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ARTICLE

Ancient Rock Paintings at Region del Cabo-BCS, Mexico: An Analytical Study

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This study focused on the examination of six rock pictorial panels and a solitary figure from four archaeological sites in the Sierra de las Cacachilas (Sector A) in the Region del Cabo, Baja California Sur, Mexico. Scanning Electron Microscopy-energy dispersive X-ray spectroscopy was utilized to analyze tiny samples of the pictorial layers, patina, rocky supports, and natural pigments. The concentrations of C, Mg, Al, Si, P, S, K, Ca, Cr, Ti, Mn, and Fe were subjected to statistical methods and the samples were divided into various clusters. Iron and calcium compounds appear to be the primary constituents of the pictorial layers. The red pigment spectra obtained through Fourier-transform infrared spectroscopy revealed the presence of inorganic compounds and the likelihood of a flora-based composite as the binding agent. The minerals identified through X-ray diffraction in the rocky supports were determined to be intrusive igneous rocks. These findings are significant for the conservation and preservation of the artwork in the Sierra de las Cacachilas.

Keywords: Archaeometry, Rock-paintings, Baja California Sur México, Raw materials, SEM-EDS, XRD

INTRODUCTION

Rock paintings are widespread and serve as a testament to the lives of prehistoric people, found in diverse places such as secluded caves and visible rock formations. The preservation of these paintings depends on various factors such as the microenvironment, the composition of the paint, and human-made events, among others. Recently, the study of rock paintings has gained increased attention and significance from various perspectives including discovery and location, documentation, and archaeometry.[1-5]

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Research conducted in Europe (France, Italy, Spain), South America (Colombia, Chile, and Argentina), and Mexico (Baja California Sur) involved the utilization of diverse analytical techniques including XRD, PIXE, RBS, EDAX, FRXT, FT-IR, MS, and EDAX. These studies aimed to determine the composition of the pictorial layer in terms of various colors, minerals, rock substrates, and organic materials employed in paint manufacturing. The results provided valuable insights for interpreting certain connections within the extensive operational process.[1-9] Despite the variations in methodologies and objectives among these studies, the overall focus remained on comprehending the operational processes involved in creating pictorial panels.

The Region del Cabo, shown in (Figure 1), is located in the southern part of the Baja California peninsula in Mexico. It is a large, barren, and remote area inhabited by hunter-gatherer-fisher groups, the Guaycuras, and the Pericues.

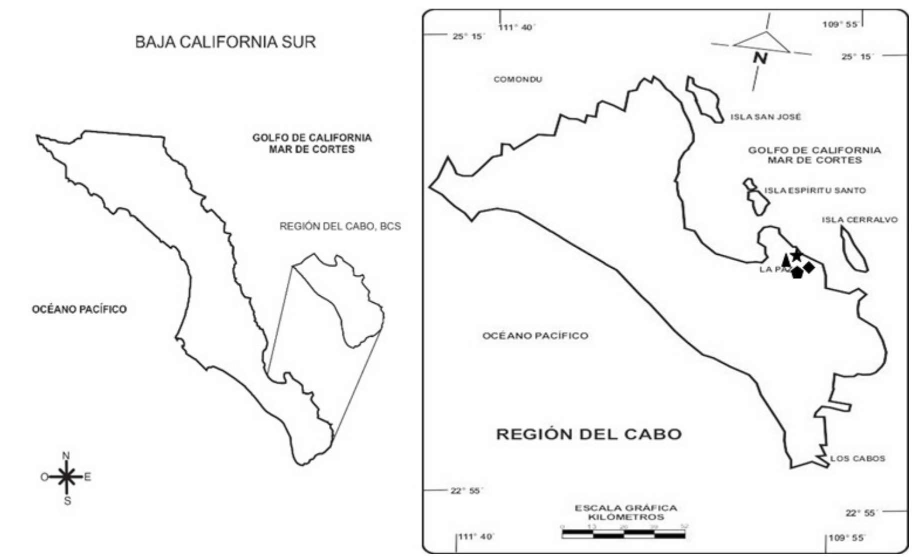

Figure 1. Map of localization of the Region del Cabo and the pictorial sites (in Sierra de las Cacachilas, Sector A): Cerro Pintada 1 (triangle) Cerro Pintada 2 (star) Castreña 2 (rhombus) Joyita de la Sierra de la Huerta (pentagon).

The pictorial rock art in this region was first recorded by Spanish missionaries in the 18th century and has since been studied by explorers and researchers, resulting in increased knowledge about the location, spatial distribution, quantity, designs, styles, and techniques used to create the art. However, no analytical studies have been conducted thus far. The main styles found in the Region del Cabo are the Cabo Representational and Cabo Abstract styles.[10,11] The ancient pictures in the Region del Cabo are a valuable contribution to Mexico's cultural heritage.

The Sierra de las Cacachilas, specifically Sector A, is part of the Region del Cabo. Among the numerous rock painting sites in this Sierra, the research selected four sites, Cerro Pintada 1, Cerro Pintada 2, Castreña 2, and Joyita de la Sierra de la Huerta (Figure 1), based on certain criteria. These criteria included the preservation status of the pictograms, the variety of styles and designs, minimal impact from the environment, ease of access to the site, and official recognition. Other factors considered were the absence of humidity, organic matter (such as fungi, bacteria, and insect nests), and contaminants (such as smoke from fires or spray paint) on the pictograms. As a result, six pictorial panels and a solitary figure were selected.

The goal of this research was to conduct a physicochemical characterization of the raw materials used in the creation of six pictorial panels, and one isolated figure found at the mentioned sites. This involved analyzing pictorial layers, patina, rocky supports, and natural pigments. The elemental composition was determined using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS). Fourier-transform infrared spectroscopy (FTIR) was used to identify the presence of organic and inorganic compounds, while X-ray diffraction (XRD) was used to determine the mineralogical composition. This groundbreaking study aims to provide new insights into the pictograms of the Sierra de Las Cacachilas, including the color palette used by prehistoric artists and the nature of the rocky supports.

MATERIALS AND METHODS

Materials

Figure 2 shows an example of one of the pictograms. Table I provides a brief overview of the characteristics of the pictorial panels at each site, including the style (Representative or Abstract), the predominant color (typically various shades of red), and the dimensions.

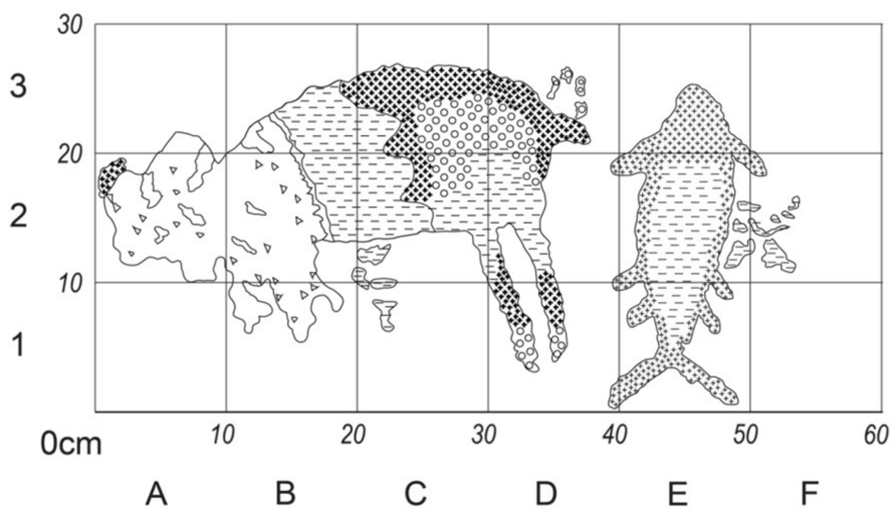

Figure 2. General view of Pictorial Panel 1: zoomorphic figures (deer and fish) and stains in Joyita de la Sierra de la Huerta. Cabo Representational style.

Table I. Description of the pictorial panels of Sierra de las Cacachilas (Sector A). (*) R: Representational; A: Abstract

Site	Zone (Nr.)	Style (*)	Design	Color	Manufacture technique	Pictorial panels	Isolated figure	Dimensions (cm)	
								Height	Width
Cerro Pintada 1	G12D8303001 (1801)	R	Zoomorphic and phytomorphic	Red (various tonalities)	Manual, hands and fingers	1		98	1.52
							1	14	24
Cerro Pintada 2	G12D8303002 (1803)	A	Crossed lines	Red (various tonalities)	Manual, hands and fingers	1		69	45
Castreña 2	G12D8303118 (46095)	R	Zoomorphic and phytomorphic	Red (various tonalities)	Manual, hands and fingers	1		59	78
						2		178	112
Joyita de la Sierra de la Huerta	G12D8303108 (46085)	R & A	Zoomorphic and stains	Red-ocher and orange	Manual, hands and fingers	1		25	55
						2		68	2.00

Methods

Photographs and videos of each piece of pictorial art were taken using a Sony Alpha 6300 digital camera. Afterward, a portable optical microscope (Dino-Lite, model AM3011, VGA) was used to perform vertical and horizontal scans of the rocky surface, with a resolution ranging from 10X to 220X. At the same time, a grid (consisting of 10 cm^2 square marked by letters and numbers) was drawn for each pictogram using Adobe Illustrator CS5A software. The conservation status of the pictorial layer and the uniformity or variation of color on the surfaces were evaluated at the points where the quadrants intersected, which helped in determining the optimal area for sample extraction.

Small samples of the pictographs (as well as three from the patina) were collected by carefully attaching a 1 cm^2 carbon strip, which was then removed using a clamp and fixed to an aluminum sample holder. To prevent any harm to the design and size of the pictographs, between four and eight samples were taken from each. The samples collected on the carbon strips were properly labeled and stored for further analysis in the laboratory. Additionally, during the inspections of the pictorial sites, some granitic rocks with vivid red and orange veins were encountered, which were analyzed as well.

Photomicrographs and X-ray spectra of pictograph and patina samples were taken with a low vacuum scanning electron microscope (SEM) JSM-6610LV with a coupled Oxford probe, for elemental microanalysis EDS. Chemical compositions were determined by EDS analysis of several points chosen at random on the photomicrographs.

Fourier-transform infrared spectroscopy analyses of four red pigment samples of pictorial layers were carried out by a VARIAN® model 640-IR. The samples were crushed in an agate mortar and then the KBr pellets were prepared. Spectrum against that of the background from 4000 cm^{-1} to 400 cm^{-1}, with 40 scans and a resolution of 4 cm^{-1}. The total number of data points was 1869.

A mineralogical analysis by XRD was performed for the rocky support samples at room temperature with a Siemens D-5000 diffractometer using Cu Kα radiation with a graphite monochromator; the diffraction pattern was collected from 2.5 to 70° 2θ with a step size of 0.02° 2θ to acquire X-ray patterns with sufficiently high intensities to identify the minerals present. For the qualitative identification of the mineralogical composition, the data file XRD JCPDS was used.

RESULTS AND DISCUSSION

Table II lists the 73 samples that were analyzed using SEM-EDS for each site and figure, with 66 samples representing the pictorial layers, three for the patina, and four for the rocky supports.

Table II. Samples analyzed by site and figure (Sierra de las Cacachilas, Sector A). The number of cluster is according to the statistical analysis of chemical compositions.

Site	Figure	Key	Cluster Nr.
Cerro la Pintada 1	Biznaga	M 17	C1
	Biznaga	M 18	C1
	Biznaga	M 19	C1
	Biznaga	M 20	C1
	Biznaga	M 21	C1
	Coyote	M 22	C4
	Coyote	M 23	C1
	Coyote	M 24	C3

(continues on the next page)

Table II. Samples analyzed by site and figure (Sierra de las Cacachilas, Sector A). The number of cluster is according to the statistical analysis of chemical compositions. (continuation)

Site	Figure	Key	Cluster Nr.
Cerro la Pintada 1	Deer	M 11	C1
	Deer	M 12	C1
	Deer	M 13	C1
	Deer	M 14	C1
	Deer	M 15	C1
	Deer	M 16	C1
	Sea urchin	M 1	C5
	Sea urchin	M 2	C4
	Sea urchin	M 3	C5
	Sea urchin	M 4	C1
	Sea urchin	M 5	C1
	Whale	M 6	C1
	Whale	M 7	C1
	Whale	M 8	C1
	Whale	M 9	C1
	Whale	M 10	C1
	Patina	M 25	C1
	Patina	M 26	C1
	Patina	M 27	C1
	Rocky support	M177	C6
Cerro la Pintada 2	Fingerprint lines	M 28	C3
	Fingerprint lines	M 29	C1
	Fingerprint lines	M 30	C3
	Fingerprint lines	M 31	C1
	Rocky support	M180	C6
La Castreña dos	Male deer	M 59	C1
	Male deer	M 60	C1
	Male deer	M 61	C4

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Table II. Samples analyzed by site and figure (Sierra de las Cacachilas, Sector A). The number of cluster is according to the statistical analysis of chemical compositions. (continuation)

Site	Figure	Key	Cluster Nr.
La Castreña dos	Male deer	M 62	C1
	Male deer	M 63	C1
	Male deer	M 64	C3
	Female deer	M 65	C2
	Female deer	M 66	C2
	Female deer	M 67	C1
	Female deer	M 68	C3
	Female deer	M 69	C3
	Female deer	M 70	C4
	Female deer	M 71	C3
	Female deer	M 72	C1
	Pitahaya	M 53	C1
	Pitahaya	M 54	C1
	Pitahaya	M 55	C1
	Pitahaya	M 56	C1
	Pitahaya	M 57	C1
	Pitahaya	M 58	C5
	Rocky support	M183	C6
Joyita de la Sierra de la Huerta	Fish	M 32	C3
	Fish	M 33	C3
	Fish	M 34	C3
	Fish	M 35	C3
	Deer (incomplete)	M 36	C3
	Deer (incomplete)	M 37	C1
	Deer (incomplete)	M 38	C1
	Deer (incomplete)	M 39	C1
	Fingerprint lines 1	M 49	C1
	Fingerprint lines 1	M 44	C2

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Table II. Samples analyzed by site and figure (Sierra de las Cacachilas, Sector A). The number of cluster is according to the statistical analysis of chemical compositions. (continuation)

Site	Figure	Key	Cluster Nr.
Joyita de la Sierra de la Huerta	Fingerprint lines 1	M 46	C2
	Fingerprint lines 1	M 47	C2
	Fingerprint lines 1	M 45	C4
	Fingerprint lines 1	M 43	C5
	Fingerprint lines 2	M 48	C2
	Fingerprint lines 2	M 50	C2
	Fingerprint lines 2	M 51	C2
	Orange stain	M 52	C2
	Rocky support	M181	C6

The X-ray spectra of EDS were used to identify and evaluate the following chemical elements C, Mg, Al, Si, P, S, K, Ca, Cr, and Fe, as demonstrated in a typical spectrum displayed in Figure 3 and Table III. Only a limited number of samples showed the presence of elements such as Ti and Mn, with Ti being found in 4 out of 73 samples (ranging from 0.3% to 4%) and Mn in 7 out of 73 samples (ranging from 0.3% to 9.3%). The average values of the element concentrations in each sample were calculated, and statistical treatments were performed by taking the log values of these average concentrations (excluding Ti and Mn).

The MURR (Missouri University Research Reactor) procedures refer to the use of a specific software, provided by that institution. This software, which is written in the GAUSS language,[12] has been used to conduct statistical analyses. The software calculates the probabilities of an individual sample belonging to various clusters, taking into consideration the Mahalanobis distance. For the analysis, the elemental concentrations are transformed into a logarithmic scale. The software also aids in visualizing these statistical outcomes. It helps in plotting principal component diagrams, which result in the artifacts being grouped into distinct clusters. Further, it enables drawing a diagram of vectors corresponding to those elemental concentrations that define the separation in clusters.

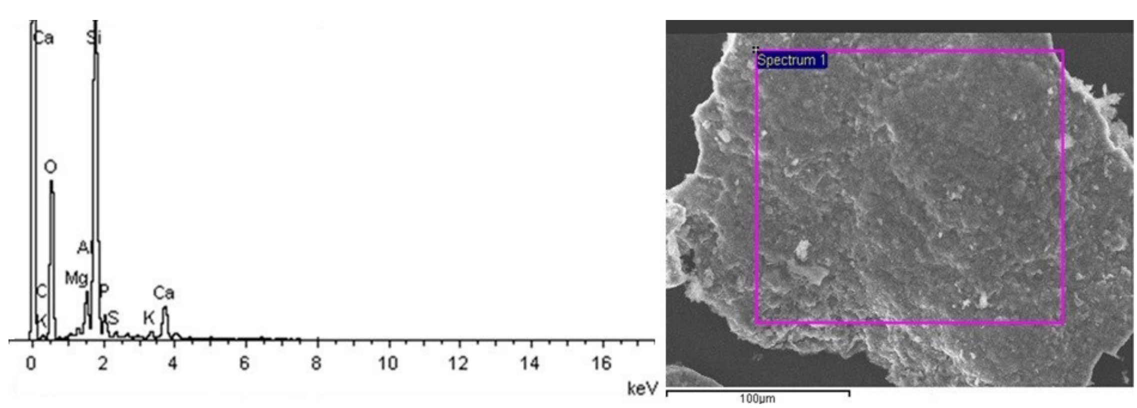

Figure 3. EDS spectrum and SEM micrograph typical of the samples of Cluster 1.

Table III. Elemental compositions of the statistical clusters formed. Data obtained by EDS, in %.

	Cluster 1 (n=39)		Cluster 2 (n=9)		Cluster 3 (n=12)		Cluster 4 (n=5)		Cluster 5 (n=4)		Cluster 6 (n=4)	
Element	**Mean**	**Min-Max**	**Mean**	**Min-Max**	**Mean**	**Min-Max**	**Mean**	**Min-Max**	**Mean**	**Min-Max**	**Mean**	**Min-Max**
C	13	5-24	<0.1	<0.1	21	8-58	17	8-25	9	6-12	16	10-24
Mg	0.7	0.1-2.7	1	<0.1-4	<0.1	<0.1	<0.1	<0.1-1	3	2-4	3	2-5
Al	3.6	0.8-9	7	3-14	4	<0.1-10	2	1-4	5	3-6	6	6
Si	21	4-31	25	15-37	12	2-21	15	9-22	21	16-26	22	15-33
P	1.7	0.1-5.3	3	<0.1-9	1	<0.1-2	1	<0.1-2	1	1-2	1	<0.1-2
S	0.4	0.1-2.8	<0.1	<0.1-1	1	<0.1-9	2	<0.1-8	<0.1	<0.1	2	<0.1-7
K	0.8	0.1-1.3	2	<0.1-5	<0.1	<0.1-1	1	<0.1-1	3	2-6	4	2-7
Ca	4	1-16	3	1-11	8	<0.1-20	2	1-7	2	1-4	1	<0.1-2
Cr	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	6	1-9	2	<0.1-6	1	<0.1-6
Fe	1.5	0.4 – 4.8	1	<0.1-8	<0.1	<0.1-1	28	4-43	10	8-13	12	6-21

Data of Table III show that trace elements were not detected and major elements (Si, Al) are similar for all samples; therefore, they are not significant for differentiation. Minor elements are the main ones for the separation of clusters. Figures 4A and 4B depict the diagrams of the principal components calculated. The first illustrates the grouping of the samples, while the second highlights the differentiation vectors. The main vectors of differentiation (Figure 4B) are based on the levels of C, Cr, and Fe, but Mg, K, P, and Ca played a role as well. Through this statistical analysis, we were able to identify six distinct clusters. Table I outlines the cluster number of each sample, and Table III presents the chemical composition data associated with each cluster. The results of the statistical analysis revealed six distinct clusters of samples.

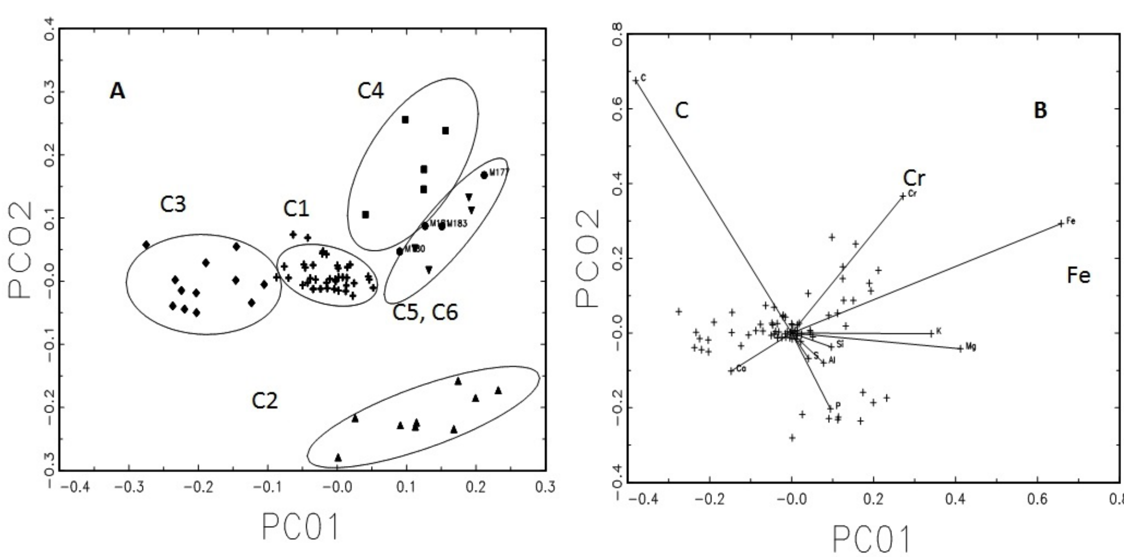

Figure 4. Principal component diagrams based on the concentration of ten chemical elements of 73 samples of pictorial layers. A) Clusters. B) Vectors.

Cluster 1 is the largest and its samples are present in all pictographs. Clusters 1, 2, and 3 do not show any significant presence of chromium, with values below the detection limit of the EDS technique. Cluster 2 has a virtually absence of carbon, while Cluster 3 has high levels of carbon and calcium, but no significant presence of iron.

The primary components of Cluster 3 could be either calcite ($CaCO_3$) or a combination of calcite and gypsum ($CaSO_4$) as sulfur was detected in some of its samples.

The highest concentration of iron can be found in the orange and red layers of C4, while the iron content in Clusters 1 and 2 is not as abundant but the samples possess a rich orange and red hue. The red and orange pigments might be composed of minerals such as hematite (Fe_2O_3), goethite (α-$Fe^{3+}O(OH)$), and/or limonite ($FeO(OH) \cdot nH_2O$).[13] There is also evidence suggesting that the pigments could be derived from clays that contain hematite.[14-15]

Figure 5 presents the FTIR spectrum of a red pigment sample; the spectra obtained from the other four samples were virtually indistinguishable. Table IV lists the functional groups of both organic compounds (alcohols, ketones, benzene, and phenols, among others) and inorganic compounds that were identified.

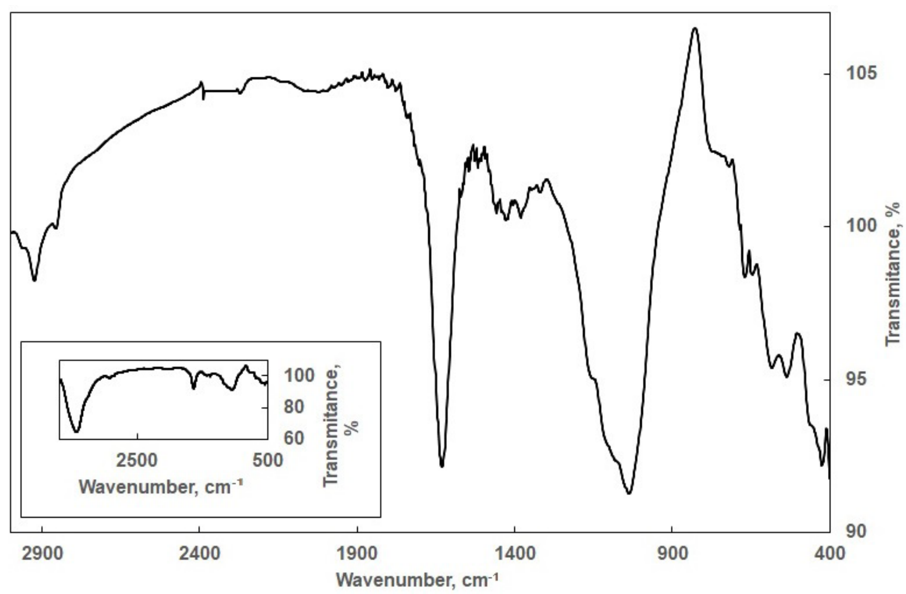

Figure 5. Typical FTIR spectrum of the analyzed pictorial layers.

Table IV. Data of the FTIR spectra of the pictorial layers

Wavenumber, cm^{-1} (*)	Functional groups (**)	Compounds
3427 (s)	-OH Str.	Alcohol
2920, 2854 (m)	-C–H_n Str.	Alkyl, aliphatic aromatic
1730 (w), 1517 (w)	-C=O Str.	Ketone and carbonyl
1630 (s)	-C=C-	Benzene stretching ring
1455 (w)	-O–CH_3	Methoxyl
1380 (w), 1317 (w)	-CH_3	Methyl
1232 (sh)	-C–O–C Str.	Aryl-alkyl ether linkage

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Table IV. Data of the FTIR spectra of the pictorial layers (continuation)

Wavenumber, cm^{-1} (*)	Functional groups (**)	Compounds
1211 (sh)	-C–O Str.	Phenol
1087 (sh)	Ca-O	Calcium carbonate
900 – 1100 (s)	Si-O Str.	Feldspar
400-800 (s)	Si-O Flx	Feldspar
400-1065 (s)	Fe-O	Hematite

(*) s: strong, m: middle, w: weak, sh: shoulder. (**) Str.: stretching, Flx: Flexing.

The Fourier-transform infrared spectroscopy spectrum was compared to those obtained from the typical components of biomass, such as cellulose, hemicellulose, and lignin. The region between 1300 cm^{-1} and 1700 cm^{-1} is indicative of the presence of lignin,[16] and the main band in Figure 5 is situated at 1620 cm^{-1} (C = C). The presence of lignin in the pictorial layer suggests the presence of plant matter. The absorption bands between 900-1000 cm^{-1} and 400-800 cm^{-1} are related to the Si-O bond of inorganic compounds such as feldspars, while the bands between 440 and 1065 cm^{-1} are linked to hematite. In contrast, the bands of calcium carbonate (1408 cm^{-1}, 873 cm^{-1}, and 712 cm^{-1})[2] are only faintly visible in the spectra.

The spectrum displayed in Figure 5 was also compared to those of the Nopal Cactus (Opuntia Ficus-Indica),[17] Nopal pectin,[18] and animal fat.[19] The spectra of these substances exhibit the bands related to carboxylic acids at 1712 cm^{-1} and 1224 cm^{-1}, which are absent in the spectrum of Figure 5, indicating that these substances were not used as the binding agent in the pictorial layer.

The minerals identified in the samples of the rocky supports (La Castreña, Boca del Álamo and Cerro Pintada) through XRD analysis, as shown in Figure 6, include mainly: quartz, pholopita, albite, and anorthoclase. These mineral phases are consistent with the granitic structure typically found in igneous-plutonic rocks, as previously identified in the northern Baja California peninsula.[2] It's important to note that the Sierra de las Cacachilas, Sector A, is located on a surface made up of intrusive igneous rocks from the Cretaceous period, primarily granite and granodiorite.

The selection of the rocky support was important in the creation of the pictorial images. Some surfaces were smoothed with stone tools, but examination of the surfaces with a handheld optical microscope showed that this was not done in the case of the rocky supports of the specified area, as no signs of carving were found.

The natural pigments of red and orange colors sourced from the granitic rocks located in the pictorial sites were abundant in iron. The SEM-EDS results showed 11-20% of iron, likely due to hematite. The presence of silicon, aluminum, potassium (potentially from feldspars), and carbon was also identified. The elemental composition of these rocks was found to be similar to that of the pictorial layers, indicating that they were used as raw materials for the creation of rock art.

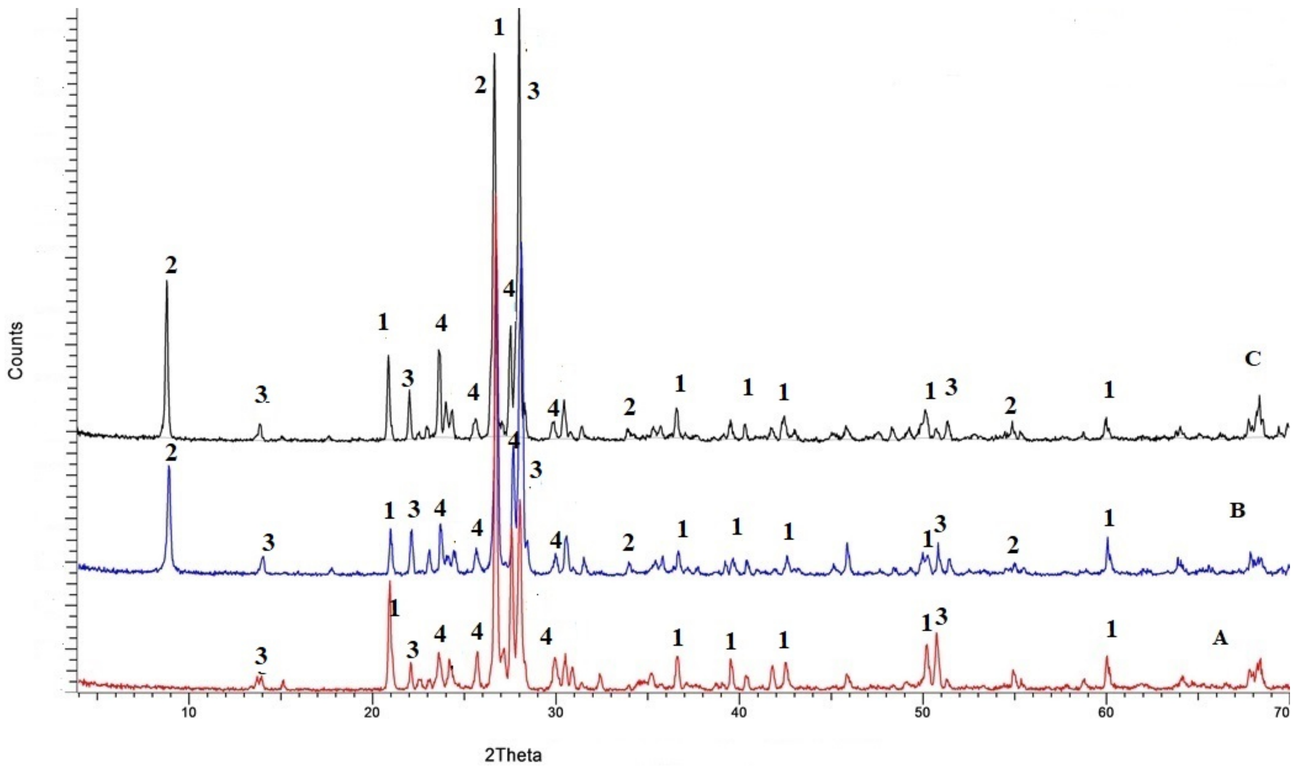

Figure 6. XRD spectra of the rocky supports from La Castreña (A), Boca del Álamo (B) and Cerro Pintada (C). The crystalline phases are: 1. Quartz, 2. Phlogopite, 3. Albite, 4. Anorthoclase.

CONCLUSIONS

This is the initial examination of the pictograms of the Sierra de Las Cacachilas. A comprehensive study using multiple techniques on small samples gave us insights into the components used in the creation of the pictograms (pictorial layers, patina, rocky supports, and pigments). The combination of the various techniques used provided a comprehensive understanding of the samples and their context.

SEM/EDS can detect C, Mg, Al, Si, P, S, K, Ca, Cr, Ti, Mn, and Fe in pictorial layers, patina, and rocky supports. Statistical calculations identify differences in element concentrations, with data grouped accordingly. Most pictorial layers had a similar chemical composition (C1), while other groups differed mainly in C, Cr, and Fe. Rocky support (C6) composition differed from C1 to C4 and was richer in Fe while scarce in Ca and Cr. The composition of C5 was similar to C6, potentially indicating a measurement of the rocky support in those samples.

Orange and red are the predominant colors in most pictorial layers, possibly due to the presence of iron compounds like hematite. Alternatively, the presence of calcium, carbon, and sulfur may suggest the presence of loading materials like calcite and gypsum. The pigments' origin may be from granitic rocks containing iron oxides found in the region where the pictorial arts were created.

Fourier-transform infrared spectroscopy analysis of red pigment grains identified both inorganic and organic compounds. Inorganic compounds included feldspars from the rocky support and hematite, supporting the previous considerations of these compounds in the pictorial layers. Organic compounds were compared with typical biomass components reveling the presence of lignin. A composite of flora may have been used as a pigment binder, but its origin remains unclear.

Based on these results: a) Dark red colors (Red 2.5YR 4/4/6) correspond to a high concentration of iron oxides (red pigment), and sometimes Ti (dark red pigment), with little evidence of carbon (binder not identified), but a high gypsum content ($CaSO_4 \cdot 2H_2O$) as loading. b) Light red colors (Red 2.5YR 4/4/8) may be a mixture with low Fe content (red pigment), high carbon content (binder not identified), and a low percentage of gypsum (loading). c) Dark colors (Greenish black 2.5/2.5/1 10G) are related to carbon content (pigment and binder) and gypsum content (loading).

Lastly, based on the mineral phases identified by XRD in the rocky supports (feldspars, quartz, and mica), it can be concluded that the structure is of granitic origin, specifically igneous-plutonic rock. The surfaces appear to be in their natural state, with no signs of previous polishing.

The findings obtained through the application of various analytical techniques provide significant knowledge for the conservation of ancient pictorial art in the Sierra de las Cacachilas region and in general they result useful for other archaeological studies.

Conflicts of interest

The authors declare that they have no conflicts of interest.

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