerold Walser (1917-2000) and conducted long after Herzfeld died [19].

A paper squeeze of a Hebrew inscription block from the Tachara at Persepolis (D)

The fourth paper squeeze has a handwritten note by Herzfeld describing it as an inscription from the Tacara in Hebrew (*Persep. Tacara Hebr*).

South of the monumental Apadana, the Tachara at Persepolis has often been referred to as the "Palace of Darius." Begun under Darius the Great (c. 550-486 BCE), the building underwent multiple changes. A large facade with a staircase was added to the west side of the building under Artaxerxes III (359-338 BCE). Like the Apadana, the function of the Tachara changed. For a brief period in modern times, before a more permanent expedition camp was built in the so-called Harem building in 1932, the Tachara was used for tents set up by Herzfeld's excavation team (Figure 7). The high quality of the carvings on the standing door- and window jambs and the polished stone floors indicate the importance of the structure in ancient times [2, 23-25]. Multiple fragments from the building's stone facades are in museums in Berlin, Detroit, and elsewhere, including a fragment of a shoe, Herzfeld himself removed from one of the door jambs and sold to the MMA in 1944 (No. 45.11.17) [23].

Figure 7. Standing doorjambs, Tacara, Persepolis *(a)*. Drawing of the Tachara by Herzfeld, unknown date [3, photo FSA A.06 05.0860] *(b)*. Example of a Late Inscription on one of the door or window jambs at the Tachara [3, photo FSA A.6 04.GN.2671] *(c)*. Sketch of Hebrew inscription in the Tachara in Herzfeld's Notebook [3, photo FS-FSA_A.6_02.01.06.025] *(d)*.

A series of sketches in Herzfeld's notebooks from 1923 preserved in the NMAA, provide additional context for these post-Achaemenid graffiti in the Tachara and Hebrew graffiti at Persepolis in general (SK V; SK VI). One notebook (N-87, pp. 18-22) lists all Hebrew inscriptions Herzfeld had recorded at Persepolis. Another notebook by Herzfeld contains modern transcriptions of some texts (N-30).

Methodologies: examining and investigating the paper squeezes

The surface of all four paper squeezes was examined using a combination of imaging and analytical instrumentation to identify possible pigments. We were especially interested in detecting further evidence of paint since the surfaces of the monuments from which the squeezes were taken were not previously studied. Multiband imaging (MBI) is a non-destructive method for investigating and differentiating materials. It involves making a series of images, each recording reflectance, and luminescence within a different limited range of wavelengths. Using a Canon R5 camera, a series of band-pass camera filters (Midopt 550, X-Nite BP1, X-Nite 330, X-Nite 830), and a set of LED lights and Tricolor lights, we recorded variations in the absorption of materials at different wavelengths. Visible (VIS), Infrared reflectance (IRR), Visible-induced infrared luminescence (VIL), and Ultraviolet reflectance (UVR) techniques were used, too. Combined, these imaging techniques can help to distinguish between the paper (substrate) and probable pigments.

The paper squeezes were also investigated under a stereomicroscope. Pigment samples were then observed under Polarized Light Microscopy (PLM) to identify the particle size of the pigments and the presence of other mineral inclusions utilizing a Zeiss Axio Imager M2M microscope, with 50×, 100×, 200×, 400×, and 500× magnifications, an Axiocam HRc digital camera, and AxioVision 4.X.X software.

Raman analyses were performed on the paper squeezes using a Bruker Optics "Senterra" spectrometer equipped with an Olympus 50× long working distance microscope objective and a charge-coupled device (CCD) detector. A Spectra-Physics Cyan solid-state laser and a continuous wave diode laser emitting at 785 nm were used as the excitation source, and two holographic gratings (1800 and 1200 rulings/mm) provided a spectral resolution of 3-5 cm^{-1}. The output laser power was 1 and 10 mW, and the number of scans, and integration time were adjusted according to the Raman response of the different particles.

As part of the materials analysis micro-samples were collected from all paper squeezes for scanning electron microscopy with energy dispersive microanalysis (SEM-EDS). This included one red (REP) and one blue grain (BEP) from the paper squeeze of the ear from Palace P at Pasargadae; one red from the rosette (RLR) and one blue particle from the feather fragment of the Lamassu crown (BLR) of Gate R at Pasargadae; one blue particle from the stone axe from the Apadana (BAA); one blue (BIT), one red (RIT), and one black (Bk.IT) from the Hebrew inscription of the Tachara at Persepolis. Selected micro samples were mounted on stubs, carbon-coated, and analyzed by scanning electron microscopy-energy dispersive X-ray spectrometry analyses (SEM-EDS) with an FE-SEM Zeiss Σigma HD, equipped with an Oxford Instrument X-MaxN 80 SDD detector. Backscattered electron (BSE) images, EDS analysis, and X-ray mapping were conducted with an accelerating voltage of 20 kV in a high vacuum. The surface of the samples was carbon-coated before the analyses.

Results

Multi-band imaging (MBI)

No pigments were specifically identified through infrared and ultraviolet imaging. VIL digital imaging, however, revealed fluorescing remnants. The fluorescing remnants visible in Figure 8d3 and d5 were mainly caused by contamination. The pink stains in Figure 3a were also detected on the rosette paper squeeze which is a result of contamination (Figure 8d5). Some other spots investigated showed fluorescent remnants (Figure 8d 1, 2, and 4).

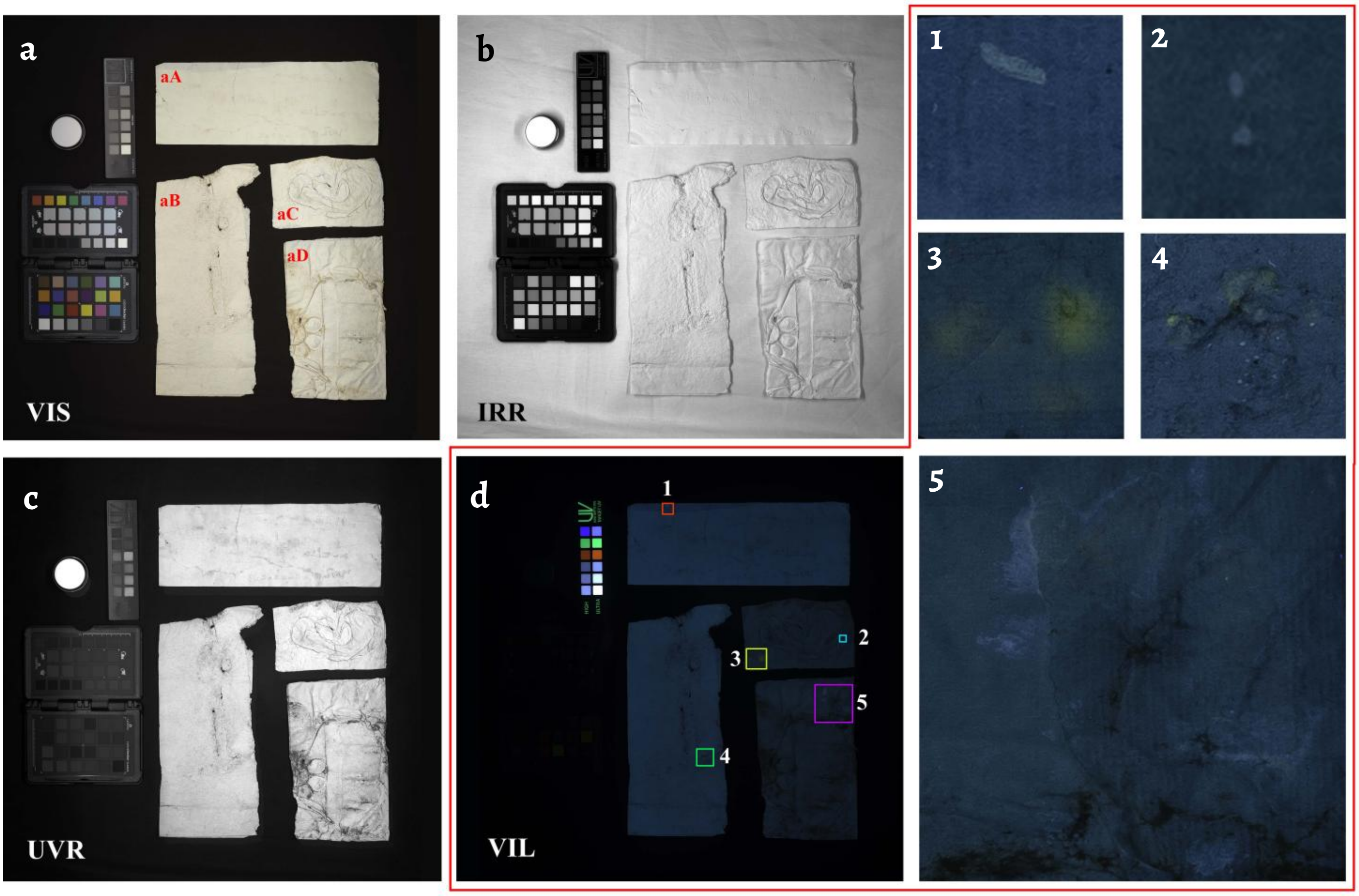

Figure 8. Multi-band images from the paper squeezes: *a)* VIS photo: aA – block with Hebrew inscription paper squeeze, aB – stone axe paper squeeze, aC – ear paper squeeze, aD – rosette paper squeeze; *b-c)* IRR and UVR photographs do not show any trace of pigments, the dark area of the rosette paper squeeze is dust in URV; *d)* VIL photograph show fluorescence particles and spots specified by numbers; *d1-5)* points 1, 2, and 4 can be traces of pigment, 3 and 5 points are contaminations.

Raman spectroscopy

Raman spectroscopy (Raman) of the paper squeeze of the limestone ear showed a density of blue (less than 100 μm in size) and two red particles. The red particles came in two varieties: dark and bright (Figure 9). The Raman spectra of the dark-red particles (225, 245, 292, 411, 496, and 610 cm^{-1}) are attributed to hematite (α-Fe_2O_3) [26] which had been identified on other architectural features from the site of Pasargadae earlier. The Raman spectra of the bright-red particles are attributed to goethite (α-FeOOH) with wavenumbers 248, 299, and 387 cm^{-1}, of which the strongest band is 387 cm^{-1} [27]. The Raman spectra of the blue samples (378, 549, and 582 cm^{-1}) are strikingly consistent with reference spectra of lazurite ($Na_8[Al_6Si_6O_{24}]S_n$) [28].

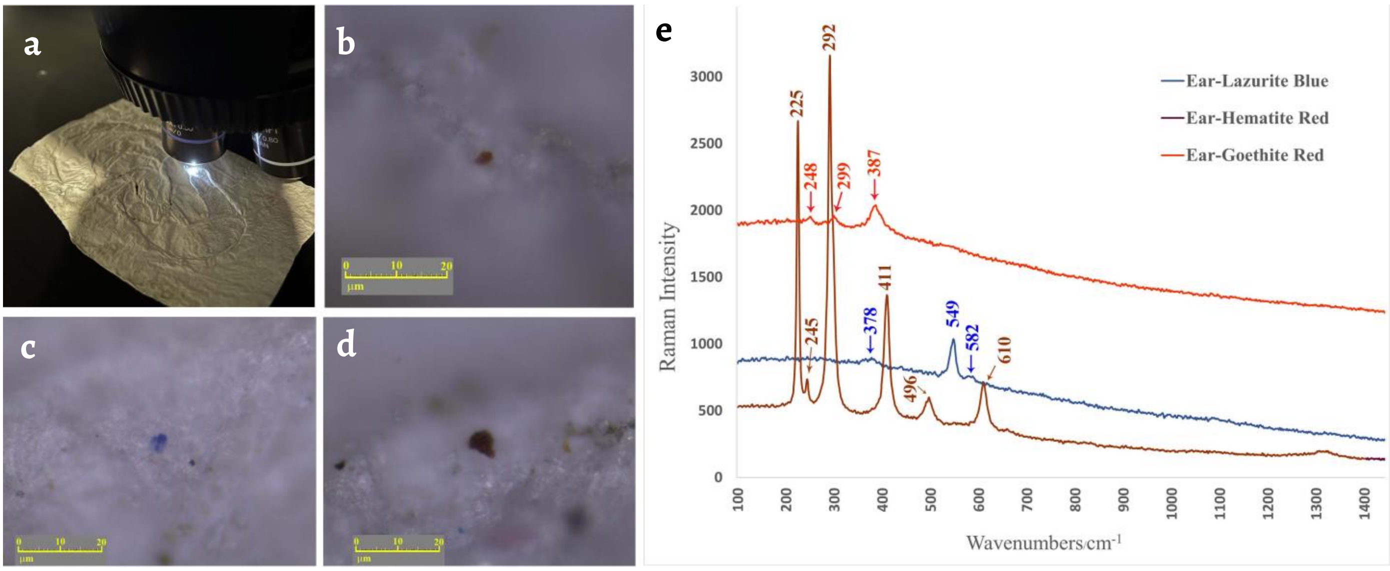

Figure 9. Raman analysis: *a)* close-up image of the paper squeeze of the stone ear; *b)* bright goethite red pigment; *c)* lazurite blue pigment; *d)* dark red of hematite grain; *e)* Raman spectra of the pigments representing hematite, goethite, and lazurite.

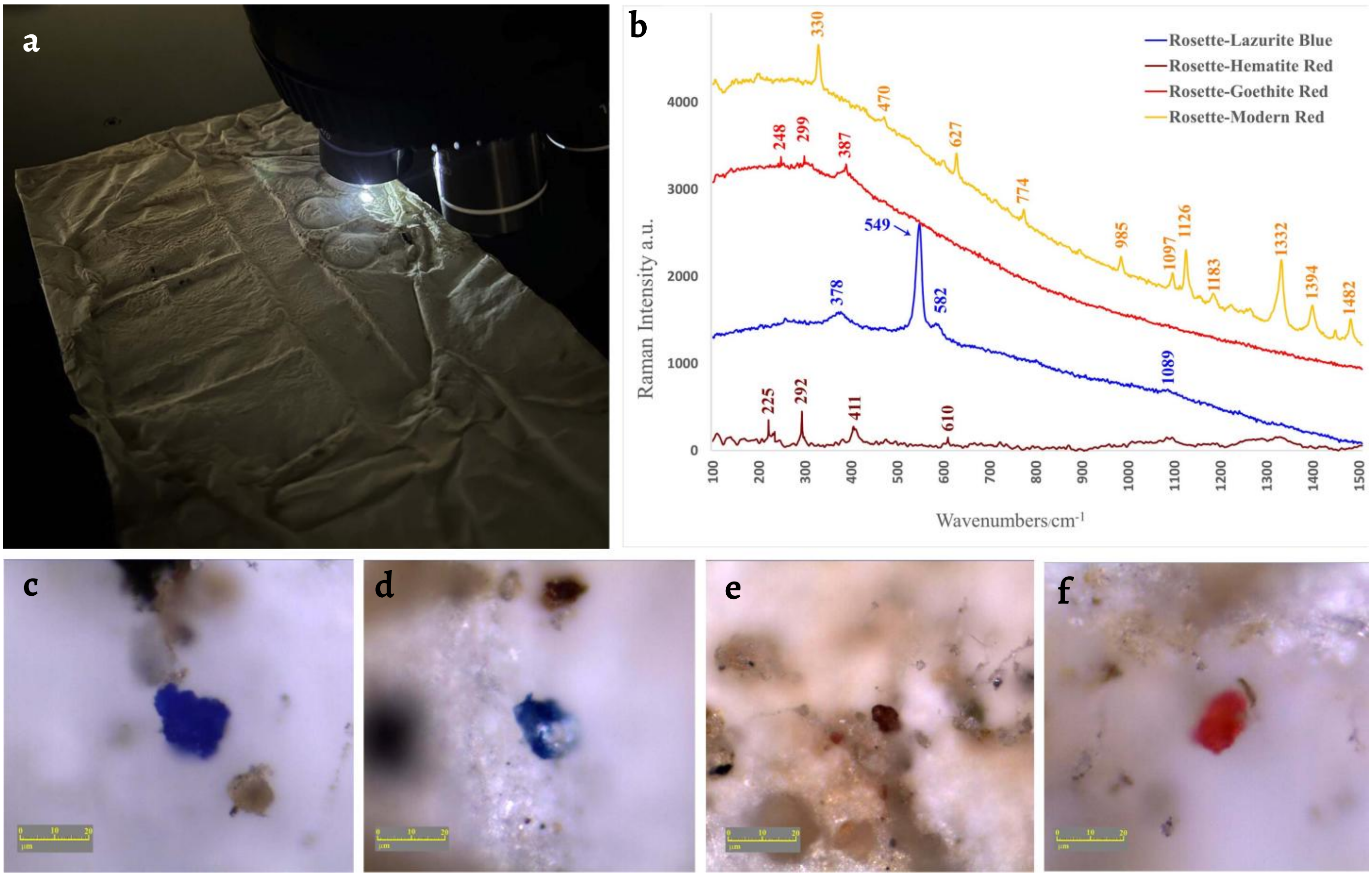

Figure 10. Raman analysis: *a)* close-up image of the paper squeeze of the rosette; *b)* Raman spectra of the grains; *c)* lazurite blue pigment on the paper; *d)* blue color of modern ink (Prussian blue); *e)* hematite red pigment; *f)* red color (modern pigment).

Microscopic investigation of the paper squeeze of the rosette showed a dense layer of red particles within the rosette pattern and blue particles on the feathers area (Figure 10). It is worth noting that there was a range of red colors in the particles, one of them pink-red. The Raman spectrum of pink-red grains in 330, 627, 774, 989, 1097, 1126, and 1332 cm^{-1} revealed a modern red pigment BR4 (Beta-naphthol) [29]. Most red grains were identified as hematite-dominant by Raman spectroscopy, one was attributed to goethite (248, 299, 387 cm^{-1}). The Raman spectra of the two blue particles were 257, 378, 549, 584, 802, and 1087 cm^{-1} of which the strongest bond (549 cm^{-1}) is consistent with lazurite, and 1087 cm^{-1} represents calcite.

Red, blue, and black particles were documented on the paper squeeze of the stone axe from the Apadana at Persepolis. The Raman spectrum of a red particle of the stone axe (Figure 11) showed 218 and 310 cm^{-1} Raman bands representing hematite (Fe_2O_3), as well as 252 and 343 cm^{-1} bands indicating cinnabar (HgS) [28-30]. Furthermore, the Raman spectrum in 380 cm^{-1} could be attributed to goethite [31].

One black particle was analyzed using Raman spectroscopy. Six Raman spectra were identified in 284, 462, 1086, 1185, 1287, and 1328 cm^{-1} respectively. These Raman spectra did not match clearly with previously identified Achaemenid black pigments such as carbon black, but 284 and 1086 cm^{-1} Raman bands could be attributed to calcite, and 462 cm^{-1} represents quartz. The Raman spectrum at 1330 cm^{-1} could refer to a carbon-black or a black earth pigment [32]. Referenced carbon-based pigments show similar Raman spectra with characteristic first-order bands in the range 1300-1600 cm^{-1}. Two broad and overlapping bands with maximum intensity at approximately 1580 cm^{-1} (G band) and 1350 cm^{-1} (D1 band) are in amorphous carbon. The position, width, and relative intensity of D and G bands can be different from sample to sample [33]. These parameters are influenced by several phenomena leading to disorder in carbonaceous materials, especially on D band intensity [34].

The black particle was analyzed in the range of 1-1500 cm^{-1}. It was not possible to run a second Raman spectrum to identify the G band. However, the fourth disorder band of carbon, D4, shows likely a carbon black pigment since D4 is found below 1290 cm^{-1} as a shoulder on the D1 band [32, 34]. The Raman spectrum in 1287 cm^{-1} (Figure 11) indicates the presence of carbon black that this D4 band observes in disordered materials such as soot and wood charcoal [32]. The additional band at 1185 cm^{-1} might be caused by impurities.

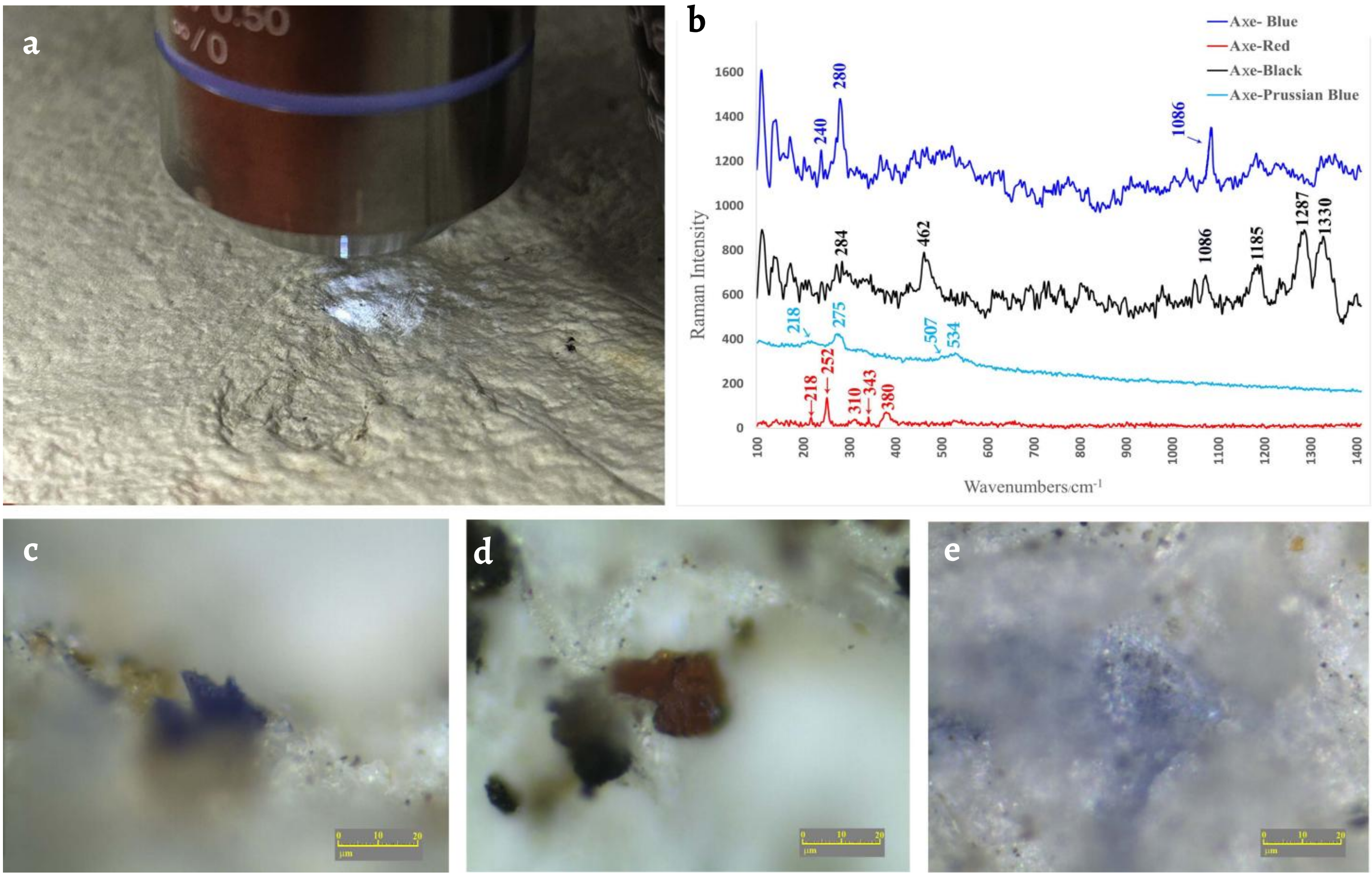

Figure 11. Raman analysis: *a)* close-up image of the curved shape of the paper squeeze of the stone axe; *b)* Raman spectra of the pigments; *c)* blue pigment within the texture of paper; *d)* hematite red and black particle within the texture; *e)* trace of Prussian blue ink absorbed inside the paper texture.

The Raman spectrum of the blue particles penetrating the paper indicated the presence of Prussian blue with Raman spectra in 218, 275, 507, and 534 cm^{-1}. The strong vibrational band of Prussian blue at 2154.96 is not there because the Raman spectra were taken from 1-1500 cm^{-1}.

Analyzing the blue pigments, we detected wavenumbers 240, 280, and 1086 cm^{-1}. These Raman spectra do not provide clear evidence for a second blue pigment, possibly due to a poorly crystalline form. However, the first band (240 cm^{-1}) could be referred to as azurite and the two bands of 280 and 1086 cm^{-1} indicated calcite. Nevertheless, because azurite shows a strong Raman band on 403 cm^{-1} [28], it is impossible to confidently identify this particle as azurite (Figure 11). During the second run, it was difficult to focus due to the curved shape of the paper squeeze. A sample was taken for elemental analysis, however (see below).

The paper squeeze of the Hebrew inscription block showed consistent microscale blue particles (less than 100 μm in size) and two red particles. Raman spectra of 225, 292, 410, and 610 cm^{-1} were identified as hematite. Raman spectra at 378, 549, 582, and 1089 cm^{-1} from the blue particle indicated lazurite on the strongest band (549 cm^{-1}) and calcite at the 1089 cm^{-1} band (Figure 12). A black particle was identified. Its texture was not like carbon black. Based on the morphology, it was rather assumed to be magnetite black. Since light and heating effects on magnetite and its transformation into maghemite and hematite with temperature increase was proven by Raman spectroscopy [35], we just carried out an elemental analysis on this sample.

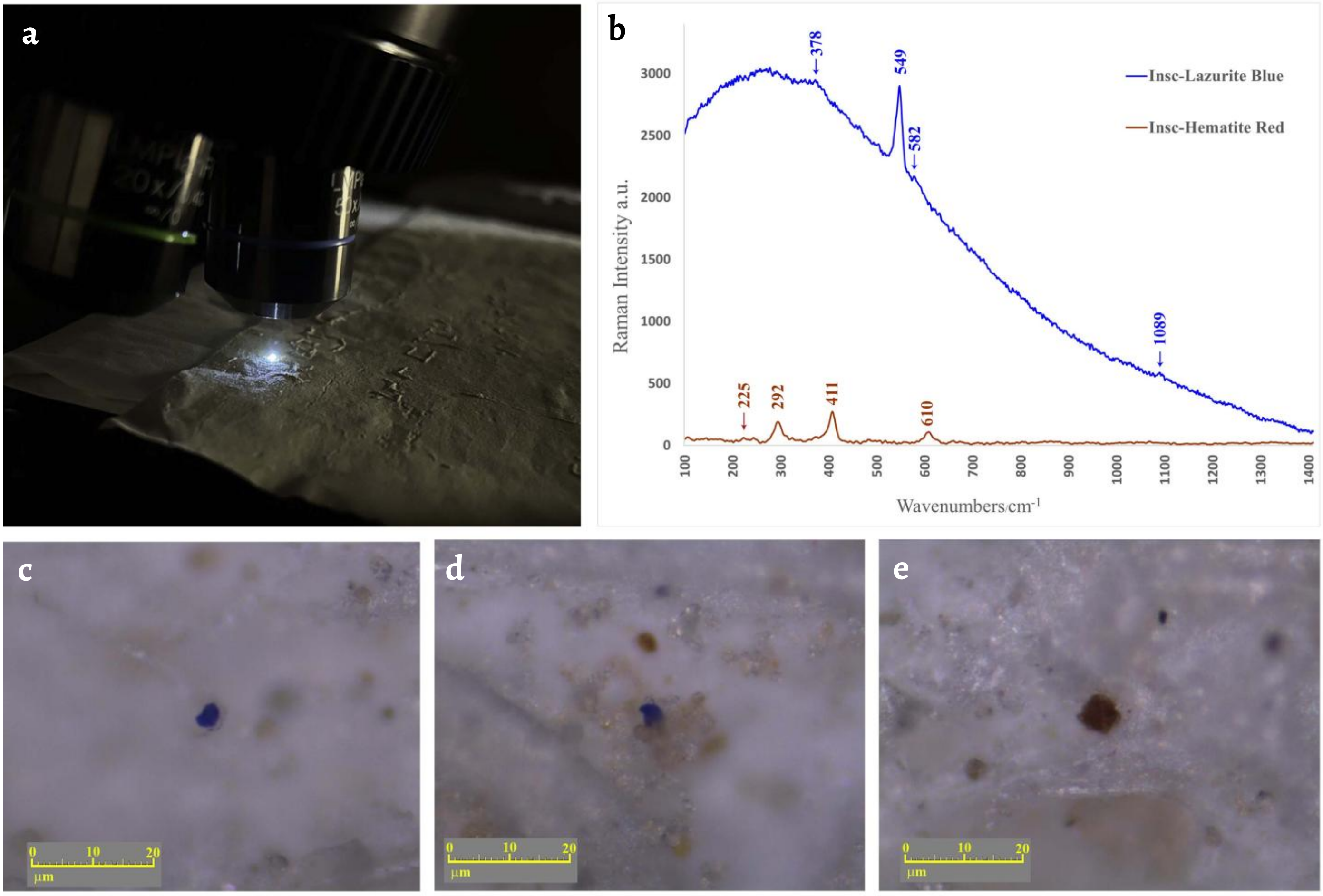

Figure 12. Raman analysis: *a)* close-up image of the paper squeeze of the Hebrew Inscription block; *b)* Raman spectra of red and blue pigments; *c-d)* lazurite blue pigments are widespread within the paper fibers; *e)* hematite red pigment.

Elemental analysis

The SEM-EDS analysis of point 1 (Figure 13) on the blue grain (BEP) identified Si, S, Ca, and Na as major constituents and Cl, K, Mg, Ti, Al, Fe, and Zn as minor constituents. Accordingly, Si, S, Ca, Na, Al, Cl could be attributed to lazurite $(Na, Ca)_8(AlSiO_4)_6(S, SO_4, Cl)_{1-2}$ verifying the result of the Raman analysis. Analysis of point 2 identified Na, Ca, P, S, K, Cl, and Si as major constituents respectively, and Ti, Al, Cu, Zn, and Fe as minor components (Table 1) that are also consistent with the presence of lazurite. The presence of Cu as a minor element could not be considered as contamination (Table 1). EDS analysis point 3 in the red particle (REP) identified Fe as a major constituent besides some earthen components such as Si, Al, and Ca indicating hematite or goethite.

Iron oxide (FeO) is the main constituent of the red particle (RLR) that was earlier identified as hematite or goethite, along with a minor silicate compound due to the presence of Si, Al, and Mg (Figure 14). A tiny blue particle (BLR) was also analyzed, and Si and Al were detected as major elements and Mg, Fe, Ca, K, S, and Na as minor constituents which could be attributed to lazurite (Table 1).

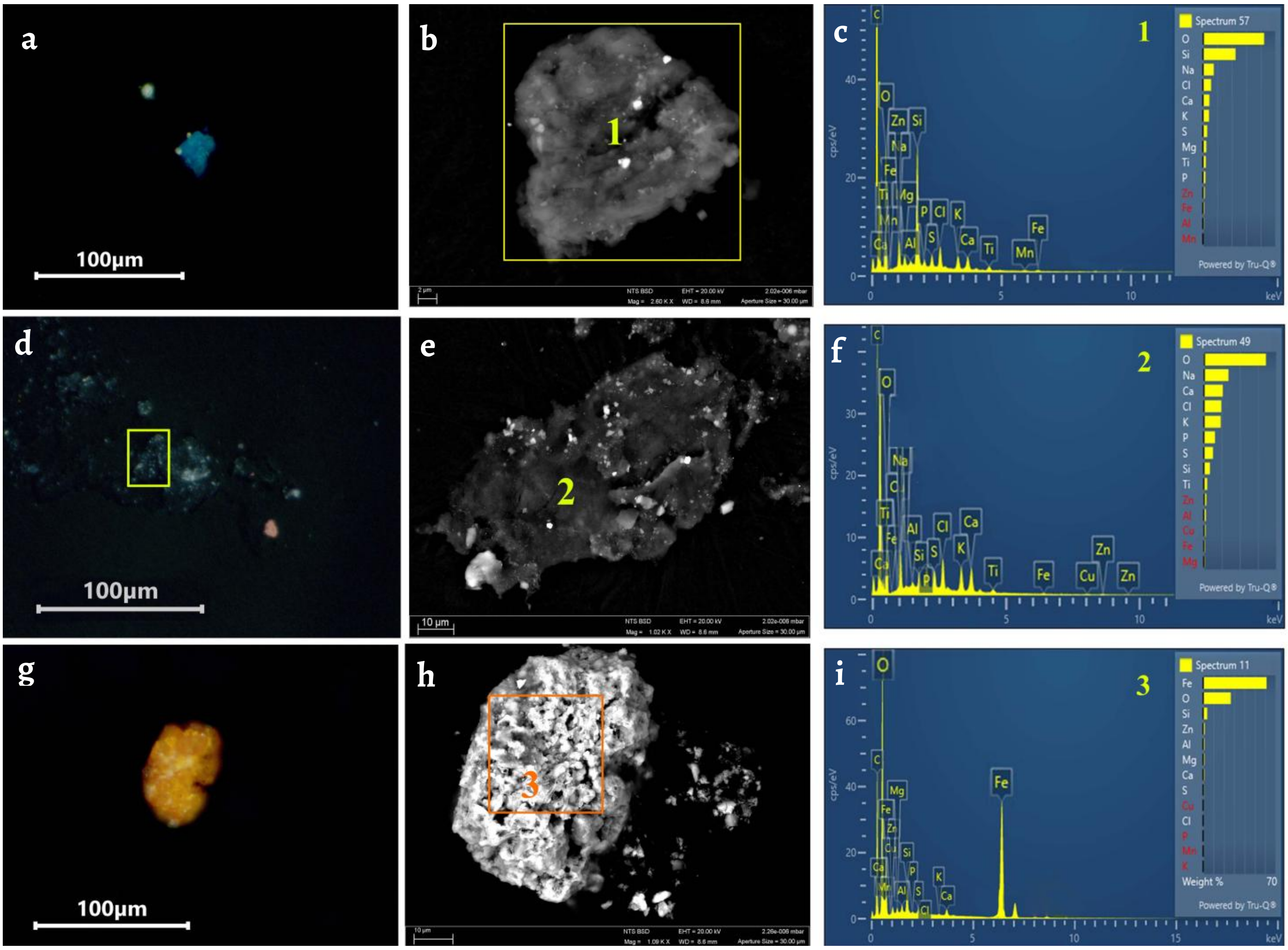

Figure 13. Paper squeeze of the limestone ear: *a)* blue particle (BEP) under PLM and *b)* SEM image; *c)* EDS spectrum of the bulk analysis of the rectangle 1 in b; *d)* shows both blue and red particles under OM and *e)* SEM image of yellow rectangle in d; *f)* EDS spectrum of point 2 in e; *g)* red particle (REP) under OM; *h)* SEM image of g; *i)* ESD spectrum of bulk analysis of point 3 in h.

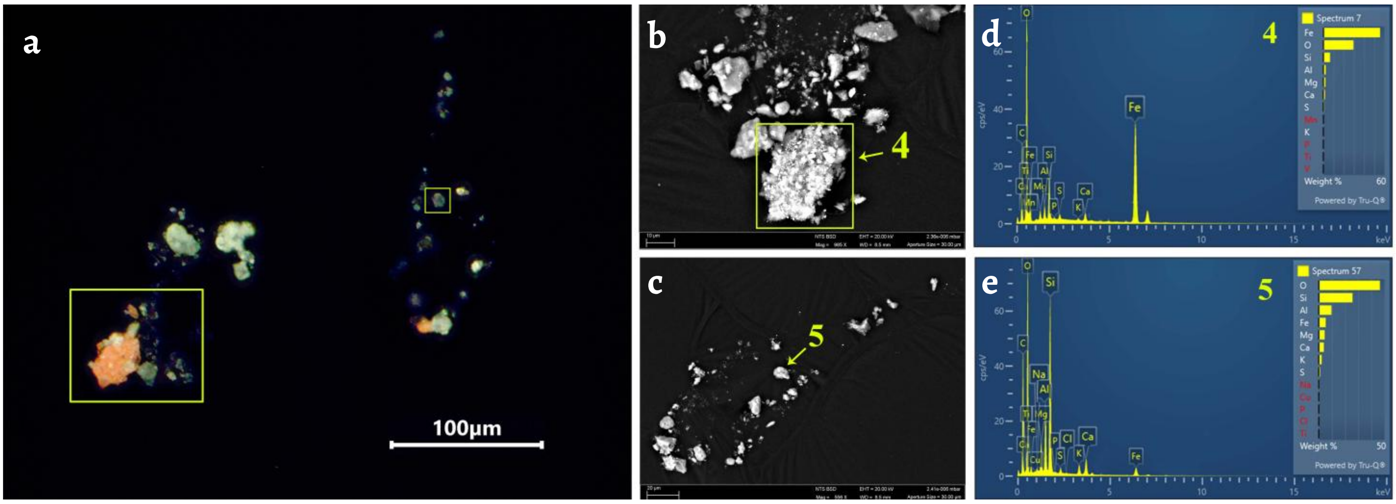

Figure 14. Paper squeeze of the rosette: *a)* red (RLR) and blue (BLR) particles under PLM; *b)* SEM image of the red particle specified with a big rectangle in a; *c)* SEM image of the blue particle specified with a small rectangle in a; *d)* EDS spectrums of point 4 in b; *e)* EDS spectrum of point 5 in c.

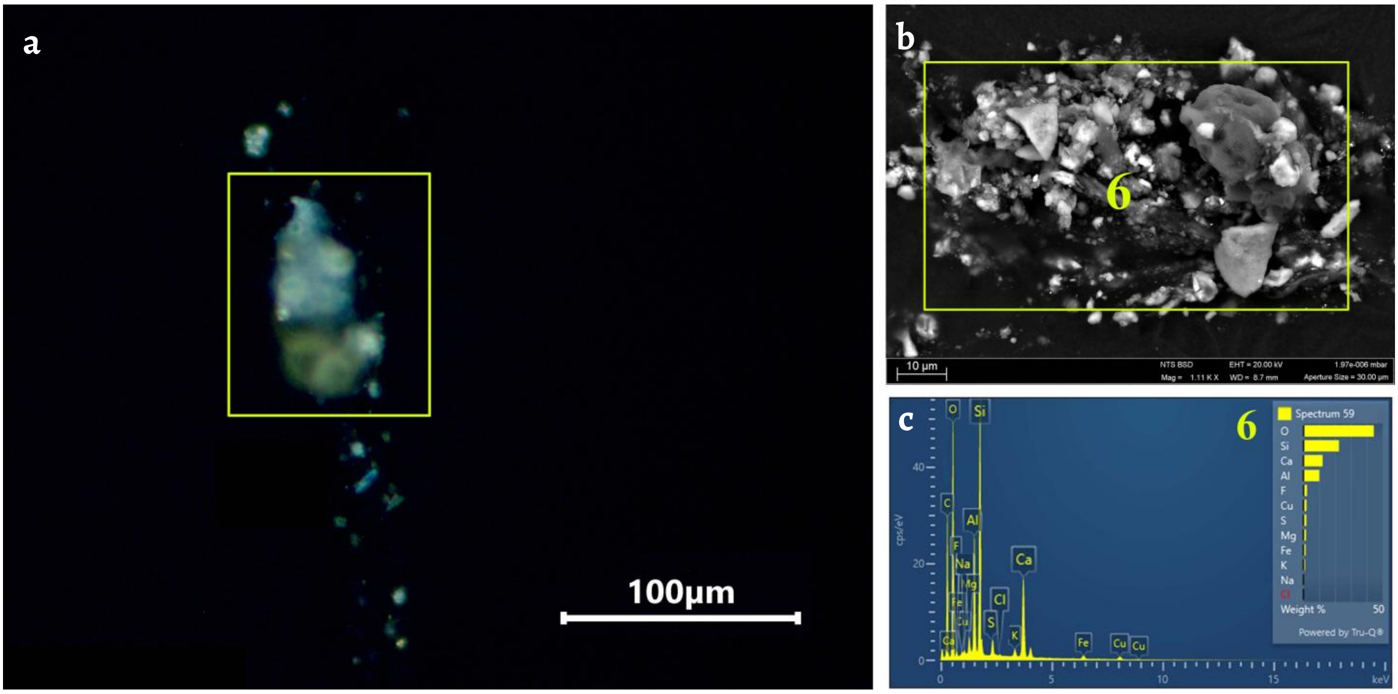

Figure 15. Paper squeeze of the stone axe from the Apadana: *a)* blue particles (BAA) under PLM; *b)* SEM image of the yellow rectangle in a; *c)* EDS spectrum of yellow rectangle in b (point 6).

EDS analysis point 6 of a blue assemblage of particles (BAA) detected Si, Al, and Ca as major and S, Na, Mg, Cu, Fe, and K as minor elements respectively (Table 1). Since it is not a single particle, probably due to the disintegration while sampling, accordingly it is composed of separate particles in the SEM micrograph. Thus, it is not possible to precisely characterize all particles or unambiguously attribute them to specific minerals. Although blue particles were observed under the microscope, these complex constituents are associated with blue particles that may be consistent with lazurite except Cu (Figure 15). Since the copper content is higher than the trace amounts found in lapis lazuli stones excavated from Persepolis [36], if we consider the same lapis lazuli resources (Badakhshan) as the source for producing pigment.

Table 1. EDS and Raman results of the pigments found in the squeezes.

Name of squeeze	Pigment	EDS*	Raman Bands (cm^{-1})	Results
Ear	Blue *(BEP, EDS: point 1)*	**Si**, **Na**, **S**, (**Cl**, **Al**, **Ca**, K, Mg, P, Ti Zn, Fe, Mn)	378, 549, 582	Lazurite
	Red *(REP, EDS: point 3)*	**Fe**, Si, (S, Ca, Mg, Al, Zn, P, Cl, K, Mn, Cu)	225, 245, 292, 411, 496, 610	Hematite
	Red	-	248, 299, 387	Goethite
Rosette	Red *(RLR, EDS point 4)*	**Fe**, Si, (S, Ca, Mg, Al, P, K, Ti, Mn)	225, 292, 411, 610	Hematite
	Blue *(BLR, EDS: point 5)*	**Si**, **Al**, (Fe, Mg, **Ca**, K, **S**, **Cl**, **Na**)	378, 549	Lazurite
	Red	-	248, 299, 387	Goethite
Axe	Blue *(BAA, EDS: point 6)*	**Si**, **Al**, **Ca**, (K, **Cl**, Fe Cu, **S**, Mg, **Na**)	240, 280	Lazurite, Azurite?
	Red	-	218, 310	Hematite
		-	380	Goethite
		-	252, 343	Cinnabar
	Black	-	1330	Carbon-Black
Hebrew inscription	Blue *(BIT, EDS: point 7)*	**Si**, **S**, **Ca**, **Al**, **Na**, **Fe**, (**Cl**, K, Mg, P, Cu)	378, 545	Lazurite
	Red *(RIT, EDS: point 8)*	**Fe**, Si, (Al, Mg, K, S, Na, Ca, Cu, Ti, Mn)	225, 292, 410, 610	Hematite
	Black *(Bk.IT, EDS: point 9)*	**Fe**, (Si, Ca, K)	-	Magnetite

* Elements responsible for the coloring are in bold; minor and trace elements are in parentheses.

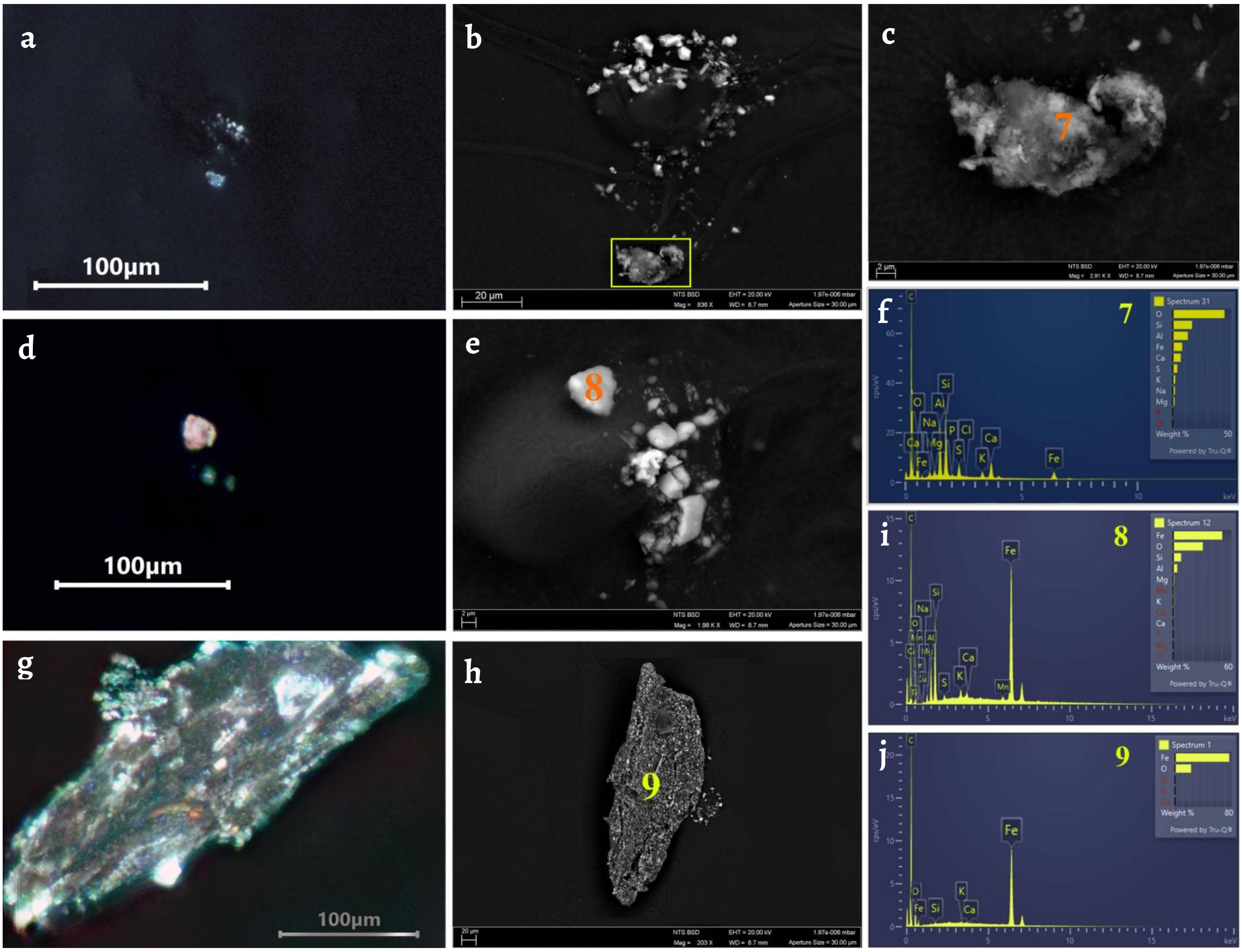

Figure 16. Paper squeeze of the Hebrew inscription block: *a)* blue particle (BIT) under PLM and *b)* SEM image; *c)* high magnification of yellow rectangle in b; *d)* red particle (RIT) besides some blue particles under OM; *e)* SEM image of d; *f)* EDS spectrum of point 7 in *c*; *g)* of a black particle (Bk.IT) under OM; *h)* SEM image of g; *i)* EDS spectrum of the red particle in e (point 8); *j)* EDS spectrum of point 9 in h.

Analysis of point 7 from the blue particle (BIT) indicated Si, Al, Fe, Ca, and S, as major constituents and Mg, K, and Na as minor elements respectively as well as traces of P, Cl, and Cu components (Figure 16). This composition is consistent with the EDS of point 8 (RIT) that identified Fe, Si, and Al as major and Mg, Mn, K, Cu, S, Ca, Ti, and Na as minor constituents respectively. The high content of iron (Fe) in point 8 could be related to hematite as it was identified with Raman analysis. The other constituent represents the lazurite blue component. Figure 16d shows how close the red particle is located next to the blue particles. This may be contaminated. EDS analysis of point 9 from black particles (Bk.IT) identified mainly iron (Fe) and trace constituents of Si, K, and Ca (Table 1). According to the EDS result, it is magnetite (Fe_3O_4).

Discussion

High-magnification microscopic investigation and microchemical analysis techniques were used to identify pigments within the fibers of four paper squeezes molded from limestone monuments at Pasargadae and Persepolis. Red, blue, and black pigment particles previously identified on the facades of certain monuments have now been documented on architectural features of four additional, previously unstudied monuments (Palace P and Gate R at Pasargadae; Apadana and Tachara at Persepolis) on the sites here, too.

An ear from Palace P in Pasargadae and a block with a Hebrew inscription from the Tachara at Persepolis were found to have been painted with widespread and abundant blue pigment particles. The surface of a rosette from the feather crown of a lamassu on Gate R at Pasargadae was covered with red and blue pigments.

Materials analyses of the blue pigments revealed a complex chemical composition indicating that lazurite was used which Raman spectrums confirmed it. Raman spectroscopy revealed that the red on the ear and the rosette from Pasargadae contained a mixture of goethite and hematite particles. Hematite was identified as red in the stone block with the Hebrew inscription from the Tachara at Persepolis. It is worth noting that the spectra of red particles from the stone axe on the Apadana showed three different minerals: goethite, hematite, and cinnabar. Magnetite was identified as black pigment on the squeeze of the Hebrew inscription stone block from the Tachara at Persepolis.

Analytical investigation showed that parts of the surface of the limestone ear from Palace P at Pasargadae and the block with the Hebrew inscription from the Tachara at Persepolis were originally painted in blue. The blue particles were mainly composed of lazurite. Lazurite was never reported as a pigment either in Pasargadae or in Persepolis. Only Egyptian blue and azurite were hitherto identified [1, 37-38].

The lazurite formula is $(Na,Ca)_8(AlSiO_4)_6(S,SO_4,Cl)_{1-2}$. The mineral responsible for the blue color of lapis lazuli is lazurite. Although lazurite is the main mineral in the composition of lapis lazuli rocks, most lapis lazuli rocks contain calcite (white phase), sodalite group minerals (blue phases), pyrite (metallic golden), and other silicates such as augite, diopside, enstatite, mica, hornblende, sanidine and nosean [36, 39-40]. Extracting a natural ultramarine, blue pigment (lazurite) from lapis lazuli was common in the past [41]. The method of purifying ultramarine has been described in Persian scientific texts on mineralogy and glazing, medicine and pharmacology, colorant making, and art resources. Badakhshan in Afghanistan has been identified as the main source of natural lapis lazuli in ancient West Asia and Egypt [42-45]. Recently, traces of lazurite were identified on paper squeezes from the Frataraka complex below the platform of Persepolis in Berlin [46]. Reference Raman spectra from samples of ultramarine (pure lazurite) from later periods in Iran show a Raman peak at 1096 cm^{-1} [47-49]. Such was not the case in our results where the Raman spectra showed a peak at 1086/1089 cm^{-1}. This could be due to a mineral inclusion related to calcite [50]. The impurities, it identified as signatures of other components of the rock matrix, both elements (Ca, Mg, K, and trace elements) and minerals (like calcite), accordingly the blue pigments cannot be a purified ultramarine. Therefore, these blue pigments are ascribed to an insufficient purification of the finely ground natural pigments. Provenance studies on ultramarine pigments indicate slight differences in the elemental composition from each source studied in the past (i.e., Afghanistan, Siberia, and Chile). Samples from Afghanistan are generally characterized by a higher concentration of potassium (K) and the trace element magnesium (Mg) [50-51]. The minor elements of the blue particles (K and Mg) found on our paper squeezes can suggest that either the blue pigment or its source originated from Badakhshan.

The fact that the paper squeeze of the ear excavated at Palace P in Pasargadae contains blue pigments makes an earlier suggestion that it was a model of the sculptor unlikely: why would a sculptor's model have been painted? If the limestone ear was originally painted it likely stemmed rather from the head of an anthropomorphic feature in an earlier building phase of Palace P.

EDS results confirmed that Cu was a significant constituent (minor) of the blue on the stone axe depicted on the Apadana and the stone block with the Hebrew inscription from the Tachara besides lazurite. Some lapis lazuli objects from Persepolis were analyzed previously and copper was reported as a trace element in their composition [36]. Accordingly, the copper identified by EDS could not be linked to the source of pigment, but it could be attributed to some blue copper-bearing pigments such as Egyptian blue ($CaCuSi_4O_{10}$) or azurite ($Cu_3(OH)_2(CO_3)_2$). Earlier examinations identified Egyptian blue as a blue pigment on a painted plaster from the same palace P at Pasargadae and on the facades of the Persepolis terrace [1, 52]. MBI technique identified tiny fluorescence particles on the two paper squeezes through VIL images (Figure 8). The fluorescence particles might represent copper and a low percentage of Egyptian blue in the blue particle. Alternatively, since a band of azurite was identified besides lazurite in one Raman spectrum (Figure 11), and since a combination of azurite and Egyptian blue was already identified in Persepolis [1], using either one of the copper-bearing pigments or a mixture of two blue copper-bearing minerals of Egyptian blue/azurite with lazurite is likely. On the other hand, this can occur by contamination by using the same paint bowls or brush containing a vestige of Egyptian blue/azurite for the lazurite blue during the painting of the stone facades. It is also possible that two different layers of blue were on top of each other. Because of the low concentration of pigments, the analytical results cannot be used to support any of these hypotheses.

The rosette of the feather crown from Gate R at Pasargadae was decorated with red and blue paint--such was also noted by the excavators shortly after the excavation at Persepolis [2, p. 95 fig. 3.3]). Both goethite and hematite (iron oxides) were identified on the rosette and the ear from Palace P at Pasargadae. The presence of both goethite and hematite may be a result of heating goethite to produce hematite [28]. It has been proven that heating the natural goethite leads to a similar spectrum as measured for the natural hematite [53]. However, one should bear in mind that natural iron minerals are sometimes poorly crystallized and transform rapidly during Raman measurements [35], although it is measured under low laser power (ca. 1 mW). On the other hand, goethite could stem from contamination from the ore, but it was reported in previous studies that show a significant content of goethite in red pigments. Therefore, it is impossible to verify this hypothesis. We can only conclude that two hematite and goethite minerals were identified as red at Gate R, Pasargadae.

Hematite was identified as a red pigment on the block with the Hebrew inscription from the Tachara at Persepolis. Interestingly, cinnabar was also identified besides goethite and hematite in a single particle of the stone axe from the Apadana. The presence of hematite and goethite follows the same idea that either hematite was produced from goethite or goethite converted to hematite under the Raman measurement.

Hematite exists in many deposits throughout Iran, often within easy reach. Cinnabar, however, is much rarer. Small deposits of cinnabar have been identified in Zarehshuran, Agh-Darreh, and Shakh-Shakh, in northwestern Iran [54]. Such a combination of pigments of hematite and cinnabar was also identified in the red-surfaced plaster floors of the Tachara at Persepolis and on the paint surface of Pasargadae [23-24, 52]. There, a thin layer of cinnabar was used on top of a hematite layer [1]. Hematite was used as a primer coat to provide a smooth surface on the plaster for the final paint layer. In this way, a rare and expensive pigment would not have been wasted on the non-visible layer. However, neither the stones of Persepolis nor the stones of Pasargadae are as porous as the plaster [55]. Therefore, hematite was not used to provide a smooth layer in this case. It has been assumed that purer hematite was used for darker red, whilst lead red was used for a reddish-pink decoration on painted plaster at Pasargadae [52]. Accordingly, the reason for combining different reds can be simply a creation of intended different red hues in a painting. The cause for observing dark-red cinnabar instead of reddish-pink, in the paper squeeze of the stone axe, could be either because of mixing hematite and goethite with cinnabar or cinnabar degradation. It is worth noting that cinnabar may have degraded and changed into the dark red metacinnabar (HgS) phase by exposure to light and weathering over a long period, the original bright red color darkens and transforms into black [55-57]. Due to the small size of the particles, it is not possible to trace this phenomenon on the paper squeezes. Different red hues open a question about the stratigraphy of the polychromy surface of the northern facade of Apadana. Scientific examination of remaining pigments on the surface of the palace or other paper squeezes would help us answer this question in the future.

The black pigment of the block with the Hebrew inscription was identified as magnetite black. It was assumed the Achaemenid black pigments are soot from the burning of organic materials. Indeed, carbon black was previously found at Pasargadae and Persepolis [52]. It is the first time that magnetite black has been reported in Achaemenid polychromy. It is impossible, however, to declare that magnetite black was a prevalent pigment as much as carbon-black during the time of the Achaemenids by finding a particle of magnetite. One should consider the possibility of hematite reduction to magnetite due to the weathering of the source rock (ore) [58]. This alteration is found in the natural deposits that high temperature and high pressure of hydrogen can accelerate its reduction reaction, although, the more stable phases of iron oxides are hematite and magnetite.

We do not want to exclude that some red and blue pigments identified on the paper squeeze of the stone axe or on the paper squeeze of the rosette could have originated from modern pen ink (Figure 11e). The ink may have been inserted either by Herzfeld and his team when they were marking the area of the molding or by archaeologists or curators who were studying and labeling the papers later.

Conclusions

Multianalytical investigations of four paper squeezes from previously unstudied stone reliefs at Pasargadae and Persepolis contribute to our existing and growing knowledge about evidence of ancient polychromy on these sites. There is evidence that an ear excavated in Palace P and a feather crown from Palace R, both at Pasargadae, have been painted. Previous examinations on the polychromy of other stone monuments close to the four architectural fragments and features introduced here provided evidence for the use of hematite as red pigment, goethite and cinnabar for red hues and carbon oxide to produce black pigment. Our study also suggests that the painters used lazurite blue and, probably, magnetite black. These findings are important in two respects. With ongoing studies on other monuments on the sites of Pasargadae and Persepolis, this investigation provides additional evidence that parts of the Achaemenid Persian stone facades were painted with blue materials probably made from lapis lazuli. The lazurite blue particles identified on the squeezes indicate the importance of the use of precious materials on the sites. Previously, only azurite and Egyptian blue were identified as the main blue pigments used for Achaemenid stone reliefs. These findings also prove that indirect scientific investigation in combination with traditional methods of documentation provides an opportunity to discover new information on ancient polychromies.

Acknowledgements

The authors acknowledge the support of Kim Benzel, Curator in Charge, Daira Eden Robert, Collections Manager, and Chloe Lovelace, Collections Specialist, Department of Ancient Near Eastern Art at The Metropolitan Museum of Art, as they facilitated access to the paper squeezes. The authors are also grateful for the support of Marco Leona, David H. Koch Scientist in Charge, Federico Carò, and Hitomi Fujii, Department of Scientific Research at The Metropolitan Museum of Art, and to two anonymous reviewers for helpful advice and suggestions.

REFERENCES

1. Stodulski, L.; E. Farrell; R. Newman, 'Identification of ancient Persian pigments from Persepolis and Pasargadae', *Studies in Conservation* **29**(3) (1984) 143-154, https://doi.org/10.2307/1506017.
2. Nagel, A., *Color and meaning in the art of Achaemenid Persia*, Cambridge University Press, Cambridge (2023).
3. *Ernst Herzfeld Papers*, Smithsonian Institution, NMAA, Gift of Ernst Herzfeld (1946).
4. Nagel, A., R. Woody, 'Excavations in an archive. An update on the Ernst Herzfeld online resources at the Freer|Sackler in Washington DC', in *A hundred years of excavations in Samarra*, ed. J. Gonnella, Reichert, Wiesbaden (2014) 18-27.
5. Root, M. C., 'The Herzfeld archive of The Metropolitan Museum of Art', *Metropolitan Museum Journal* **11** (1976) 119-124.
6. Nagel, A., 'Preserving the Achaemenid Persian legacy: aspects of conservation, technology, polychromy, and material culture in Persepolis', in *The art of empire in Achaemenid Persia: studies in honour of Margaret Cool Root*, eds. E. Dusinberre, M. Garrison & W. Henkelman, Netherlands Institute for the Near East (NINO), Leiden (2020) 113-136.
7. Booth, C., *Excavating paper squeezes: identifying the value of nineteenth and early twentieth century squeezes of ancient Egyptian monuments, through the collections of seven UK archives*, PhD dissertation, Department of Classics, Ancient History and Archaeology, University of Birmingham, Birmingham (2018), https://etheses.bham.ac.uk/id/eprint/8715/ (accessed 2024-05-07).
8. Van de Ven, A., 'The biography of the lateran squeezes: the curation of archaeological knowledge through hands-on replication', *Museum History Journal* **16**(2) (2023) 119-140, https://doi.org/10.1080/19369816.2023.2187947.
9. Burman, A., 'Paint pigment on epigraphic squeezes: a case-study from the Etruscological collections of Olof August Danielsson', *Etruscan and Italic Studies* **26**(2) (2023) 44-63, https://doi.org/10.1515/etst-2022-0017.
10. Calmeyer, P., 'Figürliche Fragmente aus Pasargadae nach Zeichnungen E. Herzfelds', *Archäologische Mitteilungen aus Iran* N.S. **14** (1981) 27-44.
11. Herzfeld, E., 'Bericht über die Ausgrabungen von Pasagardae 1928', *Archäologische Mitteilungen aus Iran* **1** (1929) 4-16.
12. Stronach, D., *Pasargadae. A report on the excavations conducted by the British Institute of Persian Studies from 1961 to 1963*, Clarendon Press, Oxford (1978).
13. Stronach, D., 'Anshan and Parsa: early Achaemenid history, art and architecture on the Iranian plateau', in *Mesopotamia and Iran in the Persian Period: conquest and imperialism 539-331 BC*, ed. J. Curtis, British Museum Press, London (1997) 35-53.
14. Ernst Herzfeld Papers, 'Note Books', in *Freer/Sackler Gallery of Art Archives*, Slideshow | /Public_Sets/FS/FSA/FSA_A.06_03.92 (accessed 2024-08-12).
15. 'Public_Sets', in *Freer/Sackler Gallery of Art Archives*, Slideshow | /Public_Sets/FS/FSA/FSA_A.06_02.01.04 (accessed 2024-08-12).
16. Roaf, M., *Sculptures and sculptors at Persepolis*, Iran XXI, The British Institute of Persian Studies, London (1983).
17. Schmidt, E., *Persepolis. Structures. Reliefs. Inscriptions*, University of Chicago Press, Chicago (1953).
18. Rehm, E., 'Die Abklatsche aus Persepolis und Pasargadae von Friedrich Sarre im Museum für Islamische Kunst in Berlin', *Mitteilungen der Deutschen Orient-Gesellschaft zu Berlin* **153** (2021) 27-55.
19. Walser, G., *Die Völkerschaften auf den Reliefs von Persepolis*, Gebr. Mann, Berlin (1966).
20. 'Persepolis, Apadana, North Stairs, Tribute Bearers, Sogdians', in *Livius.org – Articles on ancient history*, https://www.livius.org/pictures/iran/persepolis/persepolis-apadana/persepolis-apadana-north-stairs/apadana-north-stairs-tribute-bearers-sogdians/ (accessed 2024-05-17).
21. Gropp, G., 'Die Darstellung der 23 Völker auf den Reliefs des Apadana von Persepolis', *Iranica Antiqua* **154** (2009) 283-359, https://doi.org/10.2143/IA.44.0.2034381.
22. Herzfeld, E.; Sarre, F., *Iranische Felsreliefs. Aufnahmen und Untersuchungen von Denkmälern aus alt- und mittelpersischer Zeit*, Wasmuth, Berlin (1910).
23. Nagel, A., *Colors, gilding and painted motifs in Persepolis: approaching the polychromy of Achaemenid Persian architectural sculpture, c. 520-330 BCE*, PhD dissertation, Department of History of Art, University of Michigan, Ann Arbor (2010).
24. Oudbashi, O.; Shekofteh, A.; Fadaei, H., 'An exploration of a 2500-year-old monument: a reappraisal of the Achaemenian decorative flooring plasters in Persepolis world heritage site (ca. 550-330 BCE)', *Studies in Conservation* **68**(5) (2022) 491-501, https://doi.org/10.1080/00393630.2022.2062562.
25. Matson, F., 'A study of wall plaster, flooring and bitumen', in *Persepolis I: structures, reliefs, inscriptions*, ed. E. Schmidt, University of Chicago Press, Chicago (1953) 285-288.
26. Lafuente, B.; Downs, R. T.; Yang, H.; Stone, N.; Armbruster, T.; Danisi, R. M., 'The power of databases. The RRUFF project', *Highlights in Mineralogical Crystallography* **1** (2015) 25, https://doi.org/10.1515/9783110417104-003.

27. Bouchard, M.; Smith, D.C., 'Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **59**(10) (2003) 2247-2266, https://doi.org/10.1016/S1386-1425(03)00069-6.
28. Bell, I.M.; Clark, R.J.; Gibbs, P.J., 'Raman spectroscopic library of natural and synthetic pigments (pre-1850 AD)', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **53**(12) (1997) 2159-2179, https://doi.org/10.1016/S1386-1425(97)00140-6.
29. 'PR4', in *Soprano spectral library*, https://soprano.kikirpa.be/index.php?lib=sop&id=PR4_B_785_kikirpa (accessed 2024-04-04).
30. Scheuermann, W.; Ritter, G. J., 'Raman spectra of cinnabar (HgS), realgar (As_4S_4) and orpiment (As_2S_3)', *Zeitschrift für Naturforschung A* **24**(3) (1969) 408-411, https://doi.org/10.1515/zna-1969-0317.
31. de Faria, D. L. A.; Lopes, F. N., 'Heated goethite and natural hematite: can Raman spectroscopy be used to differentiate them?' *Vibrational Spectroscopy* **45**(2) (2007) 117-121, https://doi.org/10.1016/j.vibspec.2007.07.003.
32. Coccato, A.; Jehlicka, J.; Moens, L.; Vandenabeele, P., 'Raman spectroscopy for the investigation of carbon-based black pigments', *Journal of Raman Spectroscopy* **46**(10) (2015) 1003-1015, https://doi.org/10.1002/jrs.4715.
33. Tomasini, E.P.; Halac, E.B.; Reinoso, M.; Di Liscia, E.J.; Maier, M.S., 'Micro-Raman spectroscopy of carbon-based black pigments', *Journal of Raman Spectroscopy* **43**(11) (2012) 1671-1675, https://doi.org/10.1002/jrs.4159.
34. Cuesta, A.; Dhamelincourt, P.; Laureyns, J.; Martinez-Alonso, A.; Tascon, J. M. D., 'Comparative performance of X-ray diffraction and Raman microprobe techniques for the study of carbon materials', *Journal of Materials Chemistry* **8**(12) (1998) 2875-2879, https://doi.org/10.1039/A805841E.
35. de Faria, D. L.; Venâncio Silva, S.; de Oliveira, M. T., 'Raman microspectroscopy of some iron oxides and oxyhydroxides', *Journal of Raman Spectroscopy* **28**(11) (1997) 873-878, https://doi.org/10.1002/(SICI)1097-4555(199711)28:11<873::AID-JRS177>3.0.CO;2-B.
36. Oudbashi, O.; Hessari, M.; Shekofteh, A., 'Minero-chemical and provenance analysis of Achaemenian lapis lazuli cylinders from Persepolis', *Archaeometry* **66**(1) (2024) 57-75, https://doi.org/10.1111/arcm.12903.
37. Amadori, M. L.; Vagnini, M.; Vivani, R.; Anselmi, C.; Chaverdi, A. A.; Callieri, P.; Matin, E.; Mengacci, V., 'Advances in the characterization of colourful residues unearthed in Persepolis West craft zone using microscopic and spectroscopic techniques', *Microchemical Journal* **167** (2021) 106304, https://doi.org/10.1016/j.microc.2021.106304.
38. Oudbashi, O.; Hessari, M., 'A "Western" imported technology: an analytical study of Achaemenid Egyptian blue objects', *Journal of Cultural Heritage* **47** (2021) 246-256, https://doi.org/10.1016/j.culher.2020.11.001.
39. Oudbashi, O.; Shekofteh, A.; Eskandari, N., 'Provenance of the Bronze Age lapis lazuli pieces from the Early Urban Center of Konar Sandal, Jiroft, Southern Iran', *Journal of Archaeological Science: Reports* **55** (2024) 104527, https://doi.org/10.1016/j.jasrep.2024.104527.
40. Chukanov, N. V.; Sapozhnikov, A. N.; Shendrik, R. Y.; Vigasina, M. F.; Steudel, R., 'Spectroscopic and crystal-chemical features of sodalite-group minerals from gem lazurite deposits', *Minerals* **10**(11) (2020) 1042, https://doi.org/10.3390/min10111042.
41. González-Cabrera, M.; Arjonilla, P.; Domínguez-Vidal, A.; Ayora-Cañada, M. J., 'Natural or synthetic? Simultaneous Raman/luminescence hyperspectral microimaging for the fast distinction of ultramarine pigments', *Dyes and Pigments* **178** (2020) 108349, https://doi.org/10.1016/j.dyepig.2020.108349.
42. Zarkhord, S.; Nemati-Babaylou, A.; Koochakzaei, A., 'The methodology of Lzurite (Lājavard) making in ancient Persian scientific texts', *Journal for the History of Science* **21**(2) (2024) 87-114, 10.22059/jihs.2024.374980.371787.
43. Gettens, R. J., 'The materials in the wall paintings of Bamiyan, Afghanistan', *Technical Studies in the Field of the Fine Arts* **6**(3) (1938) 186-193.
44. Plesters, J., 'Ultramarine blue, natural and artificial', *Studies in Conservation* **11**(2) (1966) 62-75, https://doi.org/10.1179/sic.1966.009.
45. Holakooei, P.; Karimy, A. H., 'Early Islamic pigments used at the Masjid-i Jame of Fahraj, Iran: a possible use of black plattnerite', *Journal of Archaeological Science* **54** (2015) 217-227, https://doi.org/10.1016/j.jas.2014.12.001.
46. Nagel, A.; Aibéo, C.; Simon, S., 'New blue surfaces at Persepolis: recent observations on the polychromies of inscribed stone slabs from the Frataraka complex', in *Working on stones in the Achaemenid Persian empire*, ed. A. Nagel, J. Thomalsky & Z. Zehbari, Reimer, Berlin (in press).
47. Bicchieri, M.; Nardone, M.; Russo, P. A.; Sodo, A.; Corsi, M.; Cristoforetti, G.; Palleschi, V.; Salvetti, A.; Tognoni, E., 'Characterization of azurite and lazurite-based pigments by laser-induced breakdown spectroscopy and micro-Raman spectroscopy', *Spectrochimica Acta Part B: Atomic Spectroscopy* **56**(6) (2001) 915-922, https://doi.org/10.1016/S0584-8547(01)00228-2.
48. Colomban, P., 'Lapis lazuli as an unexpected blue pigment in Iranian Lâjvardina ceramics', *Journal of Raman Spectroscopy* **34**(6) (2003) 420-423, https://doi.org/10.1002/jrs.1014.
49. Holakooei, P.; de Lapérouse, J. F.; Rugiadi, M.; Carò, F., 'Early Islamic pigments at Nishapur, north-eastern Iran: studies on the painted fragments preserved at The Metropolitan Museum of Art', *Archaeological and Anthropological Sciences* **10** (2018) 175-195, https://doi.org/10.1007/s12520-016-0347-7.
50. Osticioli, I. A.; Mendes, N. F.; Nevin, A.; Gil, F. P.; Becucci, M.; Castellucci, E. M., 'Analysis of natural and artificial ultramarine blue pigments using laser-induced breakdown and pulsed Raman spectroscopy, statistical analysis and light microscopy', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **73**(3) (2009) 525-31, https://doi.org/10.1016/j.saa.2008.11.028.
51. Favaro, M.; Guastoni, A.; Marini, F.; Bianchin, S.; Gambirasi, A., 'Characterization of lapis lazuli and corresponding purified pigments for a provenance study of ultramarine pigments used in works of art', *Analytical and Bioanalytical Chemistry* **402** (2012) 2195-2208, https://doi.org/10.1007/s00216-011-5645-4.
52. Aloiz, E.; J. Douglas; A. Nagel, 'Painted plaster and glazed brick fragments from Achaemenid Pasargadae and Persepolis, Iran', *Heritage Science* **4**(3) (2016), https://doi.org/10.1186/s40494-016-0072-7.

53. Hanesch, M., 'Raman spectroscopy of iron oxides and (oxy) hydroxides at low laser power and possible applications in environmental magnetic studies', *Geophysical Journal International* **177**(3) (2009) 941-948, https://doi.org/10.1111/j.1365-246X.2009.04122.x.
54. Momenzadeh, M.; Nezafati, N.; Sarraf, M. R.; Shabani, K., 'Ancient gold-mercury mining in the Takht-e Soleyman area, Northwest Iran', *Metalla* **22**(2) (2016) 147-168, https://doi.org/10.46586/metalla.v22.2016.i2.147-168.
55. Shekofteh, A.; Molina, E.; Arizzi, A.; Cultrone, G.; Ahmadi, H.; Yazdi, M., 'Characterization and damage assessment of stones used in the Pasargadae World Heritage Site, Achaemenian period', *International Journal of Architectural Heritage* **13**(4) (2019) 521-536, https://doi.org/10.1080/15583058.2018.1436728.
56. Gettens, R.; Feller, R.; Chase, W., 'Vermilion and cinnabar', *Studies in Conservation* **17** (1972) 45-69, https://doi.org/10.1179/sic.1972.006.
57. Gotoshia, S. V.; Gotoshia, L. V., 'Laser Raman and resonance Raman spectroscopies of natural semiconductor mineral cinnabar, α-HgS, from various mines', *Journal of Physics D: Applied Physics* **41**(11) (2008) 115406, https://doi.org/10.1088/0022-3727/41/11/115406 .
58. Frietsch, R., *The relationship between magnetite and hematite in the iron ores of the Kiruna type and some other iron ore types*, Sveriges Geologiska Undersökning, Uppsala (1967).

RECEIVED: 2024.5.10
REVISED: 2024.12.2
ACCEPTED: 2024.12.9
ONLINE: 2025.4.27