Lithodiversity and cultural use of desert varnish in the Northern Desert of Mexico

Litodiversidad y uso cultural del barniz de desierto en el Desierto del Norte de México

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How to cite this article:

Martínez-Pabello, P.U., Menéndez Iglesias, B., López Martínez, R., Pi-Puig, T., Solé, J., Izaguirre Pompa, A., Sedov, S., 2022, Lithodiversity and cultural use of desert varnish in the Northern Desert of Mexico: Boletín de la Sociedad Geológica Mexicana, 74 (3), A100622. http://dx.doi.org/10.18268/BSGM2022v74n3a100622

Manuscript received: December 15, 2021.
Corrected manuscript received: May 5, 2022.
Manuscript accepted: June 8, 2022.

Peer Reviewing under the responsibility of Universidad Nacional Autónoma de México.

ABSTRACT

Rock varnish is a thin layer (1-40 microns every 1000 years), dark-reddish in color (30% Mn and Fe oxides, 70% clay minerals), that coats a rock surfaces in the northern Mexican deserts. This accretion has been used as a canvas by ancestral human groups to record different types of motifs (zoomorphic, geometric and anthropomorphic) in the northern Mexican desert (Sonora and Chihuahua). These petroglyphs reflect the cultural and artistic nature of past inhabitants and the varnish preserves them through the millennia. Rock varnish coats a variety of rock types, and this paper explores differences in the chemical composition and interaction of varnish and the underlying rock. We studied varnish from three different sites: Samalayuca (Chihuahua); El Álamo (Sonora); and La Proveedora (Sonora). The analytical techniques of microscopy, X-Ray Diffraction (XRD) and Laser Breakdown Spectra (LIBS), reveals a similar chemical composition (Mn, Fe, Ca and Al mainly) that it does not depend on the lithodiversity or location (Samalayuca -sandstone-, El Álamo -sandstone- and La Proveedora -granite-). We observed differences in the contact between the varnish and the underlying rock. Varnish penetrate into decayed minerals such as plagioclase; thick accumulations can occur on hard minerals such as quartz. Like prior research, we find little important contribution of material from the underlying to its varnish coating and conclude its main component derives mostly from aeolian deposition.

Keywords: desert varnish, petroglyphs, Sonoran Desert, Chihuahuan Desert, lithodiversity.

RESUMEN

El barniz de roca es una capa delgada (1-40 micrones cada 1000 años), de color rojizo oscuro (30% óxidos de Mn y Fe, 70% minerales de arcilla), que recubre las superficies rocosas en los desiertos del norte de México. Esta acreción ha sido utilizada como lienzo por grupos humanos ancestrales para registrar diferentes tipos de motivos (zoomórficos, geométricos y antropomórficos) en el desierto del norte de México (Sonora y Chihuahua). Estos petroglifos reflejan la naturaleza cultural y artística de los habitantes del pasado y el barniz los preserva a través de los milenios. El barniz de roca cubre una variedad de tipos de rocas, y este trabajo explora las diferencias en la composición química y la interacción del barniz y la roca subyacente. Se estudia el barniz de tres sitios diferentes: Samalayuca (Chihuahua); El Álamo (Sonora); y La Proveedora (Sonora). Las técnicas analíticas de microscopía, Difracción de Rayos X (XRD) y Espectroscopía de Ablación Láser (LIBS), revelan una composición química similar (Mn, Fe, Ca y Al principalmente) que no depende de la litodiversidad o ubicación (Samalayuca -arenisca, El Álamo -arenisca- y La Proveedora -granito-). Se observa diferencias en el contacto entre el barniz y la roca subyacente. El barniz penetra en minerales descompuestos como plagioclasa; acumulaciones gruesas pueden ocurrir en minerales duros como el cuarzo. Al igual que investigaciones anteriores, se encuentra poca contribución importante del material del subyacente al recubrimiento de barniz y se concluye que su componente se deriva principalmente de la deposición eólica.

Palabras clave: barniz del desierto, petroglifos, desierto de Sonora, desierto de Chihuahua, litodiversidad.

http://dx.doi.org/10.18268/BSGM2022v74n3a100622

1. Introduction

Soil is a natural resource that played a vital role in different societies and ancestral human groups throughout their history. Besides its economic significance as the base of agriculture and raw material for various industries such as ceramic production, soil has been widely used for artistic activities. Through the soil, the different human groups have built their cultural, religious and social identity. Soil has been used as a pigmentation tool, that is, a source of raw material in artistic creation for cave paintings (Álvarez Romero, 2012) and mural representations (De la Fuente, 2004). Furthermore, soil decorated human bodies in the celebration of ceremonies or rituals (Domingo *et al.*, 2009; Fiore, 2016). Soil has been used as a canvas on a large scale. The so-called geoglyphs, such as the Nazca Lines in Peru or the Acre geoglyphs in the Amazon are a clear example (Clarkson, 1997). Some interpreted the Nazca lines, some religiously referring to the arrival of water in the desert, and others make astronomical interpretations (Aveni, 1990; Klokoeník *et al.*, 2002). All these artistic expressions linked to soil reflect a human bond with the environment, a kind of bridge between human beings and nature where the soil connects to the identity to the different societies.

Petroglyphs are considered rock art, being symbols or motifs carved on different stone supports, located outdoors, and made by ancestral human groups (Whitley, 2001; Loendorf *et al.*, 2005; Keyser and Whitley, 2006). Petroglyphs are distributed globally, being found on all continents except for Antarctica (Martínez Celis and Botiva Contreras, 2004). In some settings, particularly arid environments petroglyphs are found carved in rocks covered with dark-reddish or black rock coating, engraved, and then the engraved surfaces are then coated. Several scholars have linked rock coatings like varnish to soils (Roberts *et al.*, 2018; Lebedeva *et al.*, 2019), and hence to the petroglyphs carved in rock varnish present a specific case of soil utilization for artistic purposes. These coatings can themselves record shifts in climate from arid to more humid conditions (Liu and Broecker, 2007, 2013), thus they could be considered as a specific paleopedological phenomenon.

Rock varnish is a thin, dark-reddish to black coating that develops in all terrestrial weathering environments and not just in deserts (Dorn and Oberlander, 1982; Dorn, 2009). Rock varnish grows and covers the rock in a non-uniform way, accreting a natural canvas upon which cultures and human groups carved different motifs, such as biomorphs (anthropomorphic and zoomorphic), geometric and astral (Ballereau, 1988; Villalobos, 2003; Menéndez Iglesias, 2018). Originally, these carved figures were left without varnish on what would be a "negative" canvas, leaving the rest of the coated background dark. Rock varnish owes its color to variable concentrations of iron oxides (FeOx-reddish) and manganese (MnOx-dark) that typically make up 30% of the varnish, while the other 70% is composed of clay minerals (Potter and Rossman, 1977; 1979; Perry and Adams, 1978). The growth rate of varnish in warm desert environments ranges tremendously from a few microns per millennia (Liu, 2000) to tens of microns per century (Spilde *et al.*, 2013).

Since the first academic scholarship on rock varnish (von Humboldt, 1812; Dorn and Krinsley, 2012), the processes by which varnish forms have been debated. For more than 300 years, different abiotic and biotic hypotheses (or both) have been put forward that attempt to explain the accretion of varnish (Dorn, 2009; Engel and Sharp, 1958; Krinsley *et al* 2017; Perry *et al.*, 2005, 2006; Potter, 1979). At the microscopic level, the rock varnish shows an arrangement of microlaminations (Liu and Broecker, 2013), deposited over time, where the deeper layers (those that are in direct contact with the parental rock) are the oldest, while the shallowest are the most recent. This is the reason why rock varnish and other rock coatings can be considered a cumulic micro-soil. On the other hand, the chemical distribution of different chemical elements such as Fe and Mn within the varnish microlaminations can give us information about the environments in which they were deposited

(Liu and Broecker, 2007, 2013). The role of the parent rock in varnish formation has undergone a paradigm shift. Prior to electron microscopy, geologists interpreted varnish as a decay product of the underlying rock. However, with the advent of electron microscope imagery, the accretionary nature of the coating became clear (Potter and Rossman, 1977; Perry and Adams, 1978; Dorn and Oberlander, 1982). What has not been explored in detail is the role of some iron mineral alteration in varnish processes (Martínez-Pabello *et al*., 2021a).

In Mexico, rock art, both paintings and engravings, are distributed throughout the region (Casado *et al*, 2014). However, the areas of Northern Mexico, that range from Nayarit to Sonora and Baja California through Durango, Nuevo León, Coahuila, or Chihuahua among other states, contain innumerable clusters of rock art where petroglyphs prevail (Santos and Viñas, 2005; Valadez, 2014) over pictorial representations. This is mainly due to the type of geographical relief and its geological components that make paintings and engravings, in outdoor contexts, preserved differently (Menéndez Iglesias, 2021c). Researchers are working under the hypothesis, that this art was made by groups of hunter-gatherers from the Archaic period to the Pre-Hispanic and Colonial period (Casado *et al*, 2014), although early Holocene and late Pleistocene origins have been postulated as well (Hayden, 1976).

Until recently very little information existed about the composition, origin, stability and paleoenvironmental significance of these rock coatings in Mexico – all these questions being quite important for understanding ancient utilization of the varnished rock surfaces as well as for assessment of stability and conservation of petroglyphs. Recently a detailed research of desert varnish from one of the Sonoran archaeological sites – La Proveedora attempted to fill partly this information gap (Martínez-Pabello *et al*., 2021a, 2021b). However, this research was limited to a single rock type – Mesozoic granite.

More broadly, petroglyphs across northern Mexico are found in a broad variety of geological settings. In this paper we put forward the question: do the differences in composition of host rock affect the properties of desert varnish and control its formation and stability? To answer this question, we performed a comparative study of rock varnish at three sites: the Sierra de El Álamo and La Proveedora regions in Sonora and the Samalayuca area in Chihuahua. These sites have many petroglyphs with different motifs engraved by human groups that inhabited the area, as in the case of La Proveedora, approximately 5000 years ago (Villalobos, 2003). The underlying rock upon which varnish accreted varies considerably. Thus, the present research aims to begin to understand the lithodiversity of varnish formed on petroglyphs in the region and to analyze if rock type influences its morphology and chemical composition.

2. Materials and Methods

2.1. REGIONAL SETTINGS

2.1.1. SIERRA SAMALAYUCA, CHIHUAHUA

Sierra Samalayuca is composed of around 16 km NW-SE rock strip range surrounded by other small rock hills and dunes of the Chihuahuan Desert (Figure 1). The physiographical setting corresponds to a typical insolated range of the North American Basin and Rage province (Berg, 1970; Bruno, 1995; Castulo, 1997). The current climate conditions in the area (Schmidt, 1979) matches to a very dry highland desert with hot summers (up to 41°C) and cold winters (minimal temperature -16°C). Annual average temperatures are between 12–18°C. Whitin the classification of Köppen, the type of climate corresponds to BWKx' (e') with an annual rain of 220 mm and temperature oscillation of 23°C (Comisión Nacional de Areas Naturales Protegidas). Typically, the region is known as cold desert. Predominately winds (45%) in the region come from the west with speeds of approx. 20–40 km/hr. But the fastest winds are from the South-East (approx. 50 km/hr). Representative desert plants are Larrea Tridentata (creo-

http://dx.doi.org/10.18268/BSGM2022v74n3a100622

sote bush), Artemisia tridentata (sagebrush), small choya plants and small chaparral plants.

Geologically, Sierra Samalayuca is composed mainly by green sandstones, brown, purplish-gray, and gray quartzites, purple shales, conglomerates beds and small lenticular limestone beds (Berg, 1970). The main NW-SE range corresponds to basinal sandstones group (probably alluvial fans), and surrounding hills correspond to a marine sandstone well known as La Casita Fm. This formation corresponds to the Jurassic and contains ammonite fossils (Figure 1). Copper beds are encountered along sandstones outcrops and some mineral alterations are well disseminated as silicification and chloritization (Bruno, 1995; Boily, 2013). A diorite intrusive rocks are cutting the old sandstones in the tail of the Sierra Samalayuca range, the intrusive event probably occurred during the early Cenozoic. Covering the region are alluvial, eolian and dunes sediments. Typically, a desert varnish coverture is above the entire rock area, but varnishing is strongest and thicker over the hard rocks resistant to weathering as sandstones.

2.1.2. THE SONORAN SITES: SIERRA EL ÁLAMO AND LA PROVEEDORA

The alluvial plains have many streams that, for the most part, only contain water during the rainy seasons, during the summer and in winter. In most cases these channels disappear into the desert sands before reaching the sea. In the areas of mountain ranges and rocky outcrops, it is common to find pools of water that retain a small amount of liquid a few weeks after the end of the rains and have been of great importance for the human groups that have populated the region. Due to its climate, the region is classified among the very dry semi-warm, with an average annual temperature of between 18º and 22º C and an average annual rainfall of less than 300 mm, with rains in summer and winter. The vegetation is microphyllous desert scrub, although foraging grasses have been introduced in some areas (Consejo de Recursos Minerales, 1992).

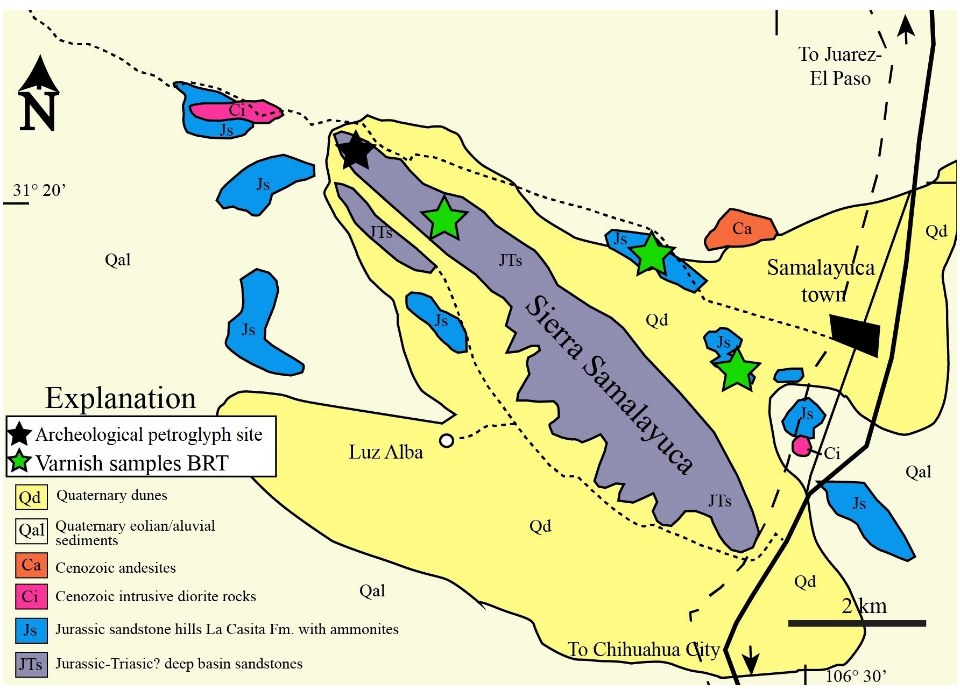

Figure 1 Geologic map of Sierra Samalayuca (modified from Servicio Geológico Mexicano map 1:250 000). Locations of BRT varnish samples in the Sierra range and small hills composed mainly by sandstones. The black star dot shown the Samalayuca Archeology and petroglyph site.

The Sierra de El Álamo study area is part of the Caborca Mining Region, which includes the municipalities of Caborca, Pitiquito, Trincheras, Altar and Benjamín Hill, within the Physiographic Province of the Sonora Desert. The geological environment that predominates is represented by Precambrian and Triassic-Jurassic metamorphic rocks, made up of gneisses, schists, shales, sandstones, and limestones (Figure 2). There are also granitic intrusive rocks from the Cretaceous, as well as volcanic rocks with ages that vary from Tertiary to Quaternary and are composed of rhyolites, andesites and basalts (Consejo de Recursos Minerales, 1992). The main geological characteristic of the Sierra de El Álamo is constituted by the El Antimonio Formation, which is "a sedimentary succession of late Permian, Triassic and early Jurassic age, which is composed of 14 sequences limited by unconformities. This unit contains systematic Permian-Triassic and Triassic-Jurassic boundaries, represented by disconformities" (González-León, 1997). This Unit lies discordantly on the Monos Formation, Late Permian (González-León *et al.*, 2017) (Figure 2).

The archaeological site La Proveedora is located 10 km west of Carborca. Cambrian rocks such as granite, granodiorite, quartzites and limestones belong to the Buelna Formation (Cooper *et al.*, 1952; Damon *et al.*, 1983). Soils such as calcisols and leptosols predominate. The detailed description of the exact location of the samples and petroglyphs are well described in the study previously done by Martínez-Pabello *et al.*, (2021a) in the area.

2.2. CULTURAL HISTORY

2.2.1. SIERRA SAMALAYUCA, CHIHUAHUA

The petroglyphs are located mainly on the Northwest and Southeast slopes of the Sierra de Samalayuca. The most outstanding representations are engravings of bighorn sheep, anthropomorphic figures mostly of humans, shamans with horned masks, arrowheads, astronomical elements, and

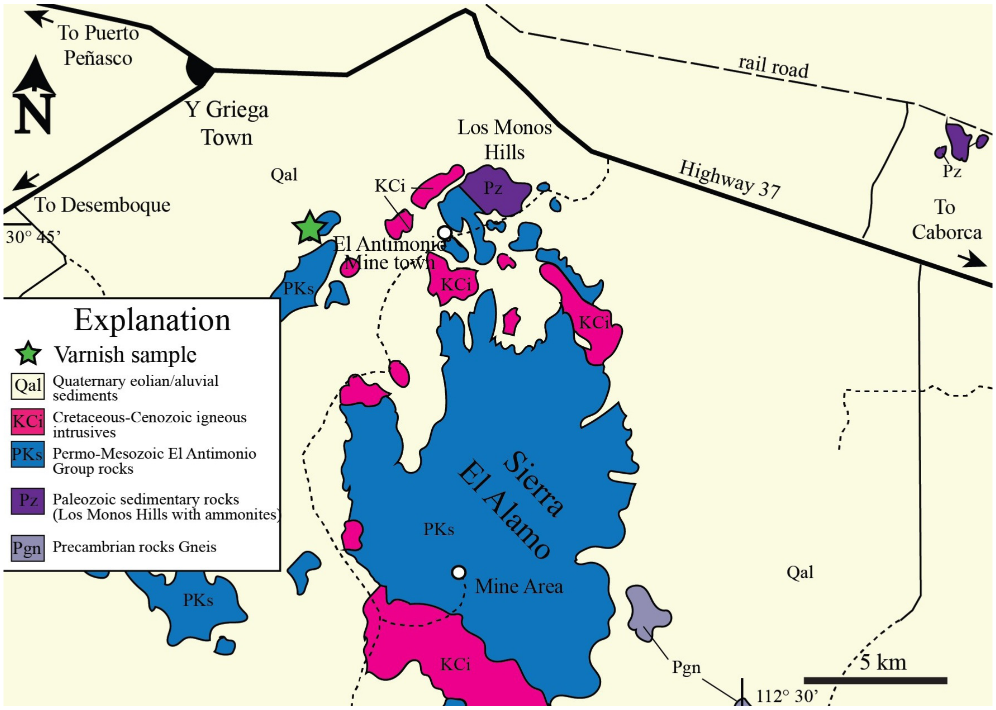

Figure 2 Synthetic geologic map of Sierra El Álamo (modified from Servicio Geológico Mexicano geologic map 1:250 000 and González-León *et al.*, 2005). Location of El Álamo varnish sample is represented by a green star dot.

the gods of antiquity such as Tlaloc, drawn with different techniques and even in cave paintings, not only in engravings. In the eastern part of the state of Chihuahua there are a good part of the sites of the so-called Candelaria style, studied by E. Gamboa (1995), with painted figures of hunters with weapons, of a naturalistic nature, such as long spears, sticks or bags (Gamboa, 1995). The figures of animals, probably bighorn sheep and pronghorn, are found aligned, forming hunting scenes, which seems to have been the main subsistence activity in the Sierra de Samalayuca. In addition, the technique seems to have been very careful in the elaboration of the rock manifestations, as well as a use of the support is observed. Cave art researchers in the area suggest that it is a cave art related to hunter-gatherers of the Late Archaic, although some sites may be from later times (Casado López, 2015). In 1991, Eduardo Gamboa carried out the *Inventory of Archaeological Sites, Engravings and Pictographies of the state of Chihuahua*, where he records the graphic-rock manifestations located in the northwest, south and southeast at the foot of the Sierra de Samalayuca. In addition, the author also points out that architectural remains were found in various locations near the Sierra de Samalayuca, as well as ceramics and lithics on the surface, providing a chronology between 1000 and 1500 BC. It seems that these representations could be linked to the Mogollón and Mimbres style of the southwestern United States of America and the Anasazi style to the north, west and southwest of this country. The chrono-cultural context of the Samalayuca petroglyphs coincide with these traditions, although based on the recovered ceramics, it is part of the cultural phases corresponding to Mimbres and Jornada Mogollón.

2.2.2. SIERRA EL ÁLAMO AND LA PROVEEDORA, SONORA

In 1987, the French astronomer D. Ballereau located and documented in the Sierra El Álamo the site known as El Arroyo de las Flechas or Aguaje de Las Palomas. This is the only known reference to the place, although the existence of several archaeological sites and caves in the area is known. Ballereau counted around 300 figures within what would be the main panel of the complex (Ballereau 1991). From his observations on the hills of La Proveedora and La Calera, he proposed a classification for biomorphic and geometric engravings. He also proposed his own definition for the style for this rock art, which he calls the "Caborqueño style". (Ballereau, 1988). According to him, El Arroyo de las Flechas would fit into this style. This site is located on a rocky front whose nature is of sedimentary origin, specifically sandstone. It is located on the right bank of the stream in a N-S direction, has dimensions of about 32 m in length and 5 m in height. The set presents a total of 766 graphic units, the central part of the rocky front being the one that concentrates the largest number of representations. All registered units are engraved except for the remains of a painted figure. The demonstrations were carried out, mainly, by means of the direct and indirect picket technique, with some pointed stone utensil and a hammer, and the fine scratching, using a metallic element for the recent glyphs. In addition, it has been observed that the groove of the engravings shows different degrees of skating between contiguous units (Menéndez Iglesias, 2021a). This would indicate that the engravings were made in different stages, as is the case of other nearby cave sites such as La Proveedora and La Calera (Amador and Medina, 2013; Martínez-Pabello *et al*., 2021a). Regarding the typology, it is very broad and contains both figurative and abstract elements: geometric, human (anthropomorphic, "lizard-men", hands, feet), instruments (bows, arrows, quivers,), animals, stars, and even historical inscriptions or graffiti, the less frequent but which reveal the presence of a place frequented until present times (Menéndez Iglesias, 2021b). Among the instruments, the arrows that have been compared with the lithic typologies of other places stand out, since we do not have diagnostic archaeological material in the cave site.

The absence of diagnostic archaeological materials does not allow us to address, with explicit evidence, the cultural affiliation of the author population of the panels with petroglyphs, nor to clarify their evolutionary development. However, the typological analogy and the formal, thematic, and technical analysis, as well as the observation of different degrees of patination between the images, allows us to present, at the hypothetical level, a chrono-cultural framework for the whole of Arroyo de las Flechas. This would be delimited by the stages of the Archaic, the Trincheras tradition, its possible relationship with the Hohokam Culture and its link to the Gila Petroglyphs styles (from the first centuries to 1450 AD) and the Great Basin Abstrac (from 1000 BC, to the first centuries AD) (Schaafsma, 1980).

There are similarities with the archaeological site La Proveedora, where more than 5000 petroglyphs have been counted. Archaeologist Beatriz Braniff was the first to provide a diverse classification for these motifs, some included anthropomorphic representations, labyrinths, and zoomorphic figures, among others (Braniff, 1992). Subsequently, other classifications have been made, which are divided into zoomorphic, anthropomorphic, and geometric (Villalobos, 2003). Different pieces of evidence and objects such as lithic fragments, spearheads, remains of ceramic objects, shells, etc., have been found in the area. These objects are part of what is known in regional cultural history as the Trincheras Tradition (Braniff, 1992, Hinton, 1955, Villalobos, 2008, 2018). There is evidence of lithic artifacts that indicates that human occupation at La Proveedora dates to the middle Holocene (ca 5000-3000 BC) (Villalobos, 2003; Martínez-Pabello *et al.*, 2021a; 2021b).

2.3. METHODS

Varnish samples were taken from 3 different sites: Sierra de Samalayuca (Chihuahua), Sierra El Álamo (also named las Flechas -Sonora, México-) and La Proveedora (Sonora, México) (Figure 3).

The rock varnish samples were collected outside, but close to, archaeological sites. The proximity to the rock sites in the collection of samples is important to enhance the likelihood that rock type and environmental influences are similar to the rock art environment. We did not analyze samples from petroglyphs. A photographic record established sample location along with registration of UTM coordinates. A description was also made of both the characteristics of the rock and its positional relationship with respect to the rock sites, that contextualizes the sampling (Menéndez Iglesias, 2020).

2.3.1. MICROSCOPIC METHODS

We observed three thin sections of 50µm thick were observed under a Zeiss Primotech with an integrated camera using the Labscope software. For the petrographic description, we used plane-polarized light (PPL) and cross-polarized light in transmitted and reflected light. Petrographic evaluation of the varnish included the thickness, relationship between varnish and the rock, and varnish habit.

2.3.2. X-RAY DIFFRACTION (DRX)

We obtained diffractograms in an EMPYREAN Diffractometer equipped with a nickel filter, a fine focus copper tube and a PIXcel3D detector. The rock samples were crushed and subsequently homogenized using an agate mortar and sieved to 200 mesh (<45 microns). They were measured using an aluminum sample holder (non-oriented fractions). The measurement was carried out in the 2θ angular interval from 4° to 80° in step scanning with a step scan of 0.003 ° (2 Theta) and an integration time of 40s per step. Quantification was performed using the Rietveld method implemented in the HIGHScore v4.5 software and the ICDD (International Center for Diffraction DATA) and ICSD (Inorganic Crystal Structure Database) databases. The varnish samples were measured in a height adjustable sample holder under the same conditions as the total rock samples.

2.3.3. LASER BREAKDOWN SPECTRA (LIBS)

The laser-induced breakdown spectra (LIBS) uses a 193 nm laser. The beam was focused on the samples in a 103 µm diameter circle at atmospheric pressure. Plasma light was collected with a mirror and a fused quartz focusing lens on a 600 µm diameter optical fiber. Ten successive pulses at a 30 Hz repetition rate were collected for each sample and time-integrated in a non-gated Ocean Insight HR4000CG-UV-NIR spectrometer. These pulses ablated an average of 1 µm depth in the sample. Solé (2014) describe the acquisition system in detail. Spectra processing used in-house software to identify the NIST database's spectral lines (Kramida *et al.*, 2019).

3. Results

3.1. MICROSCOPIC OBSERVATIONS

The characteristics of background material, observed in thin sections of the samples from the site Samalayuca reflect the sandstone rock type. It consists predominantly of sand-size grains, well sorted, among which quartz grains dominate, followed by feldspars and few altered ferromagnesian minerals. The joints between sand grains are filled with the micritic cement. In the area close to the surface of the rock fragment the cement disappears, seen clearly by the absence of the interference colors (Figure 4a). The varnish coating is dark brown to black, opaque and has quite very rugose limit with the rock base: v-shaped small depressions correspond to the sand grain contacts whereas rounded "mounds" are formed above the quartz grains. The outer surface of the varnish coating follows the same pattern (Figure 4b).

At the El Álamo site the parent rock also shows a texture typical for sandstone. Sand grains are predominantly quartz and feldspars and are poorly sorted, showing variety of sizes and have mostly subangular shapes. The spaces between sand grains are filled predominantly with the oriented clay material that shows moderate birefringence. Clay phyllosilicates sometimes also form

Figure 3 Rock outcrops with rock varnish. a) Samalayuca - Chihuahua, b) Sierra El Álamo (Arroyo Las Flechas) - Sonora and c) La Proveedora - Sonora.

sand-size clusters within the rock matrix. General morphology and thickness of the varnish coating is similar to that of the Samalayuca site. Its contact with the rock and outer surface depends upon the composition of the underlying rock: in case the contact zone consists mostly of quartz grains (Figure 4c). However, when the varnish covers concentrations of phyllosilicates, the contact between the varnish and the clays is strongly undulated and the surface becomes botryoidal (Figure 4d).

The micromorphological characteristics of the La Proveedora samples were presented previously (Martinez-Pabello *et al*, 2021a; 2021b). Here we add that the configuration of the contact of varnish with the host rock as well as it outer surface are quite rugose (Figure 4e). Dark varnish material penetrates plagioclases etch pits that follow the directions of cleavage and twinning (Figure 4f). The varnish is associated with deep depressions when it forms over the hydrothermally-altered ferruginous minerals (Figure 4g).

3.2. X-RAY DIFFRACTION

The rock F-V1 is mainly constituted by silicates, mainly quartz (~40), plagioclase (~36%), and phyllosilicates (~20%) stand out. We note small amounts of calcite-type carbonates (~1%) and magnesium calcite (~4%). Minerals of the mica-illite group are the most abundant phyllosilicates (~12%), followed by the chlorite group (~6%) and traces of kaolinite (Figure 5 - red line).

Rock P-V1 comprises only silicates, the most abundant being plagioclase (~50%), orthoclase (~15%), quartz (~14%), augite-type pyroxene, and amphibole-type, magnesium-hornblende (~7%) and actinolite (~8%). For phyllosilicates, the minerals of the group of mica/illite (~3%). Predominate, and followed by kaolinite (~1%); both clay are present in a low proportion indicating that a low degree of alteration (Figure 5 - green line).

Sample S-V1 is similar in mineralogical composition to sample F-V1. Silicates predominate again, quartz (~41%) being the most abundant mineral, followed by plagioclase (~38%), augite-type clinopyroxenes (~4%), and mica-illite-type phyllosilicates (~4%). Again, the proportion of phyllosilicates is low, showing that the rock has a low degree of alteration. Additionally, in the sample S-V1, we observed a significant proportion of calcite-type carbonates (~15%) (Figure 5 – blue line), see Table 1.

Varnish X-ray diffraction analysis yielded varied findings. In the X-ray diffraction analysis of the F-V1 varnish, the rock's important proportions of quartz and plagioclase appear, and a low proportion of pyrolusite-type manganese oxide (<1%). This mineral is poorly crystalline and was not identified as a primary mineral in the rock (Figure 6 – red line). For the varnish of the P-V1 sample, rock minerals (quartz, plagioclase) also occur, but in turn, the presence of pyrolusite (~8%) was detected; goethite (~3%) and graphite (~6%) (Figure 6 – green line). Finally, for the varnish of rock S-V1, only the goethite-type iron oxide (~2%) was identified as a mineral that is not characteristic of the primary mineralogy of the rock (Figure 6 – blue line), see table 2.

3.3. LASER BREAKDOWN SPECTRA (LIBS)

The ablation focused on the very top part of each sample in order to minimize contamination from the underlying rock. LIBS results reveal Fe, Mn, Na, Ca, Al, Li and K. In figure 7 (green line), Ca and Al (around 395 nm) exist in a greater proportion in the Samalayuca sample than in the El Álamo and La Proveedora samples. Also Fe and Mn are most abundant in the Samalayuca sample. In the case of El Álamo, prominent Na and K peaks around 590 and 770 nm respectively that may correspond to environmental contamination at the time of sampling (Figure 7 – red line). Finally, the La Proveedora sample contains similar amounts of Al (395 nm) and Mn (405 nm) to Samalayuca and lower amounts of Fe (Figure 7 – blue line). The variations between the three samples are generally minimal; the presence of Fe and Mn characteristic of the desert varnish is stable and these elements predominates in all cases.

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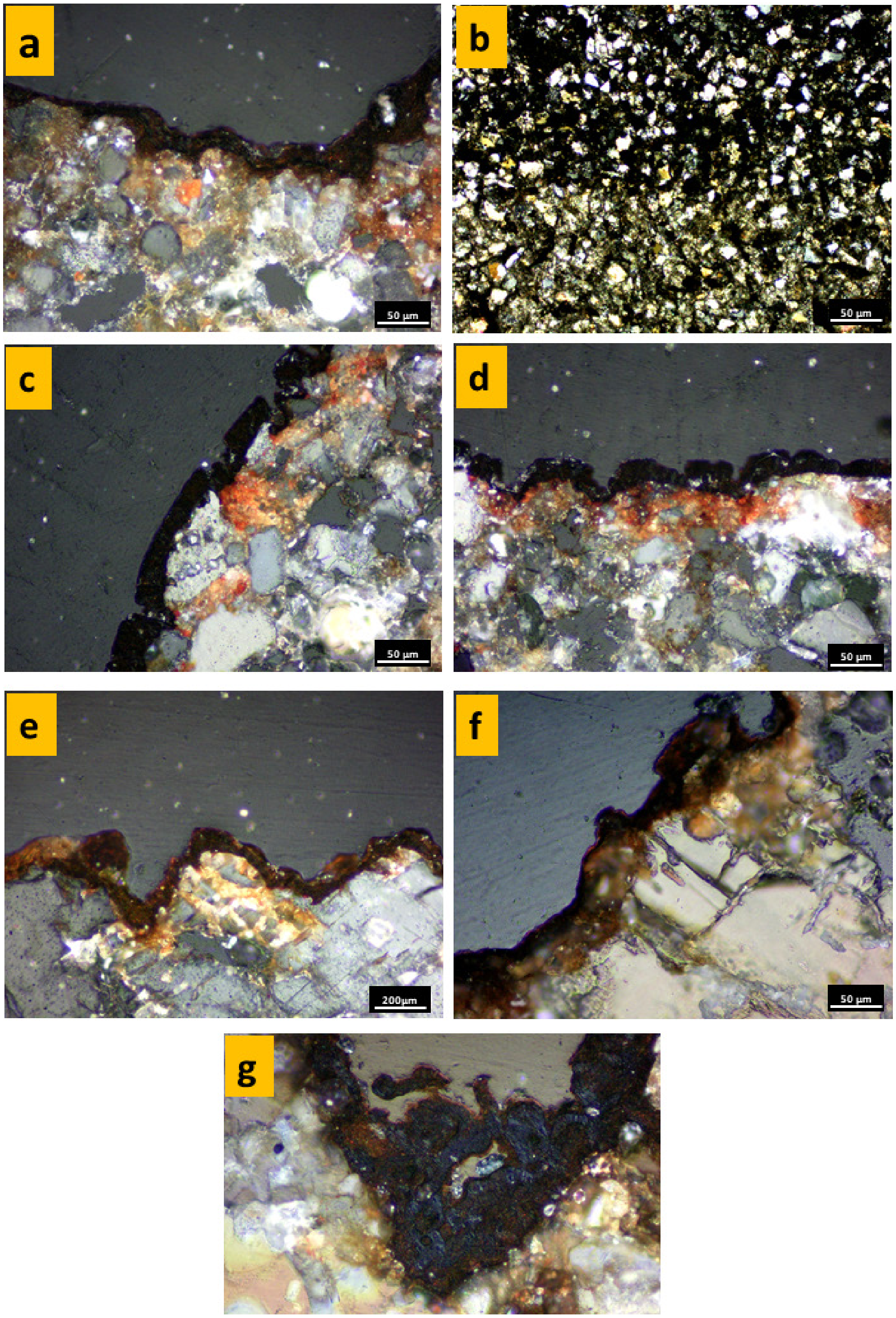

Figure 4 Micromorphology of the parent rock and varnish at different sites: a), b) Samalayuca samples: sedimentary rock of a sandstone type, predominantly quartz grains, feldespars and ferromagnesians minerals. Patina dark-brown with rugose limit with rock base; c), d) El Álamo (las Flechas) samples: sandstone structure, quartz and feldespars in different sizes and spaces filled with clay material showing moderate birefringence. Varnish covering phyllosilicates with limits undulated and botryoidal surface; e)-g) La Proveedora sample: contact between varnish and parent rock is quite rugose. Varnish penetration in plagioclases zones follow directions of cleavage and twinning. Deep depressions in presence of hydrothermally-altered ferruginouse minerals are formed. Petrography described by Martínez-Pabello *et al.*,2021a; 2021b.

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4. Discussion

The varnish of the three analyzed samples shows several similarities. Under the microscope, varnish appears as opaque rim with a sharp rock contact (Figures 4a, 4c and 4f). In figures 4a, 4c and 4e) illustrates varnish developed on three different rocks with quartz, plagioclases, and some calcareous cement in the case of Samalayuca. There are some differences, however, worth highlighting. The contact with the rock is sharp but could be very irregular depending on the rock-surface relief. Like Dorn *et al.* (2017), we observe varnish penetrating into the rock. In Figure 4e an intense weathering occurs in plagioclase affecting the cleavage planes preferentially. In this case, the varnish "infills" these areas, including some small cavities. This is more evident in a close view (Figure 4f). Note how varnish infills some pits and cleavage planes similar to observations made by Tratebas *et al.* (2004). In this figure, it is also possible to observe a well-round cavity penetrating the plane of the plagioclase. This shape could be attributed to biological activity like roots, but the relationship with the varnish is unclear, and the varnish does not infill the cavity. A similar behavior is found in Samalayuca (Figure 4a), in which the weathering affects the micritic cement preferentially, and the varnish also uses these hollows between sand and grains liberated from cement ton penetrate the rock. We conclude that in this case the geometry of patina is partly controlled by the process of decal-

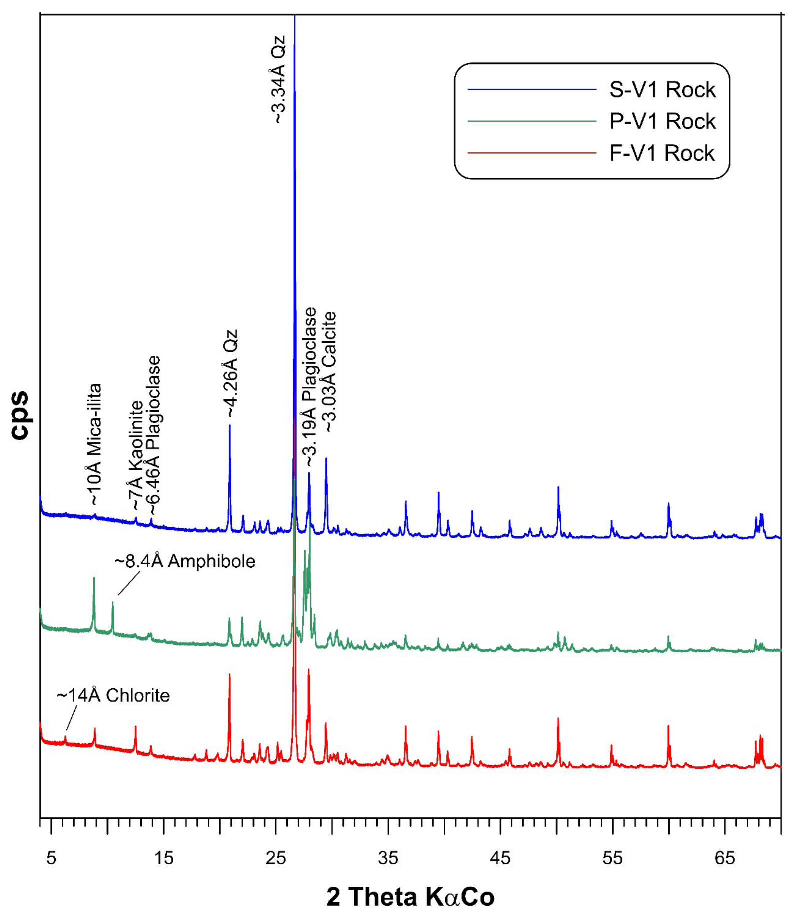

Figure 5 Diffractogram of the three parental rock samples. Samalayuca -blue line- (S-V1 Rock), La Proveedora -green line- (P-V1 Rock) and El Álamo -red line- (F-V1 Rock). The main minerals are observed in each sample.

Table 1. Mineral facies identified with XRD in underlayer rock from Las Flechas-Sonora (F-V1), La Proveedora-Sonora (P-V1) and Samalayuca-Chihuahua (S-V1) samples.

Rock		
Sample	Mineral	(%)
F-V1	Quartz	~ 40
	Plagioclase	~ 36
	Phyllosilicates	~ 20
	Calcite-type carbonates	~ 1
	Magnesium calcite	~ 4
	Mica-illite	~ 12
	Chlorite	~ 6
	Kaolinite	traces
P-V1	Plagioclase	~ 50
	Orthoclase	~ 15
	Quartz	~ 14
	Pyroxene / amphibole	~ 7
	Actinolite / hornblende	~ 8
	Mica-illite	~ 3
	Kaolinite	~ 1
S-V1	Quartz	~ 41
	Plagioclase	~ 38
	Clinopyroxenes	~ 4
	Phyllosilicates	~ 4
	Calcite-type carbonates	~ 15

cification. In Figure 4b, it is possible to observe that the calcareous cement decreases considerably in the direction of the surface in a process like the "arenization" described in quartz sandstones of Venezuela (Aubrecht *et al*., 2011).

Generally, observed varnishes does not display a well-defined internal structure or fabric, although we do note some incipient patterns. In El Álamo sample, for example (Figure 4d), some dome-like structures appear. At the spatial scale of our observations, it is difficult to define if there are clear domes as they do not display internal structure, or the dome-like structure is due to an incipient botryoidal form of the manganese oxides such as observed by Northup *et al*. (2010). In the case of La Proveedora (Figure 4g) it is possible to see a well-defined botryoidal form of manganese oxides.

In the case of the Samalayuca sample, where the XRD shows considerable amounts of calcite-type carbonates (Figure 5 blue line), when these degrade, they increase the signal around 390, 615 and 650 nm of the Ca observed in LIBS (Figure 7 - green), however, this increase in abundance cannot be considered high. The XRD analyzes made on the varnishes of the three samples show great similarities, the presence of pyrolusite (MnO_2) (Figure 6) is consistent with the characteristic composition of desert varnishes (Dorn 2009; Perry and Adams, 1978; Potter, 1979; Potter and Rossman, 1979), where the oxides of Fe and Mn predominate. Still varnishes do not have good crystallographic properties, and it is difficult to analyze by means of XRD (Northup *et al*., 2010). However, the heterogeneity of the minerals of the parent rock could be clearly observed. The elemental analysis with LIBS shows small differences between one varnish and another: Fe, Mn and Ca are present in the three samples in similar orders of magnitude (Figure 7). The Li signal ~670 nm is present in all samples. This may be due to the presence of mica (such as lepidolite) commonly found in granites. This agrees with the signal obtained with XRD at 10 Å (Figure 5), where in all samples mica is present.

These results together show that there is no clear relationship between the rock mineralogy and the chemical composition of the varnish. In that sense, it is evident that the morphology of the varnish is not affected by the mineral composition of the rock. This suggests that the origin and composition of the varnish comes from an allochthonous source, such as wind sources (Dorn, 2020) in combination with physical weather phenomena (temperature, radiation, humidity) (Xu *et al*., 2019; Perry *et al*., al., 2005) and biological activity (Lang-Yona *et al*., 2018) and not so much degradation of the parent rock. However, depending on the type of rock and mineral closest to the varnish, varnish may or may not penetrate the rock.

4.1. MODERN AND PALEOCLIMATIC CONDITIONS

The differences between the conditions under which the studied rock coatings were formed are

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Table 2. Mineral facies identified with XRD in varnish from Las Flechas-Sonora (F-V1), La Proveedora-Sonora (P-V1) and Samalayuca-Chihuahua (S-V1) samples.

Varnish		
Sample	Mineral	(%)
F-V1	Quartz*	~ 14
	Plagioclase*	~ 86
	Pyrolusite	<1
P-V1	Quartz*	~ 9
	Plagioclase*	~ 73
	Pyrolusite	~ 8
	Goethite	~ 3
	Graphite	~ 6
S-V1	Quartz*	~ 66
	Plagioclase*	~ 32
	Goethite	~ 2

* From rock.

not restricted to the type of host rock. The environmental setting changes a lot when we compare the sites in Sonora and in Chihuahua. Both areas are characterized by arid climate however their temperature regime is different. In Chihuahua winters are much colder and temperatures below 0°C are common. Until now we have not found clear evidence of the impact of these differences in the morphology or composition of the desert varnish film. On the other hand, we suppose that the low temperatures in Chihuahua could affect the stability of coatings on the rock surfaces: frost action is known to be a powerful mechanism of the physical breakdown of consolidated geological materials in deserts (Eppes *et al*., 2010; Huang *et al*., 2018; Wang *et al*., 2021).

As it was shown earlier (Martínez *et al*., 2021b) the desert varnish coating are durable surface features, developed over millennia. Thus, their formation could be controlled not only by present day but also by past environmental conditions. In this concern it is interesting to compare the main trends of environmental evolution in the two studied regions – Sonora and Chihuahua. In both regions several paleoecological records: lacustrine, packrat midden, paleopedological, are available for the Late Pleistocene conclusion e and the Holocene. They lead to the conclusion that the general trend of climate evolution was quite similar in both regions: from cooler and more humid climate at the terminal Pleistocene to abrupt aridization from the beginning of the Holocene till nowadays.

In Sonora this trend is shown by the presence of macro-botanical records; the evidence of pollen and packrat middens indicates the existence of a species of Pinyon pine-juniper-oak that predominated in the area towards the end of the Pleistocene moving from the area approximately 11 000 years ago. (Van Denver and Spaulding, 1979), In addition, there is evidence of grasses in packrat middens that indicate that there was a change in rainfall, at the end of the Pleistocene they were only present in winter and from 8 000 years ago in winter and summer (Arundel, 2002; Holmgren *et al*., 2007; Van Denver and Spaulding, 1979). Complementarily, there are studies done in lake sediment cores (Roy *et al*., 2012) and isotopy in fossil bones of mammals (Nuñez *et al*., 2010), Finally, there are studies of secondary carbonates and other pedogenetic properties in paleosols that suggest that wetter conditions existed in late Pleistocene and early Holocene. (Cruz y Cruz *et al*., 2014; 2015; Ibarra-Arzave *et al*., 2020).

In Chihuahua, the evidence of this trend is the construction of alluvial plains, the formation of paleosols, the erosion of channels (which occurred 14 000 years ago in the late Pleistocene) and the change of vegetation (grasslands), indicating the change of colder and more humid in terminal Pleistocene to relatively warm and dry climate in the Holocene (Nordt, 2003). Changes are also observed in the diatom flora, in the depths of lakes and water bodies and there is also evidence of winter rains in a wetter environment in the late Pleistocene (Metcalfe *et al*., 2002).

These data agree well with the numerous paleoenvironmental proxies obtained in the adjacent territories of the southwestern United States (Bartlein *et al*., 1998; Stute *et al*., 1995; Thompson *et al*., 1993) and Baja California (Lozano-García *et al*., 2002)

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Earlier we supposed that desert varnish in Sonora could be to a large extend the legacy of the more favorable climatic conditions of the Terminal Pleistocene. It is possible to extend this hypothesis to similar varnishes of Chihuahua and suppose that these rock coatings in the Northern Mexico are predominantly a relict surface geological and paleopedological feature.

During the Terminal Pleistocene there were more humid conditions and short-term heavy rains. This caused surface weathering on the underlying rock, forming cavities in the plagioclase grains. These cavities could later be filled by accumulation of Fe and clay from intense aeolian activity in the same period. Later, in the Holocene, the accumulation of these materials could continue to occur, but to a lesser extent (speed and magnitude). Currently there are no records or studies of aeolian sediments in the studied localities.

5. Conclusion

The manganiferous coating rock varnish has served as a natural resource for different cultural activities of human groups that inhabited the northern part of the Mexican desert thousands of years ago. This coating is composed mainly of iron and manganese oxides and clay minerals, and it accretes on different types of rocks. The varnishes studied from the state of Sonora (El Álamo and La Proveedora) and Chihuahua (Samalayuca), are present coating rocks of heterogeneous mineralogical composition and different between them. Microscopic, X-ray

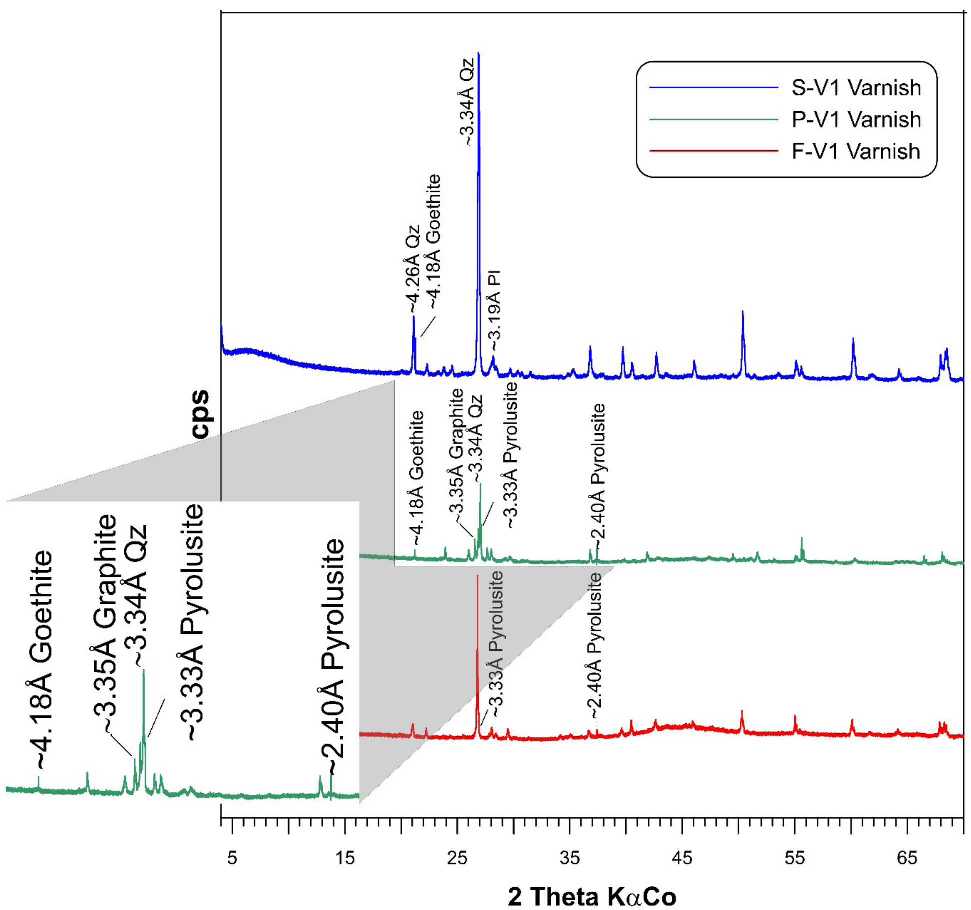

Figure 6 Diffractogram of the three varnish samples. Samalayuca -blue line- (S-V1 Varnish), La Proveedora -green line- (P-V1 Varnish) and El Álamo -red line- (F-V1 Varnish). The main minerals are observed in each sample.

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diffraction and LIBS studies of parent rocks and varnishes indicate that varnish composition or morphology varies little, despite the lithodiversity at these three sites. However, the nature of the contact between the rock and the varnish do present substantial differences. Weathered portions of minerals in the rock closest to the varnish (such as plagioclase) can sometimes be infilled by rock varnish, penetrating into and accumulating in small cavities. The hardest minerals (such as quartz) do not allow the varnish to penetrate and accumulate in thick layers. These observations are consistent with the view that varnish forms mainly from allochthonous material such as eolian sources. Finally, paleoenvironmental evidence from the northern Mexican desert suggests that varnish formation was favored in the Terminal Pleistocene, making it a relict surface geologic and paleopedologic feature.

Contributions of authors

The contribution of the authors is as follows: (1) conceptualization: PUMP, BMI and SS; (2) analysis or data acquisition: PUMP, RLM, TPP, JS, AIP and SS; (3) methodologic-technical development: TPP, JS and AIP; (4) writing of the original

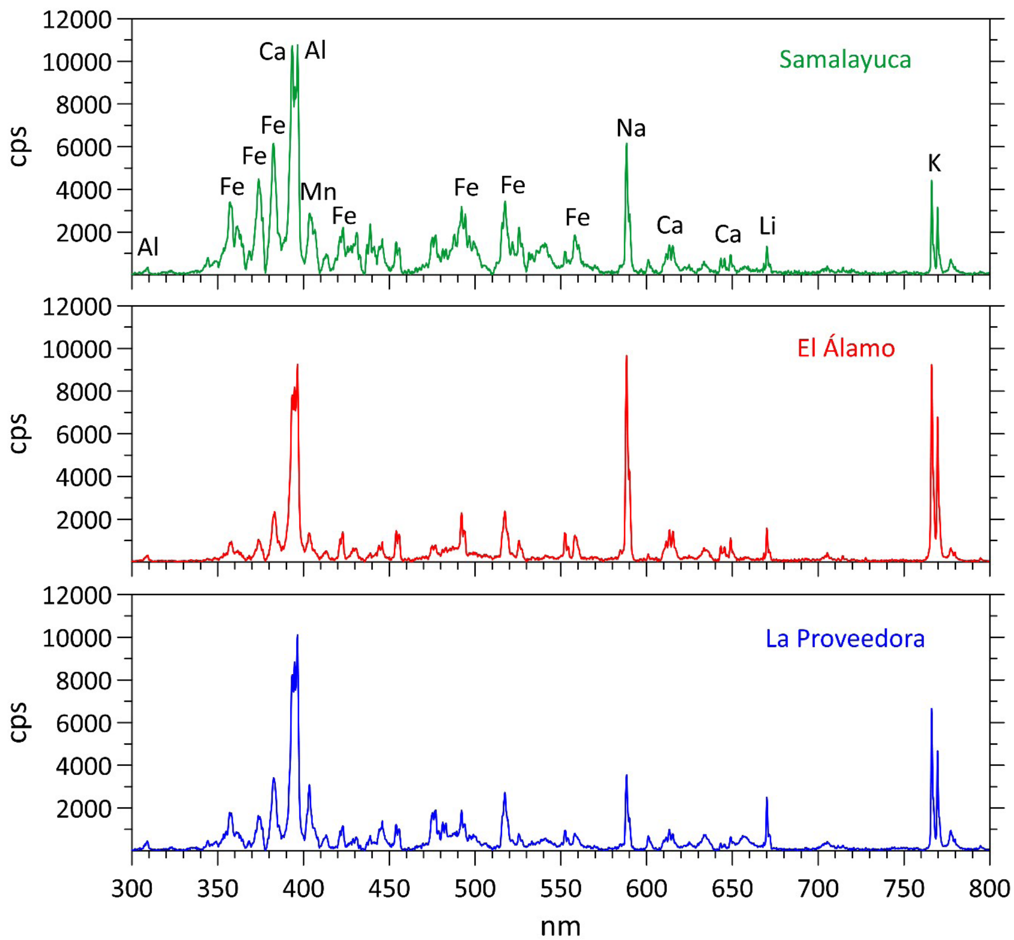

Figure 7 Laser-induced breakdown spectra of three varnish samples taken at the surface using a laser ablation system described in the text. Each spectrum was obtained with the integration of 10 laser pulses. Main spectral lines were identified, although there is some attribution ambiguity due to insufficient resolution.

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manuscript; PUMP, BMI, RLM, TPP, JS, AIP and SS; (5) writing of the corrected and edited manuscript: PUMP, BMI, TPP, AIP and SS; (6) graphic design: PUMP, BMI, TPP, JS and AIP; (7) fieldwork: PUMP, BMI and AIP; (8) interpretation: PUMP, RLM and SS; (9) financing: PUMP and SS.

Declaration of competing interest

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

Acknowledgments

Dr. P.U. Martínez-Pabello is grateful to "Programa de Becas Posdoctorales en la UNAM (DGAPA-UNAM)" for the postdoc fellowship. We appreciate the technical assistance of Jaime Díaz-Ortega. We appreciate the collaboration of Dr. César Villalobos for providing samples from La Proveedora.

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