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MULTI-ANALYTICAL CHARACTERIZATION OF RED ROCK PAINTING PIGMENTS FROM NORTH KHORASAN, NORTHEASTERN IRAN

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Abstract: This study presents the first multi-analytical archaeometric investigation of red rock art pigments from three painted shelters in North Khorasan Province, Iran — Bash Mahalleh, Zeynekanlu, and Nargeslou, whose motifs span chronologically and stylistically distinct traditions from the Late Chalcolithic/Early Bronze Age to the Iron Age and historical periods. Nine pigment micro-samples (three per site) and one local geological red-earth reference were analyzed using SEM–EDS, micro-Raman, and FTIR spectroscopy. The results consistently identify hematite (α-Fe2O3) as the primary chromophore, confirming the use of natural iron-rich ochres across all studied sites. No alternative iron oxides or synthetic red pigments were detected. Microstructural data reveal dispersed pigment particles within a heterogeneous calcareous matrix, indicating the direct exploitation of local earth resources without advanced processing or intentional refinement. Furthermore, a ubiquitous calcium oxalate monohydrate patina was identified on the painted surfaces, suggesting secondary biogenic weathering or the degradation of ancient organic materials. Despite marked stylistic and chronological differences among the painted shelters, the mineralogical uniformity of the pigments suggests broadly similar technological choices, likely constrained by the regional availability of iron-rich earth resources, thereby providing the first archaeometric framework for interpreting pigment technology in northeastern Iranian rock art. While preliminary spectral data show similarities between the rock art pigments and the geological sample, definitive provenance attribution requires expanded trace-element sourcing.

Keywords: Rock art, Red ochre, Hematite, SEM-EDS, Micro-Raman, Northeastern Iran.

چکیده: این پژوهش نخستین مطالعه چندتحلیلی باستان‌سنجیِ رنگدانه‌های سرخِ نقوش صخره‌ای را از سه پناهگاه صخره‌ای نقاشی‌شده در استان خراسان شمالی ایران، شامل باش‌محله، زینکانلو و نرگسلو، ارائه می‌کند. نقوش این محوطه‌ها از نظر گاه‌نگاری و سبک‌شناختی، سنت‌های متمایزی را از اواخر مس‌وسنگ/اوایل عصر مفرغ تا عصر آهن و دوره‌های تاریخی دربرمی‌گیرند. نه ریزنمونه رنگدانه (سه نمونه از هر محوطه) و یک نمونه مرجع از خاک سرخ زمین‌شناختی محلی با استفاده از میکروسکوپ الکترونی روبشی مجهز به طیف‌سنجی پراش انرژی پرتو ایکس ($SEM–EDS$)، طیف‌سنجی میکرو–رامان و طیف‌سنجی تبدیل فوریه فروسرخ ($FTIR$) مورد تجزیه‌وتحلیل قرار گرفتند. نتایج به‌طور پایدار هماتیت (α-Fe_2O_3) را به‌عنوان کروموفور اصلی شناسایی کردند و بدین‌ترتیب استفاده از اُخرای طبیعی غنی از آهن را در تمامی محوطه‌های بررسی‌شده تأیید نمودند. هیچ‌گونه اکسید آهن جایگزین یا رنگدانه قرمز مصنوعی شناسایی نشد. داده‌های ریزساختاری، پراکنش ذرات رنگدانه را درون یک ماتریس آهکی ناهمگن نشان می‌دهند که حاکی از بهره‌برداری مستقیم از منابع خاکی محلی، بدون فرآوری پیشرفته یا پالایش هدفمند، است. افزون بر این، وجود یک پاتینای اگزالات کلسیم تک‌آبه به‌طور گسترده بر سطوح نقاشی‌شده شناسایی شد که می‌تواند بیانگر هوازدگی زیستی ثانویه یا تخریب مواد آلی باستانی باشد. با وجود تفاوت‌های چشمگیر سبکی و گاه‌نگاری میان پناهگاه‌های نقاشی‌شده، یکنواختی کانی‌شناختی رنگدانه‌ها نشان‌دهنده انتخاب‌های فناورانه‌ای عمدتاً مشابه است که احتمالاً به‌واسطه دسترسی منطقه‌ای به منابع خاکی غنی از آهن محدود شده‌اند. از این منظر، پژوهش حاضر نخستین چارچوب باستان‌سنجی را برای تفسیر فناوری تولید و کاربرد رنگدانه‌ها در هنر صخره‌ای شمال‌شرق ایران فراهم می‌کند. اگرچه داده‌های طیفی مقدماتی شباهت‌هایی میان رنگدانه‌های نقوش صخره‌ای و نمونه زمین‌شناختی نشان می‌دهند، تعیین قطعی منشأ آنها مستلزم انجام مطالعات گسترده‌تر مبتنی بر ردیابی عناصر کم‌مقدار است.

کلیدواژه: هنر صخره‌ای، اُخرای سرخ، هماتیت، SEM–EDS، میکرو–رامان، شمال‌شرق ایران.

I. Introduction

The study of rock art, as an interdisciplinary research domain within archaeology, conservation, restoration, and archaeometry, necessitates a systematic review of previous studies and a rigorous examination of the scientific methods employed in this field. Red mineral pigments, particularly hematite, manganese oxide, and goethite, constitute some of the oldest materials associated with human symbolic activity. Archaeological evidence suggests that red coloring materials were used in the earliest examples of cave paintings discovered, dating back to the Paleolithic period (Chalmin et al., 2003). While hematite (Fe_2O_3) is widely recognized as the principal chromophore responsible for red coloration, other iron-bearing phases such as goethite, lepidocrocite, maghemite, or thermally transformed iron hydroxides may contribute to red to brown tonalities depending on crystallinity, particle size distribution, and thermal history. Natural ochres therefore represent heterogeneous geological materials rather than chemically uniform pigments (Eastaugh et al., 2008). Over the past two decades, pigment research has emphasized integrated multi-analytical approaches combining elemental, mineralogical, and spectroscopic techniques to distinguish primary pigment phases from secondary alteration products and environmental crusts. Accurate mineralogical identification is particularly important in contexts where chronological interpretations depend on stratigraphic relationships. In South-West Africa, using pXRF analysis, oxides of iron were identified in Namibia's Erongo rock paintings and confirmed their local origins (Mauran et al., 2019). In eastern Indonesia, using the uranium series method, the age of the cave paintings in Maros-Pangkep was determined to be 51,200 years. This study also identified minerals like hematite and calcite in the motifs (Oktaviana et al., 2024). Multiple methods (PIXE, NAA, SEM-EDS, FTIR, Raman) analyzed the pigments of "Virgin of Sorrows" and identified them as hematite, calcite, and organic matter. These studies indicate the importance of multiple methods in the exact analysis of pigments (Ortega-Avilés et al., 2005). In a study of the Abrigo del Lince area in Spain, sedimentation patterns and surface changes of rock patterns were investigated using SEM-EDS, Raman spectroscopy, and FTIR. The results showed that sedimentary layers were mainly composed of hematite (red pigment and the oldest layer), calcium oxalate, and gypsum as an erosion product (Nicoli et al., 2023). In Indonesia, Maryanti et al. (2022) employed laboratory-based techniques such as Raman spectroscopy, SEM-EDS, XRF, SR-XRD, XANES, and FTIR to demonstrate that hematite was used as a black pigment in the rock art of the Jufri cave (East Kalimantan). The observed crystallographic changes and octahedral symmetry distortions of the Fe^{3+} ions are attributed to thermal processes, which transformed the pigment's color from red to black and purple. These analyses reveal the complexity of prehistoric pigment production technologies (Maryanti et al., 2022). Investigated 19 pigment samples from the rockshelter of Puerto Roque in Spain using a multi-analytical laboratory approach, including Raman spectroscopy, energy-dispersive X-ray fluorescence (EDXRF), attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). The study revealed that dark pigments were composed of hematite and carbon, orange pigments originated from goethite, and light red pigments were primarily hematite. Furthermore, ATR-FTIR confirmed the role of heat treatment in enhancing the red color, while EDXRF supported the elemental similarity between the pigments and local raw materials. These non-destructive techniques highlight the importance of precise analysis of pigment composition and preparation processes in prehistoric art (Gomes et al., 2024).

Rock art constitutes a significant yet understudied component of Iran's archaeological heritage (Molaie Kordshouli et al., 2022). Despite the identification of approximately 20 pictograph sites across the Iranian Plateau—primarily in the Zagros region and sporadically in eastern Iran—research has traditionally relied on descriptive, historical-analytical, and morphological frameworks (Mohammadi Ghasrian, 2007; Vahdati, 2021a, 2021b). Although limited studies have applied elemental screening, comprehensive multi-analytical investigations integrating phase identification and microstructural analysis remain exceptionally scarce (Sadeghi et al., 2023). Consequently, significant gaps persist regarding long-term technological continuity and procurement strategies. In particular, few studies examine whether stylistically distinct assemblages within a single region share technological traditions or reflect divergent resource choices. Characterizing pigment compositions and microstructural traits in North Khorasan addresses this regional imbalance, providing essential baseline data for broader comparisons between the Iranian Plateau and well-studied global contexts.

Previous investigations across the Zagros region, Fars, northwestern, and central Iran—such as those at Sang-e Mehrdad Humian, Dusheh Cave, Tang-e Tadvan, Aghdash, and Teymareh—have primarily focused on stylistic typologies, motif categorizations, and chronological attributions relative to prehistoric ceramics (Afshari and Forouzan, 2021; Ahari Mostafavi and Asadi, 2021; Azandaryani et al., 2015; Fazel, 2011; Ghasimi et al., 2014, 2016; Karimi, 2007; Soltani, 2010). Where pigment analyses were attempted, they largely confirmed hematite or magnetite presence without evaluating processing microstructures or post-depositional weathering (Rafifar, 2002; Sadeghi et al., 2023). In northeastern Iran, recorded pictograph sites remain exceptionally rare, limited primarily to the Upper Atrak Valley and adjacent ranges in North Khorasan (Vahdati, 2021a). Among these, the shelters of Bash Mahalleh, Zeynekanlu-Mardkanlu, and Nargeslou contain the most significant concentration of red rock art in the region, featuring diverse motifs spanning from the Late Chalcolithic/Early Bronze Age to historical periods (Vahdati, 2021a, 2021b). However, despite their documentation, the technological choices and raw material procurement strategies behind these panels remain unexamined.

A pervasive shortcoming across all aforementioned studies is the complete absence of absolute laboratory dating and advanced chemical analyses of the pigments. Consequently, the chronology of rock art in Iran has relied strictly on stylistic typologies and comparative analyses with prehistoric ceramics, yielding inherently tentative and inconclusive chronological frameworks (Mohammadi Ghasrian, 2007; Karimi, 2007;

Azandaryani et al., 2015). The Upper Atrak Valley and its adjacent mountain ranges in North Khorasan contain the most significant concentration of rock paintings in northeastern Iran. Among these, the panels at Bash Mahalleh, Zeynekanlu-Mardkanlu, and Nargeslou rock shelters stand out for their motif diversity, distinctive execution techniques, and relatively good preservation. Their repertoire, ranging from geometric designs and schematic fauna to naturalistic hunting scenes, points to multiple production episodes, likely spanning from the Late Chalcolithic/Early Bronze Age into later historical periods. Although previous surveys have thoroughly documented these images (Vahdati 2021a; 2021b), technological questions regarding pigment composition and raw material sourcing have remained largely unexplored. To address this gap, we present the first analytical study of pigment samples from these shelters, following internationally established protocols for pigment characterization (Hradil et al. 2003). The present study does not attempt direct dating of pigments; rather, it provides a mineralogical and microstructural framework intended to support future chronological investigations. Against this backdrop, this study integrates SEM–EDS, micro-Raman, and FTIR spectroscopy to evaluate pigment technologies and surface weathering in North Khorasan, bridging a major geographic gap between the Zagros and Central Asia. Beyond basic identification, the study addresses three primary objectives: evaluating whether stylistic and chronological variations correlate with distinct mineralogical choices; investigating microstructural evidence for intentional processing versus direct raw ochre application; and characterizing secondary oxalate crusts to distinguish primary paint layers from post-depositional alteration. By addressing these questions, the study establishes the first comparative archaeometric framework for North Khorasan, offering insights into technological continuity and raw-material procurement on the Iranian Plateau.

II. Materials and Methods

II.1. Study Sites and Archaeological Context

Pigment micro-samples analyzed in this study were collected from three archaeologically distinct painted rock-shelters in various geographic areas within the Khorasan region of northeastern Iran (Fig. 1). The first site, Bash Mahalleh, is situated at an elevation of 2027 m asl in a narrow, V-shaped side valley of the Upper Atrak River (36°59'47.60"N, 58°6'44.23"E). The pigments were sampled from three small limestone recesses along the right bank of the Olang-e Layli stream, where motifs comprise isolated signs and geometric shapes in dark-red, light-red, and brown hues. The predominance of abstract geometric motifs and relatively schematic execution suggests a pictorial tradition distinct from the more naturalistic panels documented elsewhere in the region. Associated surface scatters of Yaz II–III pottery in the vicinity of Bash Mahalleh paintings point to an Iron Age occupation.

The second sampling area comprises the adjacent sites of Zeynekanlu and Mardkanlu, located roughly 700 m apart in another tributary valley of the Upper Atrak, along the eastern slopes of the Shah Jahan Mountain range. At Zeynekanlu (37°2'28.68"N, 58°5'15.42E; 1825 m asl), the paintings are executed on a Jurassic-Cretaceous light grey limestone substrate, featuring hunting scenes and geometric patterns tentatively assigned to the Late Chalcolithic and Early Bronze Age. The nearby Mardkanlu panels display simpler geometric markings and reddish-brown compositions ascribed to the first millennium BCE.

The third site, Nargeslou, is located roughly 20 km west of Bojnord (37°29'57.56" N, 57° 4'46.45" E; 1115 m asl). The sampled panel consists of a naturalistic hunting scene painted on a limestone face, chronologically associated with the Chalcolithic to Early Bronze Age (Vahdati 2021a). The compositional coherence of the panel, including spatially coordinated human and animal figures, suggests a deliberately planned painting episode rather than cumulative accretion through unrelated additions. The stylistic conventions and pigment characteristics at Nargeslou diverge noticeably from those documented at the Upper Atrak Valley sites.

In addition to the archaeological pigments, a geological reference sample was collected from an iron-rich red-earth deposit near Bagh Mahalleh as a preliminary proxy for potential pigment procurement (Fig. 2).

The chronological framework adopted in this study is based exclusively on archaeological evidence derived from previous investigations and should not be interpreted as direct dating of the pigments. The proposed dating relies on stylistic comparisons and associated archaeological materials reported in earlier surveys (Vahdati 2021a, 2021b). Accordingly, the Bash Mahalleh paintings are tentatively assigned to the Late Iron Age (first half of the first millennium BC), whereas the principal painted panels at Zeynekanlu and Nargeslou are attributed to the Late Chalcolithic–Early Bronze Age (ca. 3500-2500 BC). Direct chronometric dating of the pigments or associated mineral crusts will be required to test and refine these archaeological age estimates.

In total, three micro-samples were obtained from each archaeological site (Bash Mahalleh, Zeynekanlu, and Nargeslou), alongside the single geological sample from the Bagh Mahalleh vicinity (Table 1). Sampling was conducted using minimally invasive procedures to preserve the integrity of the painted surfaces.

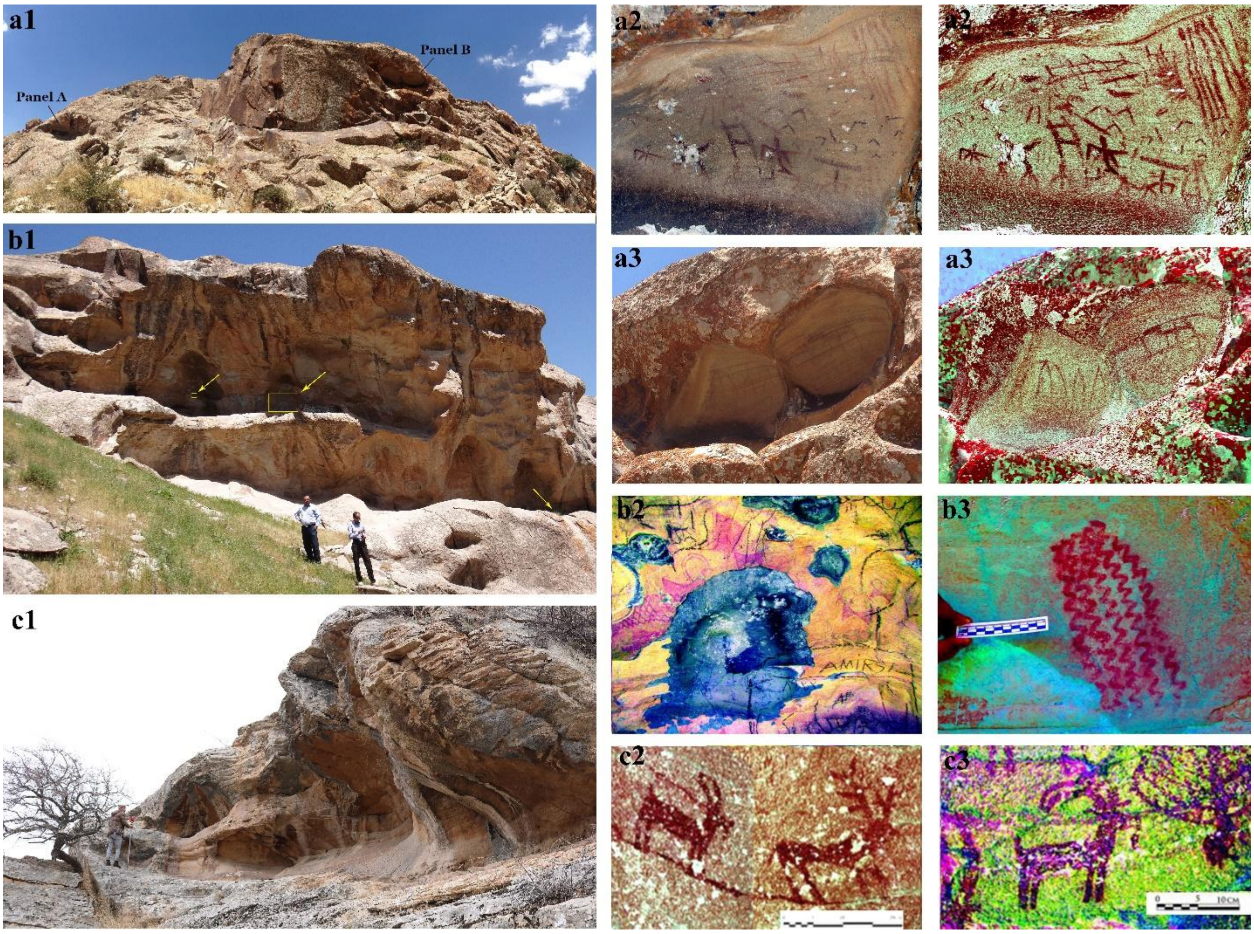

Figure 1: Images of the studied rock art showing the location of the motifs before and after image processing to enhance clarity: a) Bash Mahalleh site; b) Zeynekanlu site; c) Nargeslou site.

Figure 2: Location map of the studied sites in North Khorasan, Iran. (Left) Map of Iran indicating the position of North Khorasan Province and the city of Bojnord. (Right) Satellite view (Google Earth) showing the three rock art localities (Bash Mahalleh, Zeynekanlu, Nargeslou) and the Baghmahaleh ochre source, relative to Bojnord.

The sampling strategy was designed to maximize the representativeness of the investigated pigments while minimizing intervention on the rock art. Three micro-samples were collected from each archaeological site, targeting motifs that differed in morphology, color tone, and preservation state in order to capture the observable variability of the red painting assemblages. Sampling was restricted to areas where minute pigment losses had already occurred or where very small detached particles could be recovered, thereby avoiding unnecessary damage to intact painted surfaces. Because the investigated panels constitute protected cultural heritage, destructive sampling was intentionally kept to the minimum required for reliable multi-analytical characterization. Although the number of samples was necessarily limited, the selected specimens are considered representative of the principal red pigment technology preserved at each site.

Table 1: Sample information including site, sample ID, code, and design typology

Site	Code	Type of design
Bash Mahalleh	BM1	Simple line
	BM2	Simple line
	BM3	Complex line
Zeynekanlu	ZK1	Parallel line
	ZK2	Parallel line
	ZK3	Complex line
Nargeslou	NL1	Undetermined
	NL2	Complex shape
	NL3	Simple line
Bagh Mahalleh	BGH	Raw Ochre

II.2. Scanning Electron Microscopy with Energy-Dispersive Spectroscopy (SEM–EDS)

Microstructural features and surface morphologies were examined using a Tescan MIRA3 field emission scanning electron microscope (FEG-SEM). To accommodate the non-conductive nature of the fragile pigment fragments and preserve them for subsequent analyses, the instrument was operated in low-vacuum mode, eliminating the need for a conductive carbon or gold coating. Chemical mapping and localized elemental compositions were obtained via an attached energy-dispersive X-ray spectrometer (EDS) at an accelerating voltage of 15 kV. Multiple spot analyses were targeted on each sample, with specific point selection tailored to the local thickness and preservation state of the pigment layer.

II.3. Micro-Raman Spectroscopy

Micro-Raman spectroscopy was utilized to determine the specific iron oxide mineral phases responsible for the red coloration. Raman spectra were acquired using an Andor Technology UniDron-A spectrometer integrated with an optical microscope, utilizing 50× objective for precise laser focusing. The 532 nm line of a solid-state laser served as the excitation source, with spectra recorded over a range of 85–2085 cm^{-1} at a spectral resolution of 2 cm^{-1}. To prevent photothermal degradation or unwanted mineral phase transformations, the laser power delivered to the sample surface was strictly maintained at a minimum threshold. Prior to analysis, the spectrometer was calibrated using the characteristic Raman band of a silicon standard.

II.4. Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was performed on a JASCO 680 Plus spectrometer to characterize the functional groups of the accretion layers and alterations formed on the rock art surfaces. Micro-amounts of the scraped accretion samples were gently ground, blended with spectroscopic-grade potassium bromide (KBr), and pressed into translucent pellets. Spectra were collected in transmission mode across the 400–4000 cm^{-1} range at a resolution of 4 cm^{-1}, co-averaging 32 scans per measurement. Background corrections were systematically carried out using a pure KBr pellet under identical analytical conditions.

III. Results and Discussion

Table 2 presents the SEM-EDS elemental data for the rock art samples from Bash Mahalleh, Zeynekanlu, and Nargeslou. Across all three sites, the prominent iron (Fe) signal identifies the medium as an iron-rich earth pigment, such as red ochre. Depending on the specific micro-areas analyzed, the iron content fluctuates widely, ranging from 5% to 80%. Such variations are common, and even minimal amounts of Fe^{3+} are entirely sufficient to yield the characteristic ochre palette; hematite retains its strong tinting power, imparting red-to-brown hues at concentrations well below 2% (Mastrotheodoros and Beltsios, 2022; Rastineh et al. 2017). From an archaeometric perspective, this elemental heterogeneity provides key insights into the operational sequence of pigment production. The marked fluctuation of Fe alongside high levels of Si, Al, and Mg indicates that ancient artists utilized raw, unrefined earth materials without systematic levigation or enrichment protocols.

Although the chemical composition of the samples exhibits certain similarities to that of the Bagh Mahalleh source, the presence of measurable levels of barium in the Bagh Mahalleh sample underscores the necessity for a comprehensive assessment of the chemical profiles of other potential sources. The presence of silicon and aluminum reflects both the aluminosilicate matrix inherent to unrefined natural ochres and minor contributions from the underlying rock substrate or airborne environmental dust. While calcium is also linked to the host rock—pointing to a predominantly calcareous substrate given its high baseline relative to the silicate components—its accumulation within the outermost paint layer suggests a different mechanism. This elevated surface calcium indicates secondary precipitation triggered by long-term weathering, a phenomenon characterized in deeper detail through the FTIR analysis below.

Table 2: SEM-EDS elemental composition (wt%) of the pigment and substrate samples from the Bash Mahalleh, Zeynekanlu, and Nargeslou rock art sites.

Elt	Sample									
	BM1	BM2	BM3	ZK1	ZK2	ZK3	NL1	NL2	NL3	BGH
C	20.7	8.4	11.7	15.7	13.4	27.4	17.0	10.4	15.3	2.63
O	46.1	5.6	35.2	33.0	22.9	24.5	49.4	41.5	48.2	10.27
Na	nd	nd	nd	1.5	nd	1.4	0.1	nd	nd	nd
Mg	1.5	0.7	0.3	1.1	0.4	0.4	0.3	0.2	0.5	0.48
Al	3.9	1.2	1.3	4.6	2.5	5.5	1.3	0.8	2.3	1.52
Si	8.3	3.8	3.1	13.2	1.7	19.4	2.8	1.9	4.3	5.33
S	nd	nd	nd	14.5	17.3	4.2	0.9	1.6	0.8	0.31
K	nd	nd	nd	1.7	0.5	nd	0.2	0.2	0.8	0.44
Ca	8.6	1.3	7.5	9.8	6.8	4.8	11.4	14.6	12.2	0.47
Fe	10.8	79.1	41.1	5.0	34.5	12.4	16.6	28.8	15.7	76.06
Ba	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.49
Total	100	100	100	100	100	100	100	100	100	100

Figure 3 presents a side-by-side comparison of the backscattered (BSE) and secondary electron (SE) SEM images obtained from a sample retrieved from the Bash Mahalleh site. While hematite particles are discernible in the lower-left region, fine, sugar-like crystalline deposits are prominently observed across the majority of the specimen's surface. Microstructurally, the absence of standardized particle sizing or mechanical crushing features confirms a low-intensity processing technology, where mineral nodules were likely ground directly adjacent to the shelter sites.

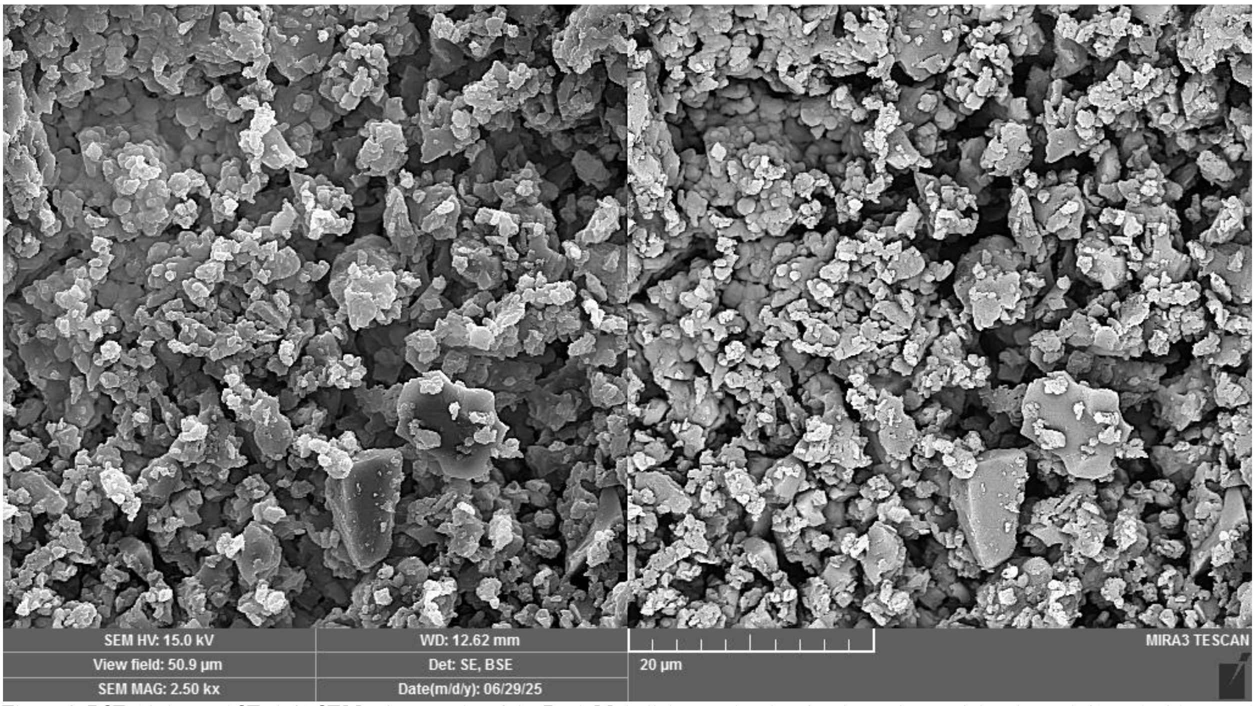

Figure 3: BSE (right) and SE (left) SEM micrographs of the Bash Mahalleh sample, showing hematite particles (lower left) and widespread sugar-like crystalline deposits.

Fourier Transform Infrared Spectroscopy (FTIR) was employed to characterize the surface deposits on the studied rock art, aiming to determine the chemical nature of these surficial materials. The FTIR spectra obtained from all six samples—comprising two specimens from each of the three study sites—displayed a remarkably consistent set of absorption bands at approximately 1628 cm^{-1}, 1316 cm^{-1}, and 780 cm^{-1} (Figure 4). Following the assignments by White (2023), these bands correspond to the asymmetric stretching (νa), symmetric stretching (νs), and bending (νδ) vibrations of the oxalate anion in calcium oxalate monohydrate. The ubiquitous presence of these diagnostic bands strongly indicates the formation of a calcium oxalate patina across both the bare rock surfaces and the pigmented areas. Such oxalate films are well-documented superficial coatings on marbles, limestones, historical monuments, and natural rock outcrops (Del Monte et al., 1987). While their presence is clear, the exact genesis of these patinas remains a subject of ongoing debate, with multiple pathways proposed in the literature. For instance, Cariati et al. (2000) demonstrated that the long-term application of organic substances to stone surfaces can undergo oxidative degradation, ultimately yielding oxalate minerals like whewellite and weddellite, depending on the nature of the original organic precursor. Beyond anthropogenic applications, biological activity represents a major driving mechanism for oxalate formation. In a study on a historic monument in India, Singh and Yadav (2023) utilized SEM to link the presence of organic filaments directly to the biological origin of an oxalate patina. They argued that microbial proliferation, particularly during intense monsoonal rains, induces the secretion of oxalic acid; this acid then leaches calcium from the stone's plagioclase feldspars, triggering the precipitation of the oxalate film. This aligns with the experimental work of Sabbioni and Zappia (1991), who concluded that such patinas primarily stem from oxalic acid secreted by stone-colonizing microorganisms, specifically lichens. This biogenic acid attacks the calcium carbonate substrate, directly resulting in calcium oxalate precipitation. This biological pathway also carries historical weight. Del Monte et al. (1987) posited that in past eras, when atmospheric conditions were more hospitable to lichen growth, the formation of oxalate patinas was a widespread natural weathering process even in urban environments. Consequently, their persistence in today's heavily polluted settings acts as a chemical record of past ecological transformations. This historical perspective suggests that similar, ancient biological activity may have driven patina formation in the Khorasan region during periods of more favorable climate. However, alternative origins involving human intervention cannot be ruled out. Rampazzi et al. (2004) identified specific organic compounds—including paraffin wax, animal lipids, and egg—using Gas Chromatography-Mass Spectrometry (GC-MS). The direct correlation between these organic residues and the oxalate content led them to suggest that the films developed from the degradation of historical surface treatments. Synthesizing the existing literature with our current FTIR findings, the formation of the calcium oxalate patina on the Khorasan rock arts can be reasonably attributed to two plausible, non-exclusive mechanisms: the biological metabolic activity of past or present microbiota, or the long-term chemical degradation of historical organic coatings intentionally applied to the stone.

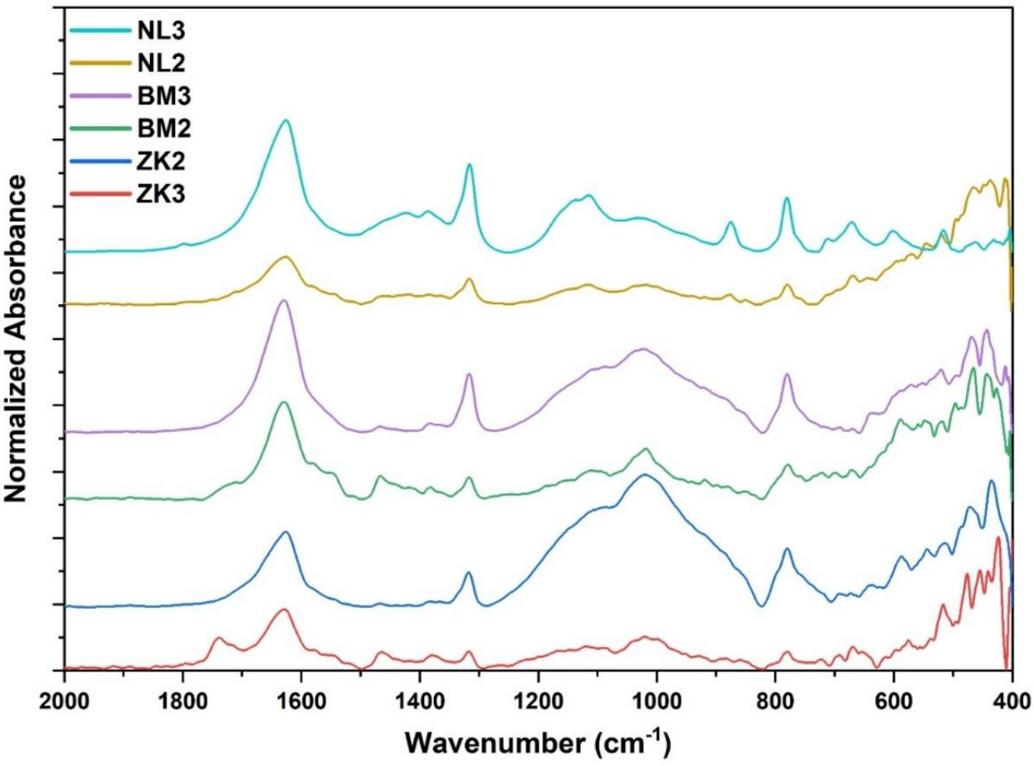

Figure 4: FTIR spectra of the surface deposits collected from the studied rock art. The diagnostic absorption bands at approximately 1628 cm^{-1}, 1316 cm^{-1}, and 780 cm^{-1} confirm the ubiquitous presence of a calcium oxalate monohydrate patina across the study sites.

Raman spectral analysis of the samples revealed a consistent pattern. Figure 5 presents the micro-Raman spectrum of the sample from Bash Mahalleh (BM3), the historical site containing the rock paintings under study, alongside the spectrum of the corresponding sample from Bagh Mahalleh, an area identified as a natural ochre source. The observed spectral features are characteristic of hematite (α–Fe_2O_3), confirming it as the primary red ochre pigment. Specifically, the prominent peak at 216 cm^{-1} is assigned to the A_{1g} mode, serving as a primary indicator of the hematite phase. The band at 287 cm^{-1} corresponds to the E_g mode, associated with the symmetric Fe–O bending vibrations. Another stable E_g mode appears at 404 cm^{-1}, further characterizing the low-frequency Fe–O vibrational profile. Additionally, a broad, intense band centered around 1315 cm^{-1} is attributed to two-magnon scattering, a well-documented diagnostic feature of hematite. The concurrent presence of the peaks at 216, 287, and 404 cm^{-1}, alongside the two-magnon scattering at 1320 cm^{-1}, unambiguously confirms the identification of the pigment as natural red ochre (Petrova et al., 2017; Pisu et al., 2025; Privitera et al., 2025).

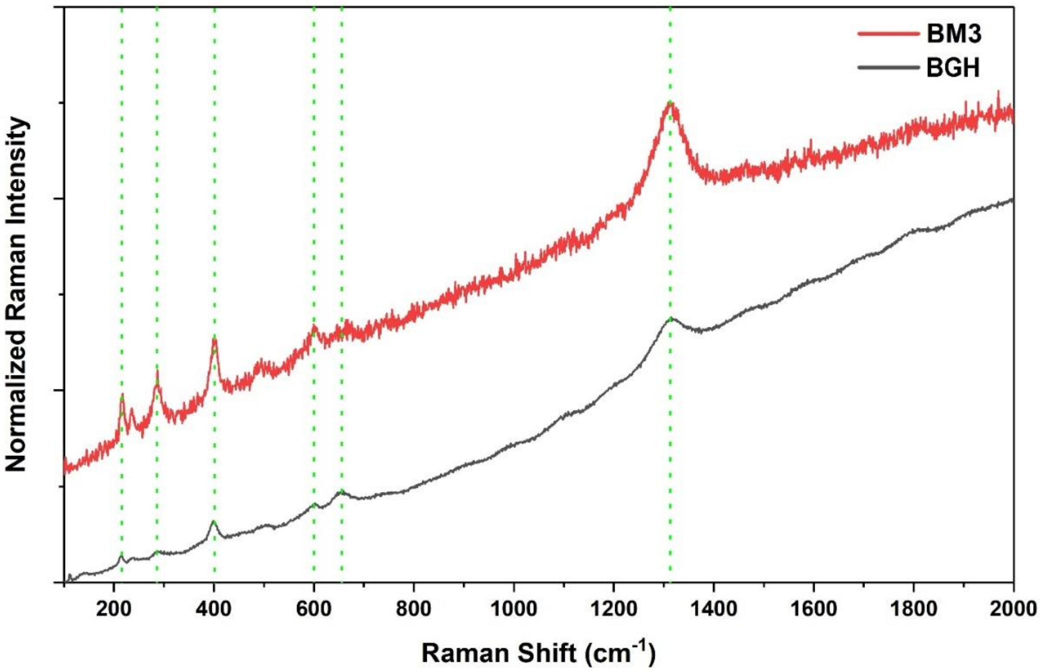

Figure 5: Micro-Raman spectra of the samples from Bash Mahalleh (BM3) and Bagh Mahalleh (BGH, natural ochre source).

When taken together, this integrated mineralogical evidence confirms that the red pigments correspond to hematite-bearing natural ochres. Raman spectroscopy consistently identifies hematite as the dominant chromophore. Alternative iron-bearing phases were evaluated. Goethite and lepidocrocite were excluded due to the absence of their diagnostic Raman bands and the lack of significant hydroxyl absorption in FTIR spectra. Maghemite and magnetite were not detected within the limits of the applied techniques. Non-iron-based red pigments such as cinnabar (HgS) and minium (Pb_3O_4) were ruled out based on SEM–EDS results, which revealed no detectable Hg or Pb. The predominant identification of hematite across these varied panels suggests a sustained preference for durable mineral chromophores, potentially reflecting a coherent technological approach based on the exploitation of local geological resources. Microstructural observations indicate dispersed pigment particles within heterogeneous mineral matrices. No clear evidence of deliberate particle refinement or systematic compositional enrichment was observed. The compositional variability among sites is most consistent with the natural heterogeneity of locally available iron-rich earth materials. Because only one geological source sample was analyzed, provenance assessment remains preliminary. Expanded geological sampling and trace-element analyses would be required for definitive source attribution.

Furthermore, the elemental composition of the samples and the unpurified nature of the raw pigments strongly indicate a natural, non-synthetic origin. Fourier-transform infrared spectroscopy further confirmed the absence of organic binders within the paint matrix. Taken together, these findings suggest that the rock art motifs were produced using straightforward application methods—such as mixing raw ochre with water or directly applying wet pigment nodules onto the rock surface. Beyond characterizing pigment compositions, this study represents a foundational step toward reconstructing regional artistic choices within the framework of the archaeology of technology.

Nevertheless, certain methodological constraints must be noted. To comply with strict heritage conservation protocols on open-air monuments, sampling was intentionally restricted to nine micro-fragments. While these capture the primary visual and compositional variations across the three shelters, evaluating broader intra-site homogeneity and definitive geological provenance will require expanded sampling of both rock art motifs and regional ochre outcrops in the Upper Atrak Valley. Additionally, while the multi-analytical suite successfully identified primary chromophores and weathering crusts, future high-precision trace-element profiling will be necessary to discriminate between compositionally similar hematite sources and reconstruct broader patterns of raw material procurement across the Iranian Plateau.

V. Conclusion

This study presents the first multi-analytical characterization of red pigments and surficial deposits from the prehistoric rock art sites of Bash Mahalleh, Zeynekanlu, and Nargeslou in North Khorasan, northeastern Iran. Integrating SEM–EDS, micro-Raman, and FTIR spectroscopy provides direct empirical evidence that hematite (α–Fe_2O_3) serves as the primary chromophore across all sampled painted motifs, confirming the exclusive use of natural iron-rich ochres. Microstructural analysis reveals a heterogeneous distribution of unrefined pigment particles, showing no evidence of systematic size reduction, mechanical refining, or thermal processing. Furthermore, FTIR spectroscopy systematically identified a ubiquitous calcium oxalate monohydrate patina across both painted surfaces and unpainted host-rock substrates. Beyond these direct analytical facts, the observed mineralogical uniformity across stylistically and chronologically distinct shelters suggests a broader regional technological tradition. Rather than employing complex processing protocols, prehistoric artists in North Khorasan relied on a minimalist technological strategy centered on the direct exploitation of accessible local earth resources. Concurrently, the ubiquitous calcium oxalate patina records long-term biogenic weathering and post-depositional environmental interactions, offering critical insights into surface conservation histories. To expand upon these baseline findings and address the inherent sampling constraints of heritage sites, future research should integrate complementary high-resolution analytical methodologies. Applying Inductively Coupled Plasma Mass Spectrometry or Laser Ablation ICP-MS to broader geological sampling will enable trace-element fingerprinting for definitive pigment provenance attribution. Additionally, direct radiocarbon dating of isolated oxalate crusts and organic binding media analysis via Py-GC-MS offer promising pathways for establishing absolute chronological frameworks and verifying ancient paint formulations across the Iranian Plateau and adjacent Central Asian corridors.

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References

Afshari, H. & Forouzan, F. (2021). The Study of the Social Life of Former Nomads Living in the Homian Plain, Based on the Study of Rock Motifs of Mehrdad Stone. *Rahpooye Honar-Ha-Ye Tajassomi*, *4*(2), 73-83. https://doi.org/10.22034/ra.2021.244948

Ahari Mostafavi, M & Asadi, M. (2021). Study on the Formal Features of the Lithographs of Luristan Dusheh Cave. *Rahpooye Honar-Ha-Ye Tajassomi*, *4*(3), 15-24. https://doi.org/10.22034/ra.2021.526731.1035

Azandaryani, E. H., Qolami, H., Mohammadi Far, Y., & Razmposh, A. (2015). Discovering New Rock Paintings at Shmsali and Gorgali Rock Shelters in Kohgiluye and Bouier Ahmad Province, Southern Iran. *Arts*, *4*(2), 61-67. https://doi.org/10.3390/arts4020061

Cariati, F., Rampazzi, L., Toniolo, L., & Pozzi, A. (2000). Calcium oxalate films on stone surfaces: experimental assessment of the chemical formation. *Studies in Conservation*, *45*(3), 180-188.

Chalmin, E., Menu, M., & Vignaud, C. (2003). Analysis of rock art painting and technology of Palaeolithic painters. *Measurement Science and Technology*, *14*(9), pp. 1590-1597.

Del Monte, M., Sabbioni, C., & Zappia, G. (1987). The origin of calcium oxalates on historical buildings, monuments and natural outcrops. *Science of the Total Environment*, *67*(1), 17-39.

Eastaugh, N., Walsh, V., Chaplin, T., & Siddall, R. (2008) *The Pigment Compendium: A Dictionary of Historical Pigments*. Oxford: Elsevier Butterworth-Heinemann.

Fazel, L. (2011). Tang Tadvan and Tang Tihui: New Discoveries of Rock Art in Fars Province. *Pazhohesh-haye Bastanshenasi Modares,* (4-5), 69-78.

Ghasimi, T., Barfi, C., & Norouzi, R. (2014). Newly found pictograms from Abdozou Rockshelter, Firouzabad, southern Zagros, Iran. *Rock Art Research*, *31*(2), 199-204.

Ghasimi, T., Ghasemi, P., Vafaei, A., & Ghezelbash, E. (2016). Recent rock art finds from north of Kavar in Fars, Iran. *International Journal of Archaeology*, *4*(6-1), 8-21.

Gomes, H., Collado, H., Garcês, S., Lattao, V., Nicoli, M., Eftekhari, N., Marrocchino, E., & Rosina, P. (2024). Archeometrical Characterization of Rock Art Pigments from Puerto Roque Open-Air Rock Art Shelter (Valencia De Alcantara, Extremadura, Spain). *Heritage*, 7, 1123–1139. https://doi.org/10.3390/heritage7030053

Hradil, D., Grygar, T., Hradilová, J. and Bezdicka, P. (2003). Clay and iron oxide pigments in the history of painting. *Applied Clay Science*, *22*(5), 223–236.
Karimi, F. (2007). A new perspective on Iranian rock carvings based on field studies, *Bastan-pazhohi*, *3*, 20-34
Maryanti, E., Ilmi, M. M., Nurdini, N., Setiawan, P., Syah, Y. M., Saiyasombat, C., Kadja, G. T. M., & Ismunandar (2022). Hematite as unprecedented black rock art pigment in Jufri Cave, East Kalimantan, Indonesia: the microscopy, spectroscopy, and synchrotron X-ray-based investigation. *Archaeological and Anthropological Sciences*, *14*, 122. https://doi.org/10.1007/s12520-022-01591-6
Mastrotheodoros, G.P., & Beltsios, K.G. (2022). Pigments—Iron-based red, yellow, and brown ochres. *Archaeological and Anthropological Sciences*, *14*, 35. https://doi.org/10.1007/s12520-021-01482-2
Mauran, G., Lebon, M., Détroit, F., Caron, B., Nankela, A., Pleurdeau, D., & Bahain, J.-J. (2019). First in situ pXRF analyses of rock paintings in Erongo, Namibia: results, current limits, and prospects. *Archaeological and Anthropological Sciences*, *11*, 4123–4145. https://doi.org/10.1007/s12520-019-00787-7
Mohammadi Ghasrian, S. (2007). Studies of rock patterns in Iran: problems and solutions, *Bastan-pazhohi*, *3*, 15-17.
Molaie Kordshouli, H., Zare, Y., & Khosravanian, R. (2022). Ancient Pictographs in Bakhtegan County of Fars Province, Iran. *Journal of Sistan and Baluchistan Studies*, *2*(2), 53-61. https://doi.org/10.22034/jsbs.2022.346804.1032
Nicoli, M., Eftekhari, N., Vaccaro, C., Collado Giraldo, H., Garcês, S., Gomes, H., Lattao, V. and Rosina, P. (2023) 'A multi-analytical evaluation of the depositional pattern on open-air rock art panels at "Abrigo del Lince" (Badajoz, Spain)', *Environmental Science and Pollution Research*, *30*, 24344–24360. https://doi.org/10.1007/s11356-022-23589-2
Oktaviana, A.A., Joannes-Boyau, R., Hakim, B., Burhan, B., Sardi, R., Adhityatama, S., Hamrullah, Sumantri, I., Tang, M., Lebe, R., Ilyas, I., Abbas, A., Jusdi, A., Mahardian, D.E., Noerwidi, S., Ririmasse, M.N.R., Mahmud, I., Duli, A., Aksa, L.M., McGahan, D., Setiawan, P., Brumm, A., & Aubert, M. (2024). Narrative cave art in Indonesia by 51,200 years ago. *Nature*, *631*, 814–818. https://doi.org/10.1038/s41586-024-07541-7
Ortega-Avilés, M., Vandenabeele, P., Tenorio, D., Murillo, G., Jiménez-Reyes, M., & Gutiérrez, N. (2005). Spectroscopic investigation of a "Virgin of Sorrows" canvas painting: A multi-method approach. *Analytica Chimica Acta*, *550*, 164–172. https://doi.org/10.1016/j.aca.2005.06.059
Petrova, O. I., Pankin, D. V., Povolotckaia, A. V., Borisov, E. V., Beznosova, M. O., Krivul'ko, T. A., & Kurochkin, A.V. (2017). Identification of pigments in colored layers of a painting by Raman spectroscopy. *Optics and Spectroscopy*, *123*(6), 965-969.
Pisu, F.A., Porcu, S., Carboni, R., Mameli, V., Cannas, C., Naitza, S., & Chiriu, D. (2025). Innovative method for provenance studies in cultural heritage: A new algorithm based on observables from high-resolution Raman spectra of red ochre. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *329*, 125581.
Privitera, A., Sardara, M., & Sodo, A. (2025). Raman approach to investigate painted decorations and manufacture technology of fake Greek and Italic pottery: a contribution to authentication. *The European Physical Journal Plus*, *140*(3), 234.
Rafifar, J. (2002). Arasbaran (Sungun) petroglyphs. *Iranian Journal of Anthropology*, *1*(1), 45-75.
Rampazzi, L., Andreotti, A., Bonaduce, I., Colombini, M.P., Colombo, C., & Toniolo, L. (2004). Analytical investigation of calcium oxalate films on marble monuments. *Talanta*, *63*(4), 967-977.
Rastineh, U.A., B. Kasiri, M., Ajorloo, B., & Ebrahimi, Q. (2017). Identification the Structure of Colorants Used on the Late Bronze Age Ceramics of Eastern Lake Urmia Based on the Specimen from Kul Tepe. Ajabshir. *Journal of Research on Archaeometry*, *3*(1), 17-27. https://doi.org/10.29252/jra.3.1.17
Sabbioni, C., & Zappia, G. (1991). Oxalate patinas on ancient monuments: the biological hypothesis. *Aerobiologia*, *7*(1), 31-37.
Sadeghi, S., Javanmardzadeh, A., Hadian Dehkordi, M., & Rezaloo, R. (2023). Evaluating the Motifs and Pigments of the Charta Pictographs in Kuhdasht, Lorestan. *Iranian Journal of Archaeological Studies*, *13*(1), 51-64.
Singh, M. R., & Yadav, R. (2023). Formation of calcium oxalate patinas as protective layer on basaltic stone surfaces of 17th century Raigad Hill Fort, India. *Heritage*, *6*(7), 5374-5392.
Soltani, M. (2010). *Iconographic and Chronological Analysis of the Petroglyphs of Qasr-e-Qand, Nikshahr.* MA thesis in Archaeology, Sistan and Baluchestan University.
Vahdati, A. A. (2021a). Hunting in the Forest Steppe: An Examination of the Painted Panel at Takke Rock-Shelter, Bojnord, Northeastern Iran. *Journal of Archaeological Studies*, *12*(24), 252–270.
Vahdati, A. A. (2021b). Newly found rock painting sites in the Upper Atrak Valley, Northern Khorasan, North-eastern Iran. *Archaeological Research in Asia*, *28*, 100317. https://doi.org/10.1016/j.ara.2021.100317
White, R. L. (2023). Infrared spectroscopic investigations of calcium oxalate monohydrate (Whewellite) dehydration/rehydration. *Minerals*, *13*(6), 783.