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THE MATERIALITY OF THINGS: FIRST RESULTS OF DIFFRACTOMETRY AND SPECTROSCOPY ANALYSES ON SECONDARY MINERAL PRECIPITATIONS ASSOCIATED WITH ROCK ART IN PIRAÍ DO SUL, PARANÁ, BRAZIL

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ABSTRACT

This study analyzed the secondary minerals precipitated in rock supports near archaeological sites with rock art in the municipality of Piraí do Sul, Paraná to detect possible mineralogical variations and their relation to rock art weathering. Results indicate several secondary minerals in important anionic groups related to physical and chemical actions. Our conclusions suggest the existence of minerals common to the weathering process indicating the alteration of rock supports due to the action of rain and interactions with pre-existing minerals and organic matter (lichens, microorganisms).

Keywords: analytical chemistry; archaeometry; mineralogy.

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A MATERIALIDADE DAS COISAS: PRIMEIROS RESULTADOS DE ANÁLISES DE DIFRATOMETRIA E ESPECTROSCOPIA EM PRECIPITAÇÕES MINERAIS SECUNDÁRIAS ASSOCIADAS À ARTE RUPESTRE EM PIRAÍ DO SUL, PARANÁ, BRASIL

RESUMO

Este estudo analisou os minerais secundários precipitados em suportes rochosos localizados próximos a sítios arqueológicos com arte rupestre no município de Piraí do Sul, Paraná, a fim de detectar possíveis variações mineralógicas e relacioná-las com o intemperismo apresentado pelos grafismos rupestres. Os resultados apontam para a existência de minerais secundários diversos alocados em importantes grupos aniónicos relacionados a açoes físicas e químicas. As conclusões apontam para a existência de minerais comuns ao processo de intemperismo que funciona como um indicativo da alteração do suporte rochoso causado pela ação da chuva e pela interação com minerais pré existentes e matéria orgânica (líquenes, microrganismos).

Palavras-chave: química analítica; arqueometría; mineralogia.

LA MATERIALIDAD DE LAS COSAS: PRIMEROS RESULTADOS DE ANÁLISIS DE DIFRACTOMETRÍA Y ESPECTROSCOPÍA SOBRE PRECIPITACIONES MINERALES SECUNDARIAS ASOCIADAS AL ARTE RUPESTRE EN PIRAÍ DO SUL, PARANÁ, BRASIL

RESUMEN

Este estudio analizó minerales secundarios precipitados en soportes rocosos, que se encuentran ubicados cerca de yacimientos arqueológicos con arte rupestre en el municipio de Piraí do Sul, Paraná (Brasil), con el fin de detectar posibles variaciones mineralógicas y relacionarlas con la meteorización presentada por el arte rupestre. Los resultados apuntan a la existencia de varios minerales secundarios ubicados en importantes grupos aniónicos relacionados con acciones físicas y químicas. Las conclusiones llevan a la existencia de minerales comunes al proceso de meteorización que funciona como indicador de la alteración del soporte rocoso provocada por la acción de la lluvia y por la interacción con minerales preexistentes y materia orgánica (líquenes, microorganismos).

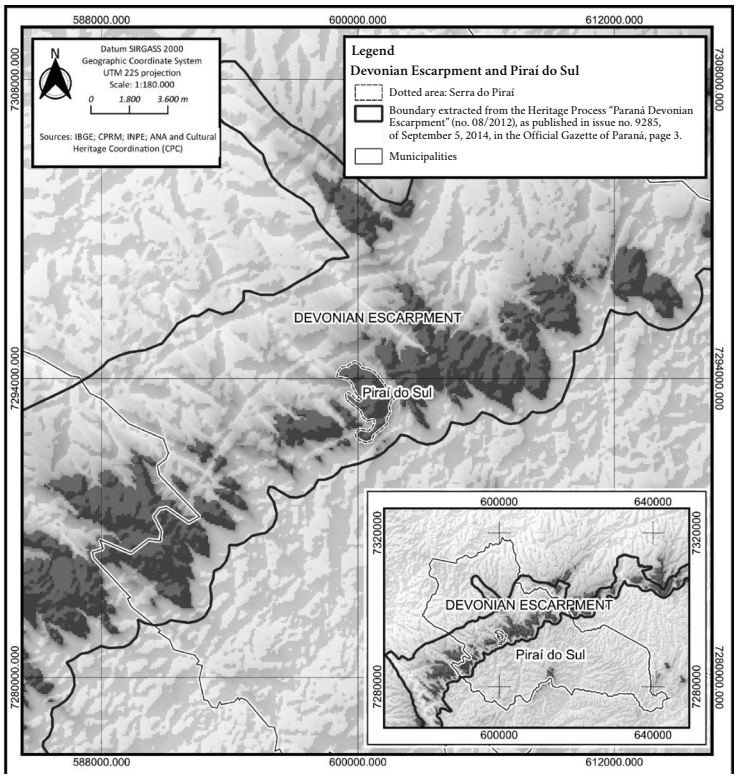
Palabras clave: química analítica; arqueometría; mineralogía.

INTRODUCTION

This study analyzed the Piraí do Sul area in the Segundo Planalto Paranaense (Second Parana Plateau) or Planalto de Ponta Grossa (Ponta Grossa Plateau), also known as Campos Gerais do Paraná (Plateau of Campos Gerais). Its lie between the Devonian escarpment to the east, at altitudes from 1,100 to 1,200 m and the Esperança escarpment (Serra Geral) to the west, whose nearby altitudes reach 350 m and 560 m (Figure 1).

Piraí do Sul is in Campos Gerais do Paraná, consisting, from the bottom to the top, of the Castro Group (Phanerozoic/Proterozoic boundary) and the Iapó (Ordovician-Silurian), Furnas (Silurian-Devonian), and Ponta Grossa formations (Devonian), with a predominance of sandstone from the Furnas Formation.

Figure 1. Location of the region with archaeological sites.



Source: Carlos Alberto Rizzi.

The area surrounding the Devonian Escarpment has large amplitudes with frequent abrupt vertical slopes, stretches of embedded rivers, and numerous waterfalls and rapids over rock beds. It has many indentations and ramifications from the Devonian Escarpment, which show landscape macrofeatures, such as hills and canyons, and meso- and microfeatures associated with ruiniform reliefs derived from active erosion processes, especially in the Furnas Formation sandstone (MELO et al., 2015).

Pontes (2019) highlights certain morphogenetic factors for the relief features in the rocks of the Furnas Formation, such as rock texture and porosity; intensity and nature of cementation (kaolinite); sedimentary and brittle structures (stratifications, bedding planes, fractures, and faults); the current topographical position of its rocks — on remnants or edges of escarpments and subject to an intense drainage of meteoric waters; and the current local climate (humid subtropical) with high rates of precipitation and insolation and a tendency toward the formation of organic acids, which accelerate the chemical weathering of its rocks.

We divided the study area into three sectors: the Serra do Piraí Nucleus, the Lola Souza Nucleus, and the Araucária Shelter.

The Serra do Piraí Nucleus has four archaeological sites on the immediately opposite side of the Devonian Escarpment (Figure 1). The area has several sandy outcrops belonging to the Furnas Formation and associated with the Devonian Escarpment. Its environmental context is well preserved and the outcrops in the studied archaeological sites (on the middle or top of its slopes) have small shelters that are normally small for human occupation but provide temporary protection.

The Lola Souza Nucleus is distributed around Morro Redondo, a remnant of the Devonian Escarpment, in Campo do Cerrado. The area has several sandstone outcrops (including conglomeratic portions) belonging to the Furnas Formation and an arboreal vegetation dispersed across valleys and between rocky outcrops. This nucleus consists of four archaeological sites.

The Araucarias shelter is an isolated archaeological site opposite to the Devonian Escarpment. The cavity at the base of the rocky wall consists of conglomeratic sandstones and the surrounding vegetation, of forests at the bottom of its valley and of grasslands.

Of the nine surveyed archaeological sites, we chose five sites for secondary mineral sample collection, as described below.

Serra do Piraí shelter 3

Located in the Serra do Piraí archaeological site, this shelter remains unregistered on the Instituto do Patrimônio Histórico e Artístico Nacional (National Historic and Artistic Heritage Institute – IPHAN). It was discovered by the University Speleological Research Group (GUPE) within the scope of its EspeleoPiraí project. It lies about eight meters from Serra do Piraí shelter 1 and belongs to the same outcrop.

Its rock art in shades of red is distributed on a small ceiling, forming small groups of digits sometimes associated with rocky features (flaking, cavities, or alveoli). The rock support shows poor conservation with advanced scaling of its sandstone rock surface, which destroyed part of the rock paintings. Ink fading is another serious problem, making recognition difficult. Figure 2 shows PIR 1 sample collection.

Figure 2. Collection of secondary minerals around Serra do Piraí shelter 3.

Source: Tatiane de Souza.

Serra do Piraí shelter 4

This small cavity lies in the archaeological nucleus of the Serra do Piraí shelter. Its central portion has rock art (next to a wasp's nest) with red pigmentation and a high

degree of weathering. We collected the PIR 2 sample from the area around the rock support, 25 meters away from the rock art.

Lola Souza nucleus 2

This site is located on the edge of the Devonian escarpment at the nucleus of the Lola Souza archaeological site. Oliveira (2014) has described this shelter as having the following dimensions: 11.5-m wide by 2-m long with a 0.67-m ceiling projection. Its main entrance faces S30W, greatly suffering from the action of the weather (rain and wind) and humidity. Its rock paintings are relatively well preserved but show moisture, infiltration, and lichens, which ended up harming their permanence and visibility on the wall due to incrustation. We collected our PIR 3 sample from this shelter.

Lola Souza nucleus 3

Mrs. Cinara Gomes de Souza (the owner of the area) discovered and recorded this site. It lies at the base of a hill wall, a remnant of the Devonian Escarpment. This shelter lacks both a prior description and official registration at the National Historical and Artistic Heritage Institute (IPHAN). Figure 3 shows aspects of the archaeological site and the collected secondary minerals (PIR 4).

Figure 3. Collection of secondary minerals around Lola Souza nucleus 3.

Source: Tatiane de Souza.

Araucaria Shelter

This site is at the base of the Devonian Escarpment wall and consists of a large shelter with several panels with red rock art. Its substrate is quite altered, showing flaking, lichen coverage, and small silicified portions, forming ideal surfaces for the elaboration of rock painting. We collected our PIR 5 sample from its surroundings.

WEATHERING AND ROCK ART

Furnas Formation rocks show karstification involving the dissolution of kaolinitic cement and quartz grains (PONTES, 2019). According to Pontes (2019), in the so-called Karst Region of Campos Gerais, unlike traditional karst, the volume initially created by dissolution manifests itself as pores distributed along the altered rock and mineral replacement may occur during this karstification process. Substitution refers to the emergence of another mineral from the chemical alteration of a pre-existing mineral.

For a better understanding of this phenomenon in rock supports with rock art, it is of extreme interest to understand that the dissolution of kaolinite occurs mainly from the

action of organic acids, especially oxalic acid (H_2C_2O4), which is produced by the degradation of certain plants. However, other influencing factors also play a role, such as temperature, water percolation movement, mineral crystallinity, aluminum content, and aerobic bacteria (CAMA; GANOR, 2006; CAMA; METZ; GANOR, 2002; MELO; GIANINNI, 2007; LASAGA, 1995; LASAGA *et al*., 1994; SUTHEIMER; MAURICE; ZHOU, 1999).

This information is important for archaeological taphonomy because the weathering process in rock supports with shelter rock art is a widespread but little explored factor in Brazil (ALVES *et al*., 2011; BELTRAO; LOCKS; AMORIM, 2002; CABRAL , 2010; LAGE, 2005; SILVA, 2007; SOUZA, 2005), being better developed in other countries (AROCENA; HALL; MEIKLEJOHN, 2008; CHALMIN, 2021; CHALMIN *et al*., 2013; MACLEAD; HAYDOCK, 2008; WATCHMAN, 1990, 1992, 1997a, 1997b). Thus, little importance has been evidently given to physical and chemical weathering as a factor of great relevance when considering changes to rock art.

The formation of secondary mineral precipitations by weathering is of particular relevance due to the typically distinct zones of alteration in rock art depending on its length of exposure to these actions.

This action has been attributed to "patina," commonly defined as a surface feature that visually differs in color or chemical composition from the unaltered rock. This is an almost colloquial term for classifying a variety of products and processes, all of which developed gradually over time by the dissolution of substances from within and on the rock surface due to weathering processes and the precipitation of these materials from solutions in the rock.

Therefore, patina indicates antiquity but researchers have accepted the word for centuries without a proper method for its study. Its categorization changed when its main component was understood as a substrate-independent production based on oxidation and reduction due to interactions between rocky substrates under different climatic conditions (BEDNARICK *et al*., 2016).

According to these considerations, this study investigates the effects of the processes expressed in the composition of rock art that are difficult to detect in rock supports as they are subject to different intensity ranges and external influences. These processes include climatic factors (humidity and temperature); chemical (deposition or removal of chemical species from painted images) and biochemical effects (chemical influence derived from fungi and bacteria); and impact mechanisms (friction, scraping).

Therefore, it is necessary to study the factors that deteriorate rock paintings in an attempt to detect the minerals commonly found in pigmented areas that cause severe degradation in most shelters.

The distinction between rock surfaces and graphical components is genuinely important. Weathering can produce calcium sulfates (gypsum, anhydrite). Their formation mechanisms are deposited by water infiltrating through rocks rich in various minerals. Gypsum is a product of the chemical alteration of sandstone due to weathering stresses (CHALMIN *et al*., 2013).

Furthermore, it is highly likely that graphism is subject to a combination of these factors. Minerals such as hematite and gypsum probably denote a change in the matrix component of sandstone to secondarily deposited minerals.

In addition to mineral combinations, other factors, such as the action of rain and intense sunlight, can increase or decrease the formation of crusts in minerals. This phenomenon may occur in more exposed shelters. In this case, leaching dominates the operational weathering regime, resulting in loss of materials and elements, unlike accretion processes, which show additions to the shelter material.

Places with rock art in Piraí show the action of several types of weathering (such as wind, humidity, light) and rock expansion and retraction, which ended up covering the art, damaging and reducing its visibility (OLIVEIRA *et al*., 2015).

Some shelters lie in river valleys, others on steep slopes, and others still at the top of slopes. The vast majority of the evaluated shelters face north to benefit from maximum sunlight, favoring salubrity conditions (temperature, humidity). The few sites on the south face of the relief have many plants and high levels of humidity, which influence the degradation of rock paintings (OLIVEIRA *et al*., 2015).

MATERIALS AND METHODS

Sampling

Several archaeological sites in the area were surveyed to identify the occurrence of secondary mineral precipitations covering or below the rock art.

After identifying these occurrences, comparative visual searches were carried out to identify such precipitations on rocky outcrops around the archaeological sites to avoid intervening in them. In total, five collection sites associated with five archaeological sites were chosen and five secondary mineral samples, collected.

Secondary minerals were scraped off the rock face with a small spatula and immediately stored in acrylic jars. Samples were generally taken from sites that had suffered previous damage and, whenever possible, from points about to exfoliate.

For this reason, sampling tended to be opportunistic rather than systematic. A photograph of each sampling area was taken. In a laboratory, samples were prepared by combining individual grains mounted on aluminum stubs with carbon tape and then covering them with a thin film of carbon.

Techniques

Techniques capable of analyzing small samples to the point of identifying their microheterogeneities were chosen: XRD, SEM-EDS, and RAMAN. Each technique had a different analysis purpose and could together answer questions regarding the presence of secondary minerals and the influence of physical and chemical weathering on the rock supports surrounding the chosen archaeological sites.

The ability to analyze a sample according to its mineralogical composition is strongly influenced by whether minerals have crystalline structures. X-ray diffraction spectrometry is based on all planes within a crystalline structure proportionally diffracting the X-rays directed at it.

As minerals have different lattice spacing or crystal planes, each will produce a unique diffraction pattern, giving them its own unique impression. However, identifying minerals in rock art is difficult because many minerals are found in a given specimen. Nevertheless, X-ray diffraction can provide information on various substances on a surface with rock paintings.

On the other hand, spectrometry (SEM-EDS) is a technique in which electrons bombard a surface and X-rays are secondarily emitted to produce the SEM (scanning electron microscopy) image. X-rays characterize chemical elements that have been affected by the impact of electrons. This is possible because each element has its own distinct X-ray energy (EGERTON, 2005; GOODHEW *et al*., 2001; CROFT JR., 2006; WHITLEY, 2001).

Raman analysis is a technique that uses a monochromatic light source that scatters upon hitting an object, generating light of the same or different energy from the incident light. Inelastic scattering is of interest as it offers important information about the chemical composition of an object based on energy differences. Low power is used to illuminate small areas of the object of interest and at the same time focus the

defined area with a small portion of this inelastically scattered radiation, i.e., many times (or wavelengths) different from the incident light (EDWARDS, 2016; FARIA, 2011; FARIA; AFONSO; EDWARDS, 2002).

Used devices

The diffractometer used was a Bruker brand, D8 Advance da Vinci model, with CuKα radiation, a LYNXEYE detector, and TWIN-TWIN optics, enabling operation with fixed optics. The SUITE DiffracEVA program and the PDF-2 database (ICDD), version 2009, from the Institute of Geosciences at USP were used to identify phases.

For EDS/SEM, a LEO 440 electron microscope from LEO Electron Microscopy Ltd. England and the Solid-State Si (Li) Energy Dispersive X-ray Spectrometer with the Inca 300 software came from Oxford Instruments Ltd, England were used. A 20 kV-voltage and a 25-mm working distance were employed as working conditions.

For RAMAN analysis, a Renishaw inVia Reflex apparatus was used coupled to a Leica DM2500 M microscope with 632.8 nm laser (He-Ne, Renishaw) - 50 mW, 785 nm laser (diode laser, Renishaw) - 500 mW, 532 nm laser (diode laser, Renishaw) - 500 mW laser; 1200-line diffraction grating (when using 632.8 or 785 nm lasers), 2400-line diffraction grating (when using 532 nm laser); and a thermally cooled CCD detector (1040×256 pixels).

RESULTS

X-ray diffraction

X-ray diffractograms enabled us to identify the most abundant minerals in each sample, whereas EDS results, their components in smaller proportions (as it is a highly specific analysis). As a rule, diffractograms are unable to find minerals in proportions smaller than 5% in a mixture (Table 1).

Table 1. Identified minerais.

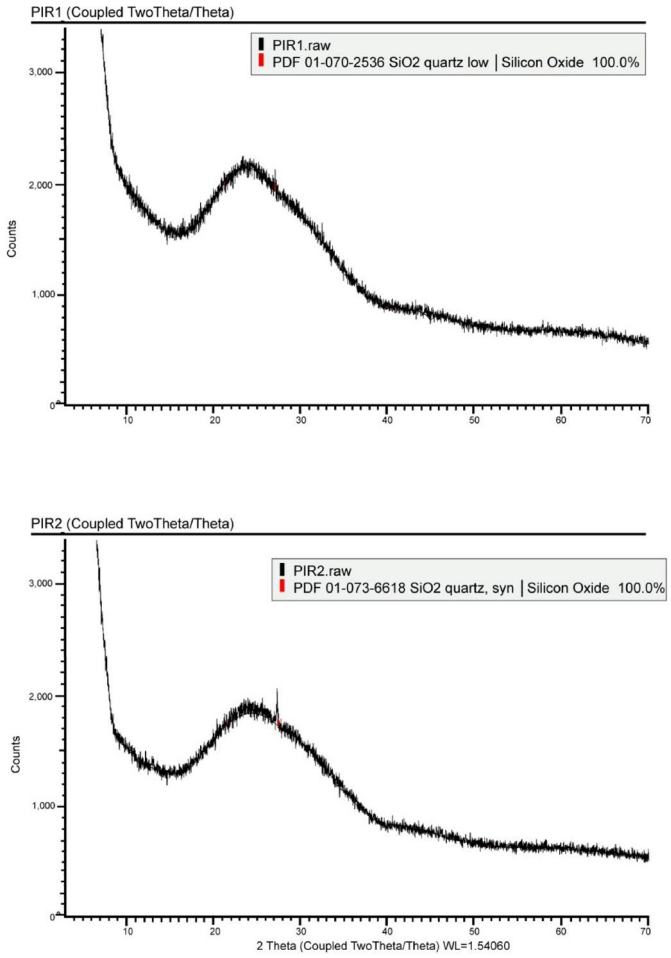
Mineral	Ideal formula
Opal	$SiO_2.nH_2O$
Quartz	SiO_2
Muscovite	$KAl_2(Si_3Al)O_{10}(OH)_2$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Barite	$BaSO_4$
Rutile or anatase	TiO_2
Goethite	FeO(OH)

Source: Daniel Atencio.

X-ray diffractograms of samples PIR1 and PIR2 (Figure 4) show background elevations resembling mountains instead of distinct peaks (except a small peak corresponding to an interplanar distance of approximately 3.3Å, possibly related to quartz). These elevations mean highly variable interplanar distances of a crystalline protostructure corresponding to amorphous minerals. Amorphous is a term that predates the discovery of X-rays, when it was thought that minerals without crystalline forms (amorphous) would also have no crystalline structures, which is absolutely

untrue. However, the word amorphous is still used to indicate the absence of crystalline structures. Incidentally, no material is completely amorphous, as per these elevations in our diffractograms. EDS results show that the material corresponding to this elevation is opal. It, as amorphous materials in general, is an unstable mineral that tends to crystallize, transforming itself into tridymite, cristobalite, and finally quartz. EDS associates compositions with very predominant SiO_2 a but whose total analysis is low, as it misses the results related to H_2O, which evade EDS analysis. Quartz corresponds to analyses in which the SiO_2 content reaches about 100% by mass. In addition to opal and quartz, EDS found muscovite and an Fe oxide (probably goethite) in PIR1 and muscovite and kaolinite in PIR2.

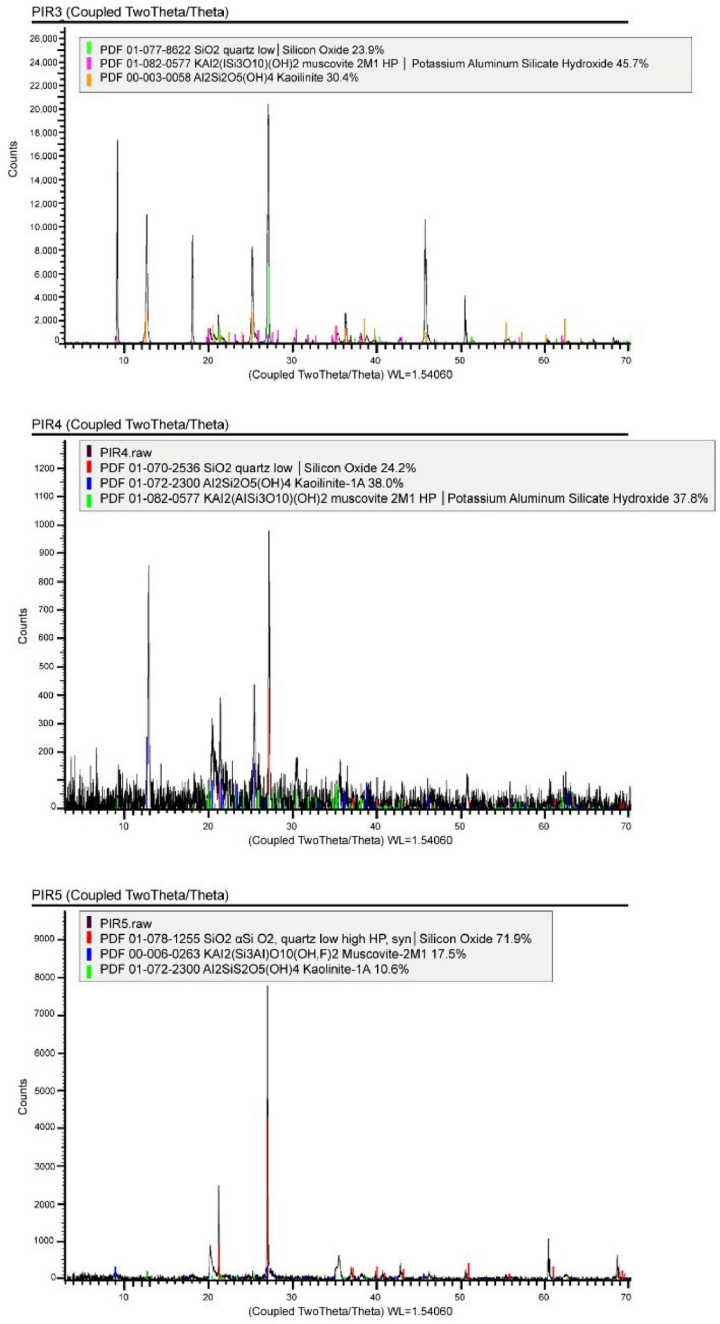
Figure 4. X-ray diffractograms of samples PIR 1 and PIR 2.



Source: Tatiane de Souza and Daniel Atencio.

The main minerals we found using X-ray diffraction in PIR3, PIR4, and PIR5 are quartz, muscovite, and kaolinite. In addition to these minerals, EDS found several others (Figure 5). PIR3 had barite, a mineral with a TiO_2 composition probably referring to rutile or anatase (the most common minerals with this composition). PIR4, in addition to a compound with a TiO_2 composition, had two minerals that avoided identification: an Al phosphate with Sr and an Al phosphate-sulfate with Sr. PIR5, in addition to barite, an iron oxide (probably goethite), and the aforementioned TiO_2 compound, also showed an Al phosphate-sulfate with plenty of Sr and REE and a K and Al mineral with a very low analytical total.

Figure 5. X-ray diffractograms of PIR3, PIR4, and PIR 5.



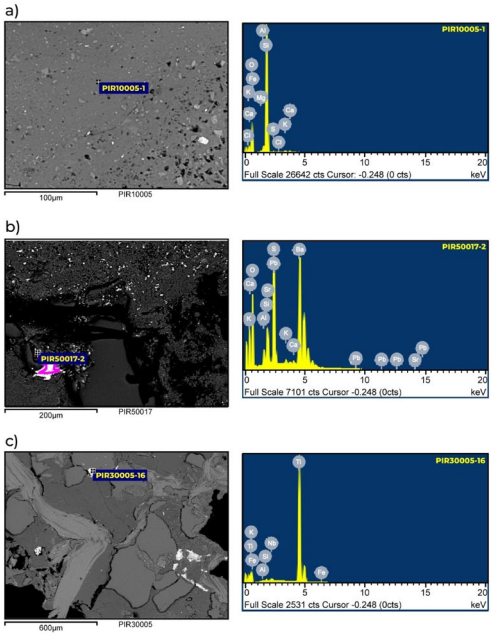
Source: Tatiane de Souza and Daniel Atencio.

SEM/EDS

Scanning electron microscope offers images of backscattered electrons, in which different shades of gray indicate varying chemical compositions. The lighter the hue, the heavier the elements in the mineral. In contrast, the darker the hue, the lighter its elements. These differences enable the verification of different phases and the obtention of specific chemical analyses in its different phases. In Figures 6, 7, and 8, side-by-side images of backscattered electrons are represented with the location of the analyzed points and graphs with the chemical elements detected at said points. We generated a couple of pictures for each identified mineral.

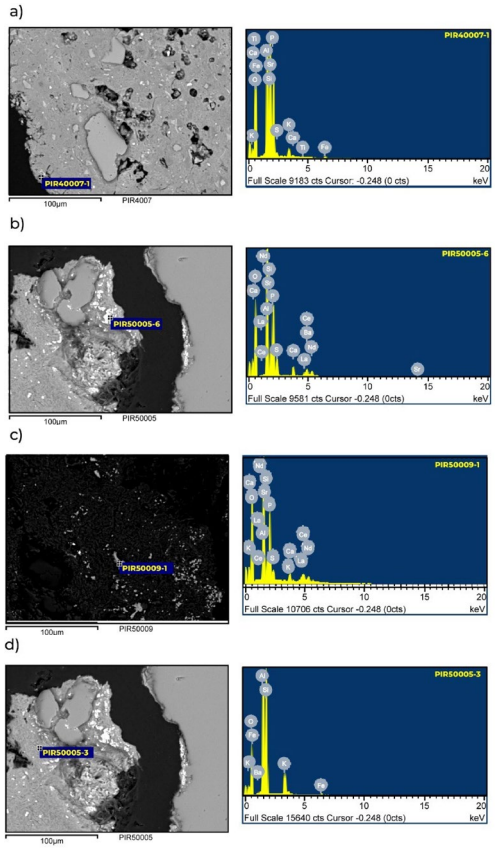
The following figures show such spectra:

Figure 6. SEM/EDS data a) opal; b) barite; c) rutile or anatase.



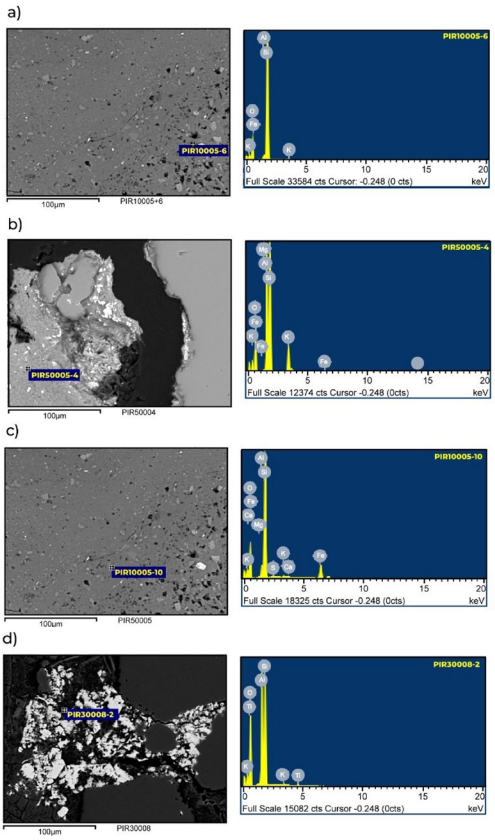
Source: Tatiane de Souza and Daniel Atencio.

Figure 7. SEM/EDS data a) Unidentified Al phosphate with Sr; b) Unidentified Al phosphate-sulfate with Sr c) Unidentified Al phosphate-sulfate with Sr and REE; d) Unidentified mineral with K and Al.



Source: Tatiane de Souza and Daniel Atencio.

Figure 8. SEM/EDS data a) quartz; b) muscovite; c) goethite; d) kaolinite.

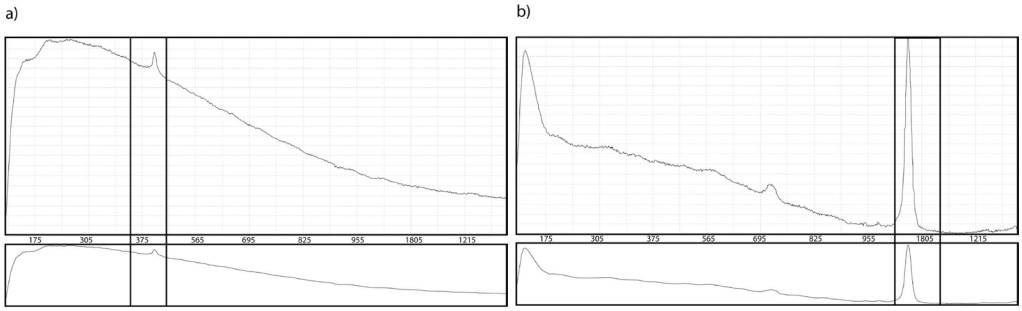


Source: Tatiane de Souza and Daniel Atencio.

RAMAN

Using the RRUFF website (https://rruff.info/) and comparing data with academic papers searched in its attached database, the mineral spectra found in the graphs below corroborate our XRD and SEM/EDS analyses. Analysis consisted of removing baselines and identifying the exact offset values. Figure 9 a), with a peak close to 465 km, strongly indicates the presence of quartz, whereas Figure 9 b), with the highest peak around 1080 km, a carbonate or sulfate. It is impossible to know which specific carbonate we found but it could also be sulfate since its peak is between carbonate (~1080) and sulfate (~1005/1010). This corroborates the large number of clusters detected using SEM/EDS with significant amounts of phosphates or sulfates in combination with various chemical elements, including REE.

Figure 9. Raman detection of quartz (a) and carbonate or sulfate anionic group (b).



Source: Evandro Pereira da Silva.

CONCLUSIONS

The minerals we found represent associations of primary minerals in sandstone and secondary minerals (formed in the crusts of the latter). These crusts, arising from aqueous solutions due to chemical weathering, encompass rock minerals from physical weathering. The primary minerals we found are quartz, muscovite, and kaolinite. Kaolinite is a diagenetic mineral and functions as a cement, whereas quartz and muscovite are minerals from sediments. Note that some of the quartz may be secondary and resulting from opal crystallization. The mineral with a TiO2 composition (rutile or anatase) also belongs to a primary mineral assembly. All other minerals (barite, goethite, the unidentified phosphates and sulfates, and the K and Al mineral) are secondary and have a very low analytical total, having formed as superficially precipitated materials.

It is important to identify the limitations of the carried out mineralogical analyses. The scanning electronic microscopy (SEM) equipment we used with coupled EDS forbids the analysis of chemical elements with low atomic numbers, from 1 (hydrogen) to 8 (oxygen). Therefore, it is unable to observe water in a hydrated mineral (as is the case with opal). If a mineral contains OH (as is the case with kaolinite), it will be unable to attest to the presence of the hydroxyl. Moreover, if a material has carbonates or nitrates (as may be the case with the mineral in which we only found K and Al), these analytic techniques will be unable to find that anionic group as there is no way to analyze carbon or nitrogen. As the built-in sample section for analysis is carbon plated, the observed carbon peak will refer to this metallization. We can only suspect of light elements as a result of the low totals in our analyses, which would be complete with the addition of percentages referring to H_2O, CO_3, etc. However, these low totals may be due to several factors, such as rough surfaces (i.e., with cavities), which are practically unavoidable in sections of secondary minerals, which are generally fragile.

Raman analyses can evaluate structural details, such as chemical bonds in anionic groups, for example. An anionic group consists of a cation surrounded by anions. This set works as a single anion. Examples of anionic groups include silicates, phosphates, nitrates, sulfates, carbonates, etc. These structure components are used for systematic classification since, in general, all silicates are similar to each other, just as all phosphates are similar to each other, and so on. Thus, we suspected the presence of carbonate in our samples, which would have been impossible to verify using EDS but was possible with Raman.

X-ray diffraction can obtain crystal structures, which are related to crystalline compounds; in this case, minerals. One of its limitations, as mentioned, is that it is unable to identify compounds in smaller quantities (EDS can find such substances). Likewise, isostructural compounds show X-ray diffractograms that are very similar to each other (as they have the same structure), making identification difficult.

Therefore, we conclude from the discussion above that the application of only one mineral analysis method is insufficient for a complete study. Even the association of several methods is unable to solve all these problems, as evident in this study.

As for the identified compounds, in addition to rock minerals (sandstone, in this case), we attested to the presence of weathering minerals, some of which are ephemeral due to their solubility. The composition of these secondary minerals formed by aqueous solutions at room temperature involves the chemical elements of rock minerals, but may also receive the contribution of organic matter (e.g., nitrates and oxalates) which are included in the solutions that percolate the rock.

The study of rock minerals and material alterations enables the elaboration of several hypotheses. One line of reasoning is that these minerals served as material to prepare cave paintings. Another is that they can react with paintings, configuring agents of their

destruction by, for example, dissolving them. The production and dissolution of secondary minerals is continuous and can act for long periods, chemically weathering paintings. In addition, physical weathering may occur due to the penetration of solutions into, under, or over the paintings, peeling them. On the other hand, secondary minerals precipitated on paintings may eventually protect them as if they were a varnish. This depends, of course, on the composition and stability of the newly formed minerals.

Physical and chemical weathering are the main agents for the formation of secondary minerals at the researched archaeological sites. Their action is highly important for archaeology as they can perform several functions, from degradation by dissolution to adding crusts that cover rock supports and even preserve rock paintings by covering and protecting them from climatic influence over millennia.

Another important factor is the possibility of their use in the production of the rock art repertoire. As many of these minerals come from alterations to several other minerals, hypotheses suggests that these solutions, added to rock supports, could have been used to form a base for applying paint to rocky shelters.

The performed analysis was of vital importance to detect secondary minerals and weathering processes. Our analyses enabled us to infer that the evaluated rock paintings show a mineral chemical composition unlike that of their rock supports due to their persistence and the aggressive actions instilled on them, or, if the minerals on their rock supports were somehow used to prepare pigments, their producers knew that certain properties of these minerals could determine their composition.

Thus, we wonder why these supports were chosen for these paintings and to what extent the positioning of secondary minerals in rock supports can suggest how these populations observed the effect of climatic conditions on the production of paintings and what measures they took to minimize physical and chemical weathering.

Finally, the production of rock paintings in large quantities, regardless of unfavorable climatic factors, is highly significant. Thus, we wonder whether the climate remained stable until the present day or whether paleoenvironmental actions were modifying the environment, altering the composition of rock supports and the rock art we can currently observe.

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REFERENCES

ALVES, Tetisuelma Leal *et al*. Pigmentos de pinturas pré-históricas do sítio letreiro do Quinto, Pedro II. *Química Nova*, v. 34, n. 2, p. 181-185, 2011. DOI: 10.1590/S0100-40422011000200002.

AROCENA, Joselito. M.; HALL, Kevin; MEIKLEJOHN, Ian. Minerals Provide Tints and Possible Binder/Extender in Pigments in San Rock Paintings (South Africa). *Geoarchaeology*: An International Journal, v. 23, n. 2, p. 293-304, 2008. DOI: 10.1002/gea.20215.

BEDNARICK, Robert *et al*. Paleoart and materiality: the scientific study of rock art. Canberra (AU): Archaeopress, 2016.

BELTRÃO, Maria; LOCKS, Martha; AMORIM, Jacqueline. Projeto central: preservação dos sítios arqueológicos com arte rupestre. *FUNDHAMENTOS II*, v. 1. São Raimundo Nonato. FUMDHAM, 2002, p.243-253.

CABRAL, Carlos Henrique Romeu. A influência dos intemperismos na conservação e apresentação da pintura rupestre no semiárido pernambucano. *In*: ENCONTRO DA ASSOCIAÇÃO NACIONAL DE PESQUISADORES EM ARTES PLÁSTICAS "ENTRE TERRITÓRIOS", 19., 2010, Cachoeira, BA. *Anais* […]. Cachoeira, BA: [*s. n.*], 2010. p. 1-9.

CAMA, Jordi; GANOR, Jiwchar. The Effects of Organic Acids on the Dissolution of Silicate Minerals: A Case Study of Oxalate Catalysis of Kaolinite Dissolution. *Geochimica et Cosmochimica Acta*, v. 70, n. 9, p. 2191-2209, 2006. DOI: 10.101/J.gca.2006.01.028.

CAMA, Jordi; METZ, Volker, GANOR, Jiwchar. The Effect of pH and Temperature on Kaolinite Dissolution Rate under Acidic Conditions. *Geochimica et Cosmochimica Acta*, v. 66, n. 22, p. 3913–3926, 2002. DOI: 10.1016/S0016-7037(02)00966-3.

CHALMIN, Emilie *et al*. How to Distinguish Red Coloring Matter Used in Prehistoric Time?: The Contribution of Visible Near-Infrared Diffuse Reflectance Spectroscopy. *Color Research and Application*, v. 46, n. 4, p. 653-673, 2021. DOI: 10.1002/col.22647.

CHALMIN, Emilie *et al*. Investigation of Organic Matter Entrapped in Synthetic Carbonates: A Multimethod Approach. *Microscopy and Microanalysis*, v. 19, n. 1, p. 1-13, 2013. DOI: 10.1017/S1431927612013773.

CROFT JR., William. *Under the Microscope*: A Brief History of Microscopy. Singapore: World Scientific, 2006. (Popular Science, 5).

EDWARDS, Howell G.M. Raman Microscopy in Art Archaeology. *Spectroscopy*, v. 17, n. 2 p. 1-3, 2016.

EGERTON, Ray, F. *Physical Principles of Electronic Microscopy: An Introduction to TEM, SEM and AEM*. New York (US): Springer Science + Business Media, 2005.

FARIA, Dalva L. A. de. *Entenda o que é espectroscopia Raman*. [*S. l.*: *s. n.*], 2011. Disponível em: https://www.crq4.org.br/sms/files/file/Espectroscopia_Raman_4.pdf. Acesso em: 14 abr. 2023.

FARIA, Dalva L. A. de.; AFONSO, Marisa C.; EDWARDS, Howell G. M. Espectroscopia Raman: uma nova luz no estudo de bens culturais. *Revista do Museu de Arqueologia e Etnologia*, v. 12, p. 249-267, 2002.

FORD, Bruce; MACLEOD, Ian; HAYDOCK, Phil. Rock Art Pigments from the Kimberley Region of Western Australia: Identification of the Minerals and Conversion Mechanisms. *Studies in Conservation*, v. 39, p. 57-69, 1994. DOI: 10.1179/sic.1994.39.1.57.

GOMES, Cinara de Souza. *As representações geométricas e zoomorfas da tradição planalto*: a arte nos Campos Gerais. Curitiba: Imprensa Oficial do Governo do Estado do Paraná, 2011.

GOODHEW, Peter J; HUMPHREYS, Jhon; BEALAND, Robert. *Electron microscopy and analysis*. New York: Taylor and Francis, 2001.

LAGE, Maria Conceição S. M.; BORGES, Joina Freitas; ROCHA JR., Simplicio. Sítios de registros rupestres: monitoramento e conservação. *Mnme*: Revista de Humanidades, v. 6, n. 13, p. 28-51, 2004-2005.

LASAGA Antonio C. *et al*. Chemical Weathering Rate Laws and Global Geochemical Cycles. *Geochimimica ET Cosmochimica Acta*, v. 58, n. 10, p. 2361-2386, 1994. DOI: 10.1016/0016-7037(94)90016-7.

LASAGA, Antonio C. Fundamental Approaches in Describing Mineral Dissolution and Precipitation Rate. *In*: WHITE, Arthur F.; BRANTLEY, Susan L. (ed.). *Chemical Weathering Rates of Silicate Minerals*. Washington, DC (US): Mineralogical Society of America, 1995. p. 23-86.

MACLEOD, Ian; HAYDOCK, Philip. Effects of Water Vapour and Rock Substrates on the Microclimates of Painted Rock Art Surfaces and Their Impact on the Preservation of the Images. *AICCM Bulletin*, v. 31, n. 1, p. 66-86, 2008. DOI: 10.1179/bac.2008.31.1.007.

MELO, Mario Sergio de *et al*. Kaolinite, Illite and Quartz Dissolution in the Karstification of Paleozoic Sandstones of the Furnas Formation, Paraná Basin, Southern Brazil. *Journal of South American Earth Sciences*, v. 63, p. 20-35, 2015. DOI: 10.1016/j.jsames.2015.06.011.

MELO, Mario Sergio; GIANNINI, Paulo Cesar F. Sandstone Dissolution Landforms in the Furnas Formation, Southern Brazil. *Earth Surface Processes and Landforms*, v. 32, p. 2149-2164, 2007. DOI: 10.1002/esp.1520

OLIVEIRA, Fernanda Cristina Pereira de *et al*. As pinturas rupestres na região de Pirai da Serra, Paraná. *Ra'e Ga*: O Espaço Geográfico em Análise, v. 33, p. 171-197, 2015.

PONTES, Henrique Simão. *Patrimônio geológico cárstico em rochas areníticas e políticas públicas de geoconservação com base em estudo de caso do município de Ponta Grossa (PR)*. Tese (Doutorado em Geologia) – Setor de Ciências da Terra, Universidade Federal do Paraná, Curitiba, 2019.

SILVA, Vanda D. S. *Alteração de rochas e a conservação do patrimônio arquitetônico: estudo de caso de Pórtico da Igreja do Outeiro da Glória-RJ*. Monografia (Bacharelado em Geologia) – Universidade Federal do Rio de Janeiro, Rio de Janeiro, 2007.

SOUZA, Harley Anderson. *O desgaste da pintura rupestre e dos abrigos sob rocha na reserva particular do patrimônio natural (RPPN) Pousada das araras em SerranopólisGoiás*: Condicionantes Naturais. Dissertação (Mestrado Profissional em Gestão do Patrimônio Cultural) – Pontifícia Universidade Católica de Goiás, Goiânia, 2005.

SUTHEIMER, Susan; MAURICE; Patricia A.; ZHOU, Qunhui. Dissolution of Well and Poorly Crystallized Kaolinites: Al Speciation and Effects of Surface Characteristics. *American Mineralogist*, v. 84, n. 4, p. 620-628, 1999. DOI: 10.2138/am-1999-0415.

WATCHMAN, Alan. A Conservation Scientist's Perspective on Rock Art Sampling Standards. *Rock Art Quarterly*, v. 3, p. 17-22, 1992.

WATCHMAN, Alan. A Review of Studies into the Composition of Pigments Used in Australian Rock Paintings. *In*: BRUNET, J.; VIDAL, P.; VOUVE, J. (ed.). *50 Ans après la découverte de Lascaux*: journées internationales d'étude sur la conservation de l'art rupestre: Dordogne Périgord (France). Périgueux (FR): Atelier de recherches et d'études en Périgord, 1990. p. 57-64.

WATCHMAN, Alan. Dating the Kimberley Rock paintings. *In*: Kenneally, Kevin Francis (ed.). *Aboriginal Rock Art of the Kimberley*. Perth (AU): Kimberley Society, 1997a. p. 39-46.

WATCHMAN, Alan. *Kimberley and Hann*: River Paint and Accretion Compositions. [*S. l.*]: Australian Institute of Aborigional and Torres Strait Islander Studies, 1997b. Unpublished report.

WHITLEY, David S. *Handbook of Rock Art Research*. California (US): Altamira, 2001.