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**THE CASE OF COMMON AND NEW MINERALS IN ROCK ART
SUPPORTS ASSOCIATED WITH THE ROCK REFUGE
METAMORFOSE – PIRAI DO SUL, PARANA, BRAZIL**

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3 **THE CASE OF COMMON AND NEW MINERALS IN ROCK ART SUPPORTS**
4 **ASSOCIATED WITH THE ROCK REFUGE METAMORFOSE – PIRAI DO**
5 **SUL, PARANA, BRAZIL**
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10 **O CASO DE MINERAIS COMUNS E NOVOS EM SUPORTES DE ARTE**
11 **RUPESTRE ASSOCIADOS AO REFUGIO RUPESTRE METAMORFOSE–**
12 **PIRAI DO SUL, PARANA, BRASIL**
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18 **Abstract:** The existence of common and new minerals occurring in the canyon
19 surrounding the rock art refuge Metamorfose, located in Pirai do Sul, Paraná, Brazil.
20 Spectrometric and spectroscopic methods were used. The results were the discovery of a
21 nitrate-based mineral identified for the first time, in addition to the identification of
22 common white minerals. The minerals in the environment of the refuge are the result of
23 diversified interactions between a chemical and geological environment that produce
24 severe weathering whose change in paintings rock is not always related only to humidity.
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27

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29 **Keywords –** spectrometry, spectroscopy, rock art, weathering
30

31 **Resumo:** Aborda-se a existência de minerais comuns e novos ocorrendo no cânion que
32 circunda o refúgio de arte rupestre Metamorfose, localizado em Pirai do Sul, Paraná,
33 Brasil. Foram utilizados métodos espectrométricos e espectroscópicos. Os resultados
34 foram a descoberta de um mineral à base de nitrato e que está em estudo, além da
35 identificação de minerais brancos comuns. Os minerais no ambiente do refúgio são
36 resultado de interações diversificadas entre um ambiente químico e geológico que
37 produzem intemperismos severos cuja mudança nos grafismos nem sempre está
38 relacionada apenas à umidade.
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41 **Palavras-chave –** espectrometria, espectroscopia, arte rupestre, intemperismo
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Introduction

The IMA (International Mineralogical Association) Minerals List – updated in July 2023 presents 5,955 currently valid mineral species (IMA, 2023). Only about 10% of these species occur more abundantly in the Earth's crust, in such a way that the vast majority of them are rarities or species of extremely unusual origin (Branco & Chaves, 2006).

It should be noted that the limits of the definitions of a mineral are marked by its trajectory in the history of science. The mineral concept, as other concepts, has evolved over time.

For the purposes of understanding this work, it is important to say that in a third period beginning in the second decade of the 20th century, the internal structure of a mineral, three-dimensional and three-period was demonstrated through interaction with X-rays, in which they began to be valued, jointly, the chemical and structural properties, which is known as Crystallochemistry (Gomes, 2022).

Among many causes, minerals can be formed by anthropic action and this action is contained within a new geological period called Anthropocene. According (Artaxo, 2014), the Anthropocene began with the Industrial Revolution, in the second half of the 18th century, so that a new agent of change was added to the geological transformations. The rapid human population growth, associated with the excessive use of natural resources from 1950, had implications for the terrestrial ecosystem.

In cases of archaeological sites with support art, many different processes related to unbridled economic development can impact these fragile records, such as the installation of large developments, vandalism, fires and uncontrolled tourism, the extent of the damage is not yet known.

Exploitation of forests, mining, carbon dioxide emissions and fires are just a few examples of anthropogenic processes that can accelerate degradation or alteration, cause the destruction of rock art contexts, modifying the relationships of the elements that make up the rock supports and rock art.

The conditions for these minerals to form are also dictated by natural conditions and, in this sense, a brief overview of the geological and paleoenvironmental conditions of Ponta Grossa, Paraná, and adjacent regions since the end of the Pleistocene are presented as conditions for possible climate changes.

In Piraí do Sul, Paraná, some of these characteristics are conducive to the formation of minerals due to the characteristics of the Devonian Escarpment. They result from an

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3 interaction of factors of different nature and scale: the texture and mineralogy of the
4 sandstones, the current humid subtropical climate and the effect of macro and
5 microorganisms.
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8 Among the authigenous minerals are quartz (SiO_2), kaolinite ($\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$) and
9 its polymorph dickite ($\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$), illite, a variety of muscovite
10 ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$), albite ($\text{Na}(\text{AlSi}_3\text{O}_8)$), and anatase (TiO_2) (Ramos & Formoso,
11 1975; De Ros, 1998). Otherwise, there is diagenetic kaolinite, with crystals up to 50 μm
12 in length (Melo & Giannini, 2007).
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15 The studies by Melo & Giannini (2007) confirmed the importance of dissolution in
16 surface and underground erosion processes in sandstones. This diagenetic evolution leads
17 to two characteristics of the Furnas Formation sandstones that greatly influence its
18 erosion: relatively low average porosity (9%) and intense kaolinitic cementation (up to
19 more than 20%, with an average of 13%) (Melo et al., 2015).
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22 According (Zalán et al., 1990), the Furnas Formation was exposed for a period of 10
23 Ma before being covered by the transgressive marine deposits of the Ponta Grossa
24 Formation. This long period of exposure would allow an extensive circulation of meteoric
25 waters, which would explain the intense dissolution of feldspars and the kaolinitization
26 observed in the formation, as well as the eogenetic cementation of quartz (Carneiro,
27 2009).
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30 Kaolinite occurs in the Furnas Formation in two ways: as cement, precipitating in
31 secondary, intergranular pores and between slices resulting from muscovite alteration
32 exhibiting different stages of alteration depending on the kaolinitization process that
33 generates openings in its structures according to its basal cleavages, where kaolinite
34 cement precipitates and, in more advanced stages, reduction of grain birefringence and
35 formation of grayish masses (Carneiro, 2009).
36
37

38 As described by (Cruz, 1987), rare are the cases of observing kaolinite directly
39 replacing detrital feldspar grains, but the aluminum and silicon necessary for its
40 precipitation were probably derived from the dissolution of these grains (Carneiro, 2009).
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43 These are small-scale features indicative of mineral dissolution and reprecipitation
44 processes in the Furnas Formation sandstones. Considering that exfoliations with
45 telodiagenetic kaolinite affect rock art, this is an indication that dissolution and
46 reprecipitation are younger than the rock art (Melo et al., 2015).
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49 Paleoenvironmental data (Lorscheitter & Takeda, 1995) reconstitute the oldest to the
50 most recent periods, so that the data point to a low pollen rate before 11,000 BP, sparse
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3 and little modified vegetation. The analysis shows a semi-arid climate during the late
4 Pleistocene. For these authors, between 11 and 8,000 BP the data corroborate more varied
5 grassland vegetation, with improvements in environmental conditions, due to the increase
6 in temperature and humidity, the vegetation of the forests begins its slow and progressive
7 development.
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11 An important reconstruction for this area was carried out by (Moro et al., 2004) in
12 Lagoa Dourada. According to the author, this site is a round sinkhole with a diameter of
13 300 m located in the Vila Velha State Park, close to Ponta Grossa. The present study of
14 physical, chemical and biological data indicates that during the late Pleistocene, Lagoa
15 Dourada experienced a cold and dry period.
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20 The following period was characterized by several fluctuations in level, with short
21 and intense droughts and longer intermediate wet periods. The following conclusions
22 about the climatic history of Lagoa Dourada can be drawn from the diatom records as
23 follows: (1) distinct climatic changes have been reported during the last 11,000 years at
24 the studied site; (2) the Late Pleistocene climate was drier and cooler than the present; (3)
25 the beginning of the Holocene is marked by increased humidity; (4) around 8710 yr BP
26 became arid and cold; (5) the following period was characterized by several water level
27 oscillations, with short and intense dry events and longer intermediate wet periods; and
28 (6) in the last 100 years, the region has experienced a hotter and drier climate compared
29 to the previous one (Moro et al., 2004).
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37 These situations act directly on archaeological sites. However, few investigations so
38 far have focused on the characterization of rock supports devoid of rock art, which are
39 essential to determine how the producers of rock art related to them and the operating
40 environmental conditions (Chalmin et al., 2007; Chalmin et al., 2021; Hoerle et al., 2011).
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45 For the degradation of graphisms, a characteristic that is highly emphasized by almost
46 all researchers is moisture in its various forms, which intervenes in almost every type of
47 chemical change as a solvent or carrier (moving items such as salts or acids) or as a direct
48 agent (hydration), so that rain washes the rock surface and pore water acts physically
49 and/or mechanically, as in swelling or shrinking of minerals, hydraulic pressure, and
50 removal of surface grains and paints (Chalmin et al., 2007; Chalmin et al., 2021; Hoerle
51 et al., 2011).
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56 However, a study carried out by (MacLeod & Haydock, 2008) measured the
57 deterioration that occurs in the dry season and changed the perception that the rainy
58 season brings the most significant changes in the deterioration of graphics. These authors
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demonstrated that even in the dry season there are significant changes in the amount of moisture in the rock. As measuring devices were inserted, measurements of the sandstones were carried out and the huge temperature peaks associated with some of the rocky sites are indicators of rapid increases in the local air movement and with it the loss of heat due to the desorption of the water that is in the surface layers of the rock and in the graphics (MacLeod & Haydock, 2008; MacLeod & Haydock, 2002).

This type of study of the scarce microclimate of rocky supports is essential for making inferences about the type of mineral formed and the environmental conditions exerted on the rocky supports that shelter them in contact with rock art.

Theoretical Framework

This research fits into what has been called Archaeometry in recent years. Archaeometry is a field of archaeological science that uses methods, techniques and theory from the physical, chemical, biological and earth sciences to clarify archaeological problems. Archaeology and the exact, biological and earth sciences seek to empirically collect, analyze, synthesize and interpret data related to the archaeological record that contains inorganic and organic material. Investigations involve both experimental and non-experimental approaches and research of very small fraction materials (e.g. minerals and their constituents) as well as chemical and biological substances and residues from the molecular scale to macroscopically observable artifacts and ecofacts (Wells, 2014).

Study Area

The Metamorfose refuge is located on the plateau, an elevated area of plains in Campos Gerais, exactly at an altitude of 1031m (figure 1), characterized by a succession of canyons or extensive walls formed by erosion processes over millions of years, being sculpted mainly by the action of winds and waters and fitted and aligned in a straight line, being interpellated by field vegetation and large Atlantic forest trees, having at its base a sedimentary basin cut by a succession of rivers in radial typology that runs through the area. To the north, on the plateau, there are trays covering the crystalline foundations of an escarpment that is one of the most dissected areas in the region. The system of alluvial plains is associated with the embedded trays and valleys interspersed by the system of dissected domains and structural steps, with harmony between the emerged lands and the floodplains.

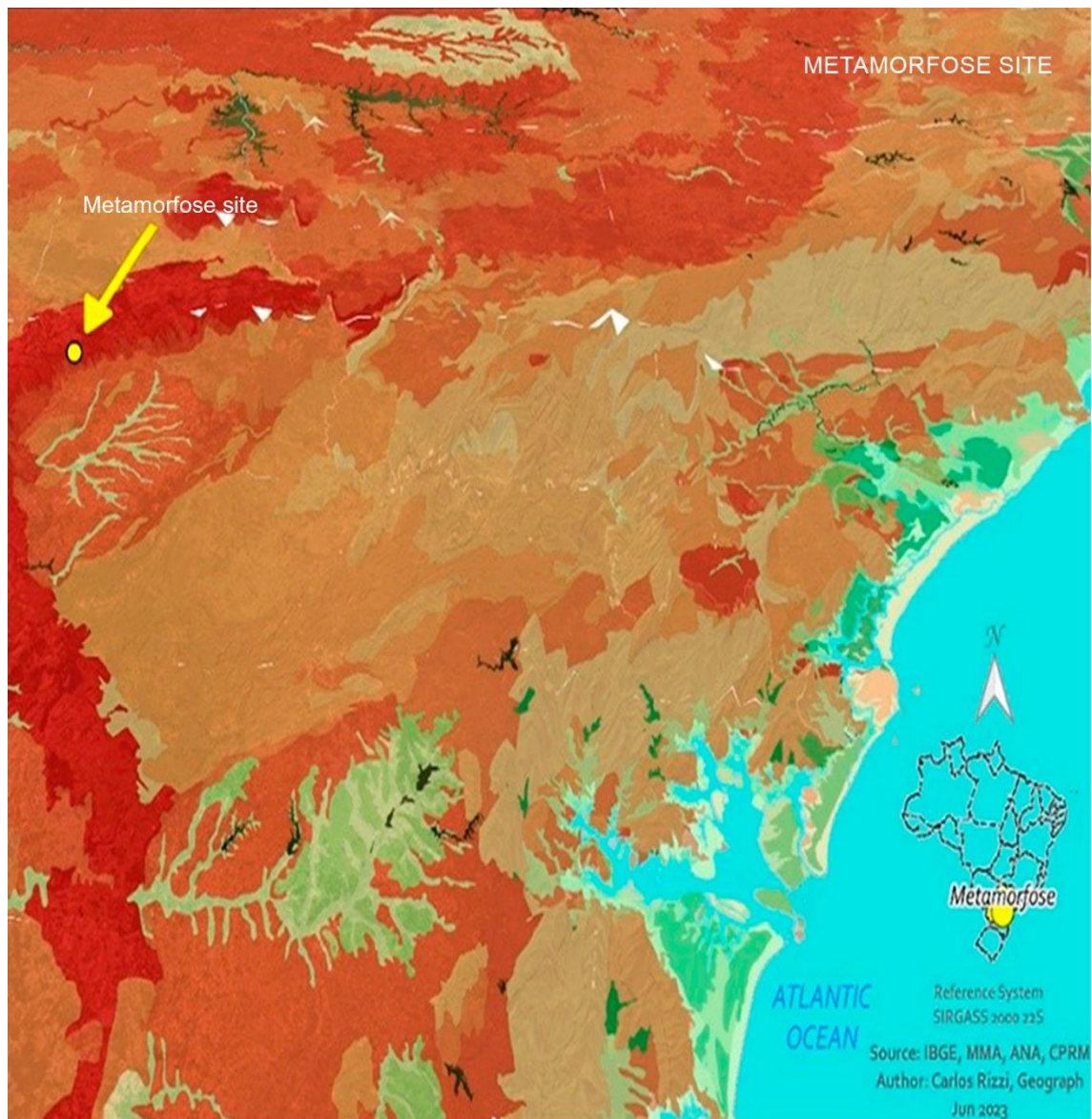


Figure 1 – Metamorfose Refuge, Pirai do Sul, Paraná. Image created by Carlos Rizzi (2023).

The Metamorfose archaeological refuge

This site was recently characterized in terms of rock art by the SpeleoPirai speleological project on a classificatory approach based on morphology and quantification of rock art through the image enhancement technique provided by the Dstretch application, ImageJ.

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3 From the taphonomic point of view, it was noted that most of the refuge is dry, but
4 wet fields located above the steep wall provide points with dripping and constant
5 humidity, especially after rains, so that the panels produced on the first level (lower floor)
6 are predominantly affected by this natural action (Pontes et al., 2022).
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10 The refugium microclimate is in line with what has been said about secondary
11 mineral precipitation in the research area. The characteristics of high dissolution and
12 reprecipitation of minerals in the sandstones of the Furnas Formation are present, but to
13 some extent these are preserved mainly in the rocky walls protected from the action of
14 rain, solar incidence, microorganisms and submillimeter reliefs that can be developed,
15 such as alveoli where rainwater runs off (Melo et al., 2015).
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20 Although rock shelters are, from a geomorphological point of view, a privileged
21 category in terms of physical-chemical preservation or modification in relation to the
22 deposition of secondary minerals, the nature of these minerals is combined with the
23 human action exerted on them, which interferes with the uptake, production, use and
24 conservation thereof.
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30 A new mineral in the Pirai do Sul area

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32 In two of the samples collected around the Metamorfose refuge, the presence of an
33 unusual mineral was verified, at first supposed to be scarbroite ($\text{Al}_5(\text{CO}_3)(\text{OH})_{13} \cdot 5\text{H}_2\text{O}$)
34 because its X-ray diffractogram bears some resemblance to that of this mineral. The
35 chemical data, however, suggest it is an Al nitrate and not an Al carbonate as expected if
36 it were scarbroite. Additional studies are being carried out and are needed to characterize
37 this new mineral.
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43 The suspicion that it could be a new mineral came after the exhaustive Raman
44 analyzes in which we tried to obtain scarbroite peaks without success, so that we began
45 to suspect that it was not scarbroite, but that it was very similar to nitrate peaks.
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48 The mineral is conditioned to a rocky support in the canyon that surrounds the
49 Metamorfose refuge and appears as a thick layer of white color and botryoidal texture. It
50 covers an entire support of rock support and is exposed to adverse weather conditions
51 such as wind and rain (figure 2).
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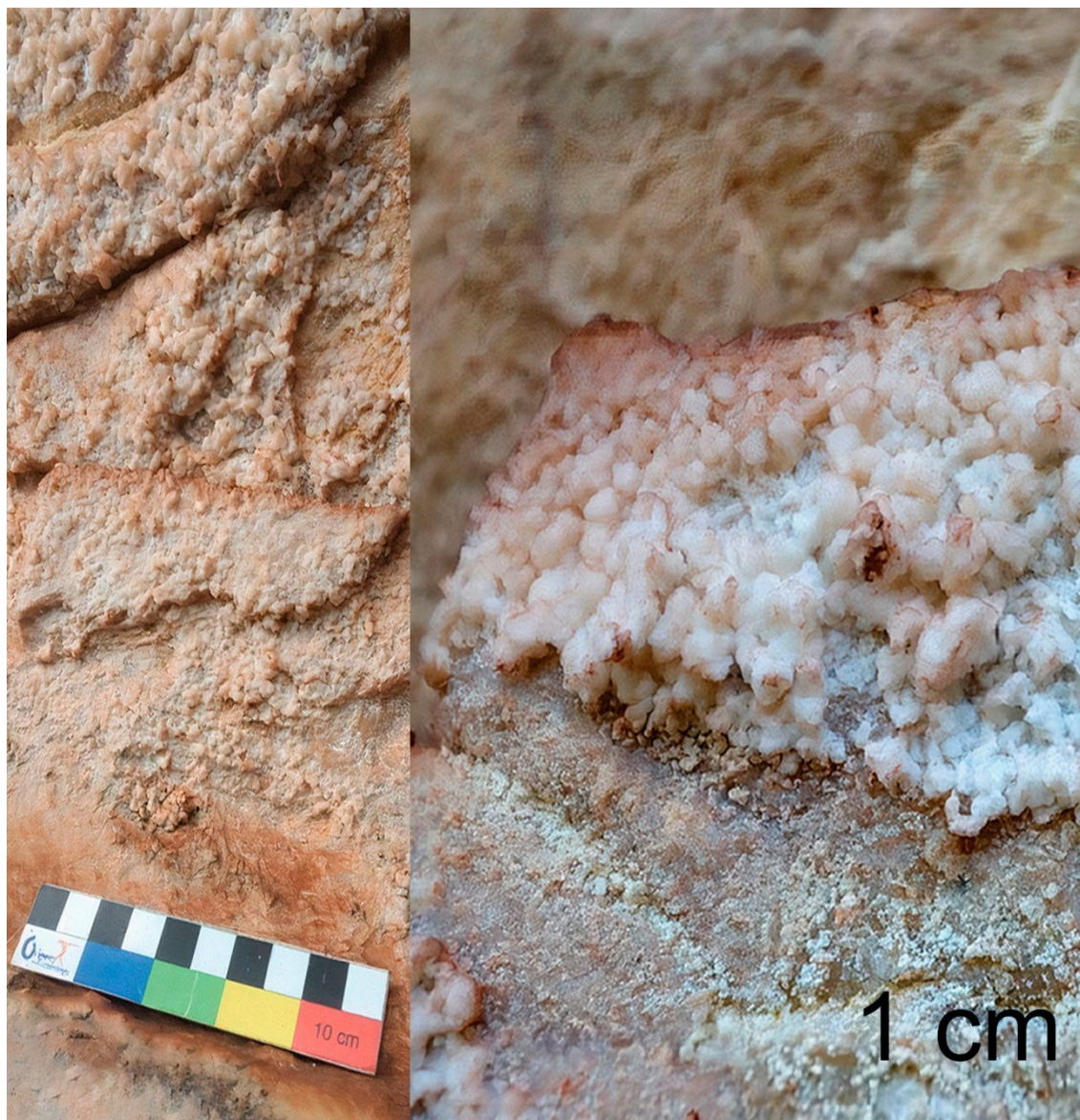


Figure 2 – New mineral detected in the Metamorfose refuge canyon, Piráí do Sul, Paraná. Image created by Tatiane de Souza (2022).

White Minerals in the Metamorphosis refuge

It is noted in the Metamorfose refuge that there is a deposition of white minerals on zoomorphic figures and on concentric circles filled with white pigmentation (figure 3).



Figure 3 – White mineral on zoomorphic painting rock and concentric circles in the Metamorfose refuge. Image created by Tatiane de Souza (2022).

Research has been carried out in studies published in the state of Paraná on white rock pigmentation (Laming-Emperaire, 1956; Arnt, 2002; Blasi et al., 2002; Cavalheiro, 2004; Parellada, 1993a, 1993b, 1994, 1997, 2001, 2003, 2009) without reaching any positive result.

Red, brown, black and rarely yellow colors were highlighted (Parellada, 2009), in more recent works carried out in the Ponta Grossa region, red, yellow, orange, purple and black tones were found (personal communication by Henrique Pontes).

A brief survey was carried out regarding white pigments found in Brazil, so that these are present in the central west region, in Cidade de Pedra, Rondonópolis (Vialou,

2006), in the northeast more broadly (Cavalcanti, 1986) and in special relevance for this research, in the south, in Santa Catarina (Comerlato, 2005).

No analysis of the rock paintings was carried out; however, important information is that these minerals are resistant to weathering within a range found in rock art circuits. Given the characterization of these minerals, comparisons were also made with work carried out in various parts of Australia (Stuart and Thomas, 2017; Chalmin et al., 2017; Clarke, 1976), which have a variety of white-toned minerals and influence interactions with different microclimates.

Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), huntite ($\text{CaMg}_3(\text{CO}_3)_4$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and/or calcite (CaCO_3), for example, are minerals present in Australian white pigments. The oxalate minerals in the white ink are believed to be the result of microbiological alteration of huntite and calcite.

Other analyzes of pigments from rock art sites in Western Australia, in the Napier Ranges in the Kimberley region, have focused on identifying the white pigments that dominate this area. The white pigments were found to consist mainly of huntite, gypsum and the oxalates whewellite ($\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$) and weddellite ($\text{Ca}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$). The conversion, or not, of huntite into oxalates makes it possible to identify variations in the mineral composition of pigment specimens.

Materials and methods

6.1 Sampling:

Several locations around the Metamorfose refuge were visited to identify the occurrence of secondary mineral precipitation in association with rock art. Considering the Metamorfose refuge as the reference center of rock art, comparative visual searches were carried out to identify such precipitations in rocky outcrops located in the surroundings in order not to carry out interventions in it. Gathering sites associated with the refuge were chosen and thirteen samples of minor minerals were collected.

Minor quantities of minerals were scraped from the rock face with a small spatula and stored directly in acrylic pots. 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. In the laboratory, samples were prepared by combining individual grains mounted on aluminum stubs with carbon tape, which were then covered with a thin film of carbon.

6.2 Techniques:

6.2.1 XRD - X-ray diffraction

As different minerals have different lattice spacings or crystalline planes, each will produce a unique diffraction pattern, giving each mineral its own unique impression. However, identifying minerals in support with rock art is difficult because many minerals are found in a given specimen. In addition, the technique presents a limitation in relation to this type of sample because it is destructive, through the powder method, and it is very important to acquire the sample from places where there is no insertion of rock art.

6.2.2 SEM-EDS – Energy dispersive X-ray spectroscopy (EDS) coupled to the scanning electron microscope (SEM)

In the analysis, the EDS-SEM (Energy-dispersive X-ray spectroscopy) provides valuable information about the chemical composition of the the minerals, which is fundamental in the mineralogical determination of the samples. Subsequently, through the EDS, the elemental analysis of the surface of the sample was carried out. In the scientific literature, we observed few works applied in archeology with the use of EDS coupled to the SEM (Scanning Electron Microscope), being practically null the characterization of the minerals in the rocky supports with rupestrian graphics.

6.2.3 RAMAN -

Raman spectroscopy is a technique in which scattered light is used to measure the vibrational energy modes of a sample. Raman spectroscopy can provide chemical and structural information, as well as the identification of substances through their fingerprint. Raman analysis uses a monochromatic light source that scatters when hitting an object, generating light of equal or different energy than the incident light (Faria et al., 2002; Edwards & Vandanabeele, 2016; Faria, 2011).

6.3 Devices used:

The diffractometer used was a Bruker brand, model D8 Advance da Vinci, CuK α radiation with LYNXEYE detector and TWIN-TWIN optics, which allows operation with fixed optics. The SUITE DiffracEVA program and the PDF-2 database (ICDD) version 2022 from the Institute of Geosciences at USP were used to identify the phases.

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3 For EDS/SEM - The Electron Microscope was a model LEO 440, brand LEO
4 Electron Microscopy Ltd. England, and the Solid State Si(Li) Energy Dispersive X-ray
5 Spectrometer with Inca 300 software was from Oxford Instruments Ltd, England. The
6 working condition was a voltage of 20 kV and a working distance of 25 mm.
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10 For RAMAN analysis, a Renishaw inVia Reflex apparatus was used, coupled to a
11 Leica DM2500 M microscope, containing lasers with excitation at 785 nm (diode laser,
12 Renishaw) - 500 mW - and at 532 nm (diode laser, Renishaw) - 500mW. The equipment
13 also contains two diffraction gratings, one of 1200 lines (when using the 785 nm laser)
14 and one diffraction grating of 2400 lines (when using 532 nm laser), in addition to a
15 thermoelectrically cooled CCD detector (1040x256 pixels). Wire 4.4 software was used
16 during data collection. Baseline subtraction was performed using Fityk 1.3.1 software.
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23 Results

24 At first, was focused closely on the “scarbroite”. In analyses, samples 4 and 11
25 were the ones that contained this Al-rich composition. The database card 12-0627 PDF2,
26 (ICDD) (International Centre for Diffraction Data) cited by (Duffin & Goodyear, 1960;
27 Brindley & Comer, 1960) showed some similarity. The peaks stand out in intensity and
28 broadening in sample 11, more defined peaks and presence of gibbsite were observed in
29 sample 4 (figure 4).
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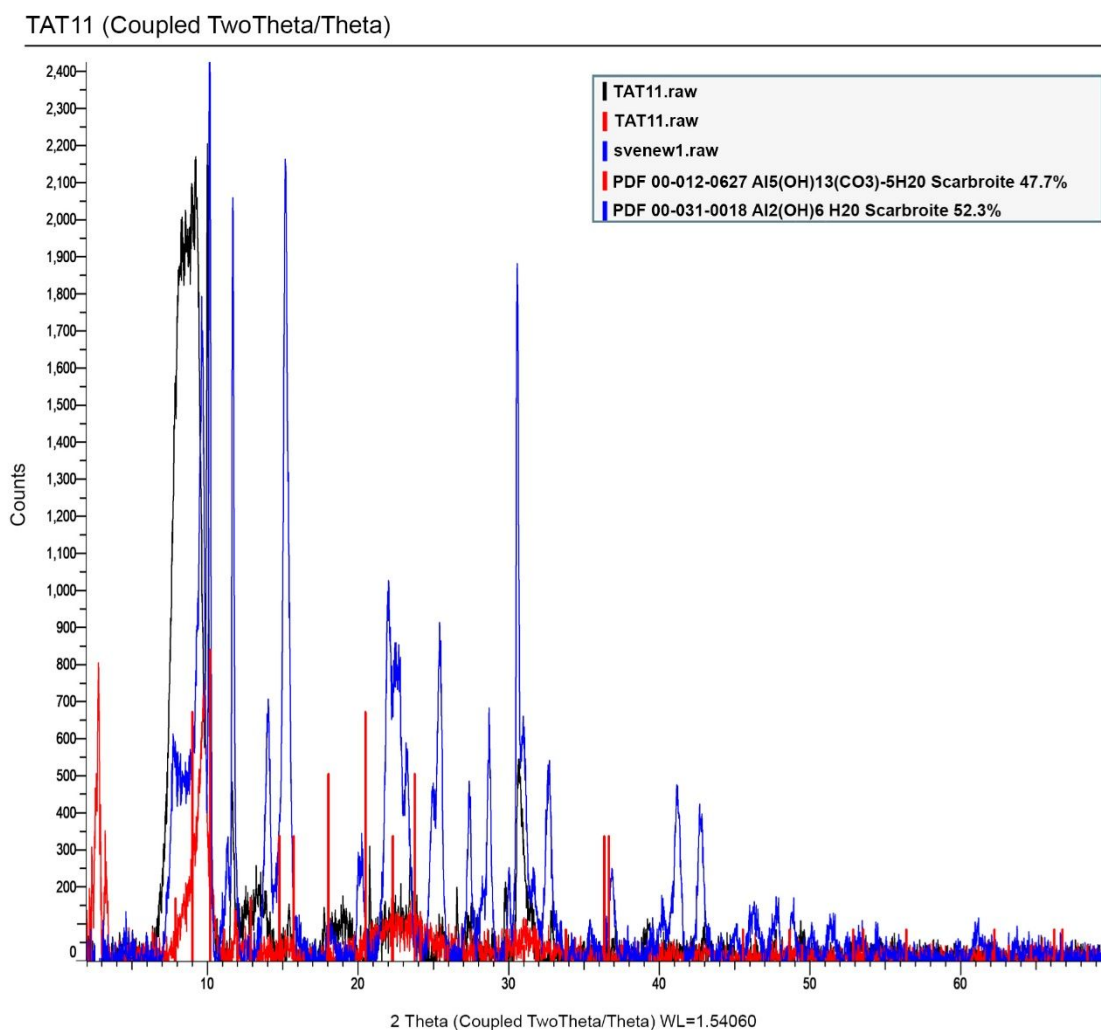


Figure 4 – Identification of a new mineral in XRD in sample 11. Image created by Daniel Atencio (2023).

Samples of common minerals were also compared with data from the cards (ICDD). In our samples, quartz was found (SiO_2), gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, kaolinite $(\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4)$, muscovite $(\text{KA}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2)$ and alunite $(\text{KA}_3(\text{SO}_4)_2(\text{OH})_6)$. The differences found were completely acceptable when considering that they refer to a growth of quartz peaks and a decrease in the intensity of other minerals, making them smaller and less defined. With the exception of group 3 where there is evenness between mineral peaks, all identified minerals are very close to the background of the graph.

Four groups were put together based on the similarity of common minerals found. What was called group 1 is composed of quartz, gypsum and kaolinite, with quartz

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3 intensity and discrete peaks of kaolinite and gypsum. What was considered group 2 is
4 composed of quartz, gypsum, kaolinite and muscovite with intense quartz peaks and
5 discrete kaolinite and gypsum and muscovite peaks. What was called group 3 is composed
6 of gypsum, alunite, quartz and kaolinite. They are peaks almost identical in intensity.
7
8 Finally, group 4 is composed of quartz and minerals that are atypical in the samples, such
9 as kingite ($\text{Al}_3(\text{PO}_4)_2\text{F}_2(\text{OH})\cdot 7\text{H}_2\text{O}$), unidentified aluminum phosphates and tinsleyite
10 ($\text{KAl}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$), with very low peaks.

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15 The energy dispersive X-ray spectroscopy (EDS) coupled to the scanning electron
16 microscope (SEM) was performed due to the supposed presence of scarbroite and we
17 repeated the analysis a few times to verify that it was a mineral whose main composition
18 was the aluminum.
19

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22 The points of convergence are the existence of a mineral whose main composition
23 is aluminum in all the listed samples, silicon, sulfur and magnesium and perhaps calcium
24 and lead.
25

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27 Two laser excitation lines were used: 532 and 785 nm, whose selection criterion
28 consisted of minimizing undesirable fluorescence effects that could impair the
29 identification of characteristic Raman bands. All Raman spectra were compared with the
30 RRUFF (project website containing an integrated database of Raman spectra, X-ray
31 diffraction and chemistry data for minerals) (<http://rruff.info/>) and with the literature, with
32 the aim of identifying the composition of the unsuccessfully studied mineral.
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37 The peaks we find are always around 1050. Values above 2000 are bending and
38 stretching associated with water, either in the form of HOH or OH (figure 5). It is
39 noteworthy that the peak of 1050 has a strong correspondence with nitrate. Just as oxalate
40 has a biogenic origin, nitrate may also have a similar origin, and may be produced by
41 nitrifying organisms, reducing other species such as Fe^{3+} . Furthermore, this is not the
42 only possible source of nitrate, a metagenomic analysis of a quartzite cave in Minas
43 Gerais showed the presence of genes from nitrifying organisms (Bendia et al., 2021).
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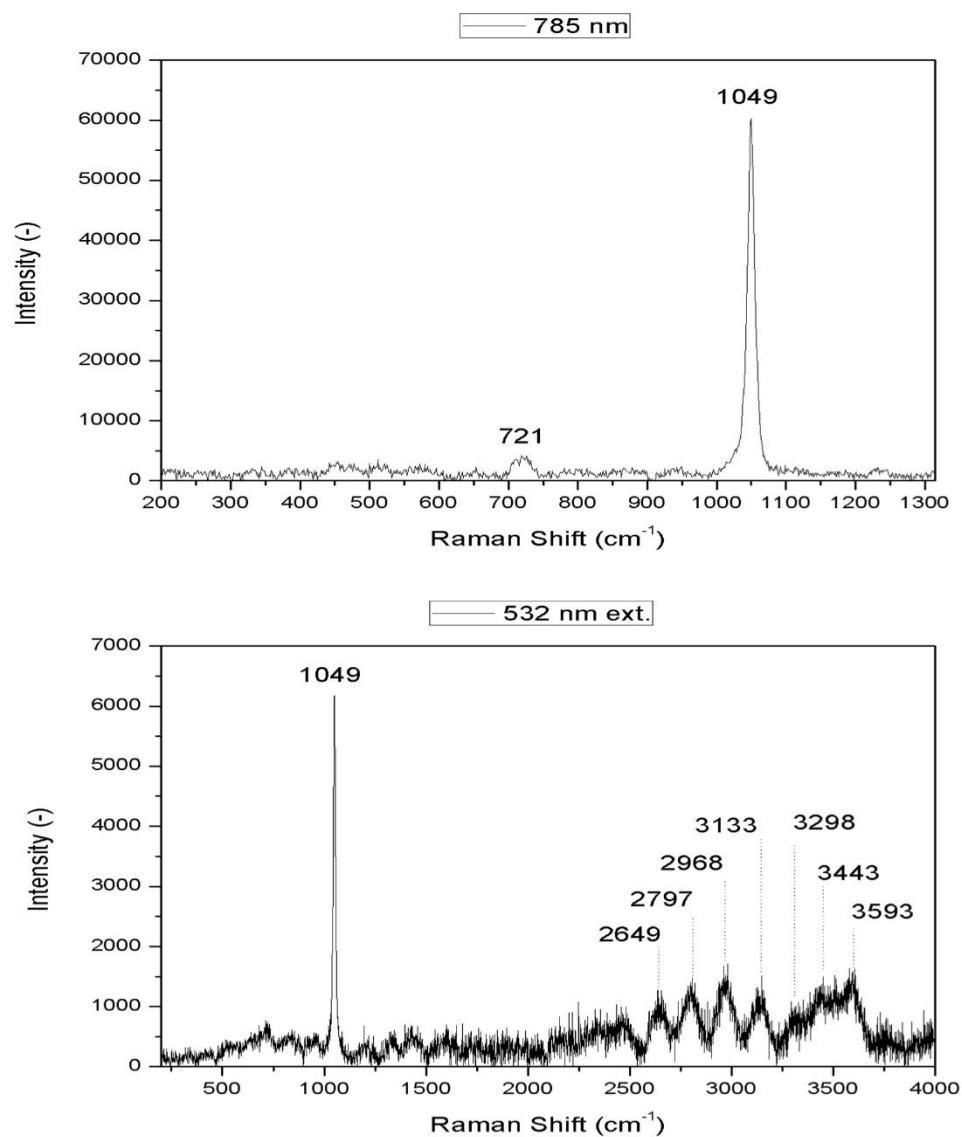


Figure 5 – Detection of the Raman spectrum of the new mineral. Image created by Gabriel Gonçalves Silva (2023).

Only in one study comparative measures were found for scarbroite and the peaks were completely different from those found in our Raman analysis. A measured sample of scarbroite yielded a significant spectrum rich in peaks among which we highlight carbonate (Raman shift at 1107) and others attributable to hydroxyl (Raman shifts at 3593, 3614 and 3668) (Boscardin et al., 2009), data that did not are corroborated by the peaks found in the analyzed samples (figure 5).

Discussion

The new mineral identified in the canyon that surrounds the Metamorfose refuge is being investigated, when we detected that it was not scarbroite, other analyzes are in progress for its chemical and structural identification.

Otherwise, common minerals participate in the process of modifying rocky supports with rock art, as shown in Figure 3, but diagenetic kaolinite is perhaps the most important alteration due to dissolution in sandstone surface erosion processes. A long period of exposure to water would explain the intense dissolution of feldspars and the kaolinitization of rocky supports, but this would not be the only explanation.

It is interesting to remember that weathering occurs with different pressure and temperature in hydration and hydrolysis reactions. An understanding data for white minerals is that the stability of gypsum, quartz, muscovite, presents slower weathering rates, when hydration caused by meteoric water. Gypsum loses 3/4 of its water of crystallization during the calcination process, converting to calcium sulfate hemihydrate, the mineral bassanite, ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) which, when mixed with water, can be molded and worked before hardening and acquiring the mechanical consistency of the rehydrated stable form (Baltar et al., 2008).

Meanwhile, muscovite is one of the most important and common rock-forming silicates (characteristic of acidic rocks), being also very resistant to weathering (which allows its presence in almost any type of rock) and alunite is product of alteration of aluminous rocks by strongly acidic and oxidizing solutions. Alunite formed by the weathering of sulfide-rich deposits hosted by Al-rich rocks, or by the circulation of meteoric water through aluminous rocks or pyrite-rich shales, are also common.

According to the paleoenvironmental analyzes carried out in the area, it is possible that mineral relationships with rock supports developed after the Pleistocene when rainfall increased and these minerals resisted the action of wet periods. In fact, taking advantage of this characteristic to form and deposit in rocky refuges in the area. However, as we have already said, it is not exactly dry conditions that prevent the degradation or deposition of minerals, but the surface temperature of the sandstone, as demonstrated in experimental studies. It would not be an exaggeration to consider that these minerals could have appeared in a brief period, as for example in the last 100 years when the region experienced a hotter and drier climate compared to the previous one, being accelerated by the weather conditions that became more acute.

Conclusion

It is concluded from this study that the region is rich in minerals with different characteristics depending on environmental conditions. From new to well-known minerals, peculiarities of the region favor an interaction between products derived from the formation of secondary minerals that sometimes jeopardized the existence and continuity of rock art, sometimes could participate in the production chain, being of vital importance to clarify directly what is the mineralogy of the pigments present in rock art to determine their association with common minerals found in rocky supports.

Given these considerations, a study that encompasses the identification of minerals existing in the graphics and rock supports can form a broader production chain and place rock art in context and not just focused on distinctions or quantification of signs.

It is interesting to note that the minerals present are considered stable in the face of severe weather conditions, with the exception of new mineral and alunite, so that what we found underwent a process of important environmental modification and that this modification affected the way in which the human groups that frequented the Metamorfose refuge chose specific areas to shelter. the signs still seen today.

High rainfall and humidity during the Holocene period and conditions for the formation of secondary minerals possibly went together and this may indicate that the minerals that exist today are the most resistant to this weathering situation and that they could be used as raw material in the production of mixed graphics material to other minerals to compose different shades.

It is also possible that in drier periods, human groups inserted a large part of the production of graphics in unprotected areas, which may suggest that at that time the climatic conditions were stable enough for them to be applied to the rocky support of the refuge without the concern that they would be lost with the humidity.

Otherwise, it is interesting to investigate the existence of colors as white as those existing in the concentric circle of the Metamorfose refuge, which seems to have been filled with pigment and is not reported to be present in the research area or in the state of Paraná.

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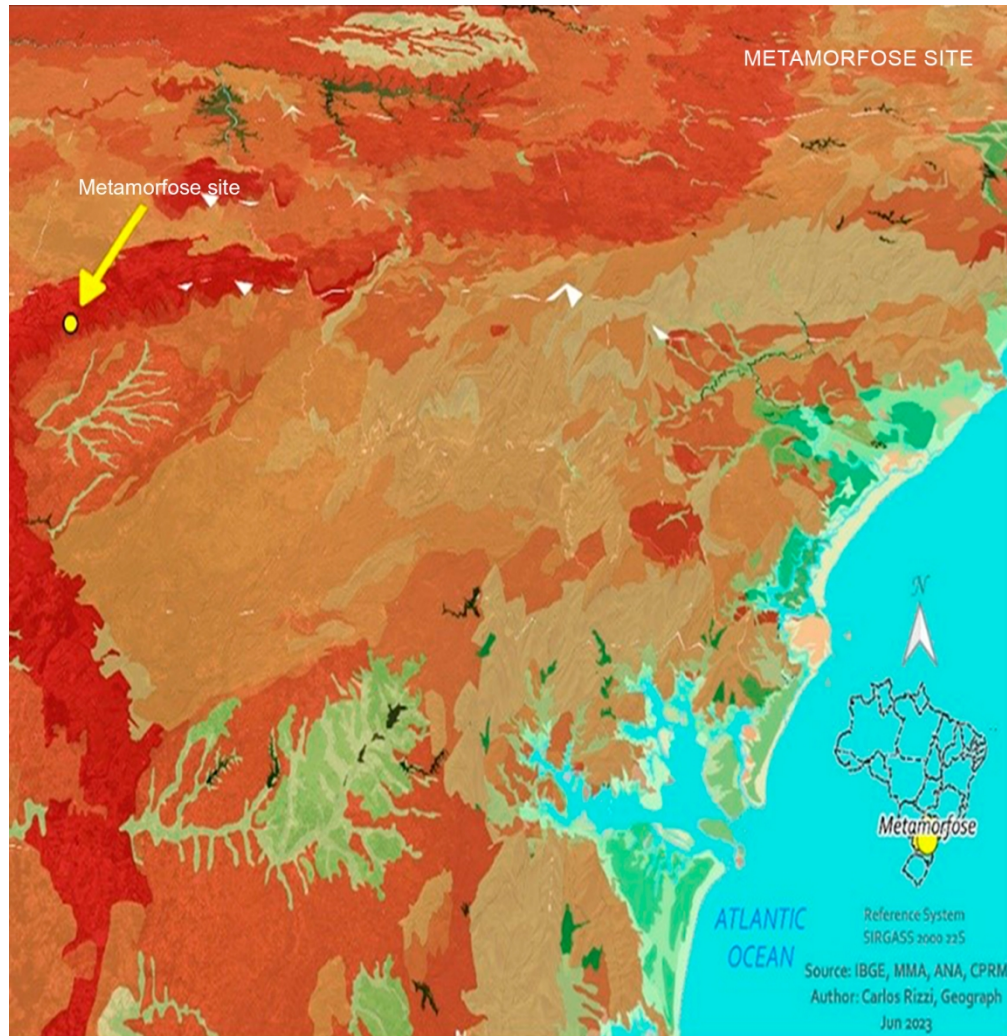


Figure 1 – Metamorfose Refuge, Piraí do Sul, Paraná

165x170mm (300 x 300 DPI)

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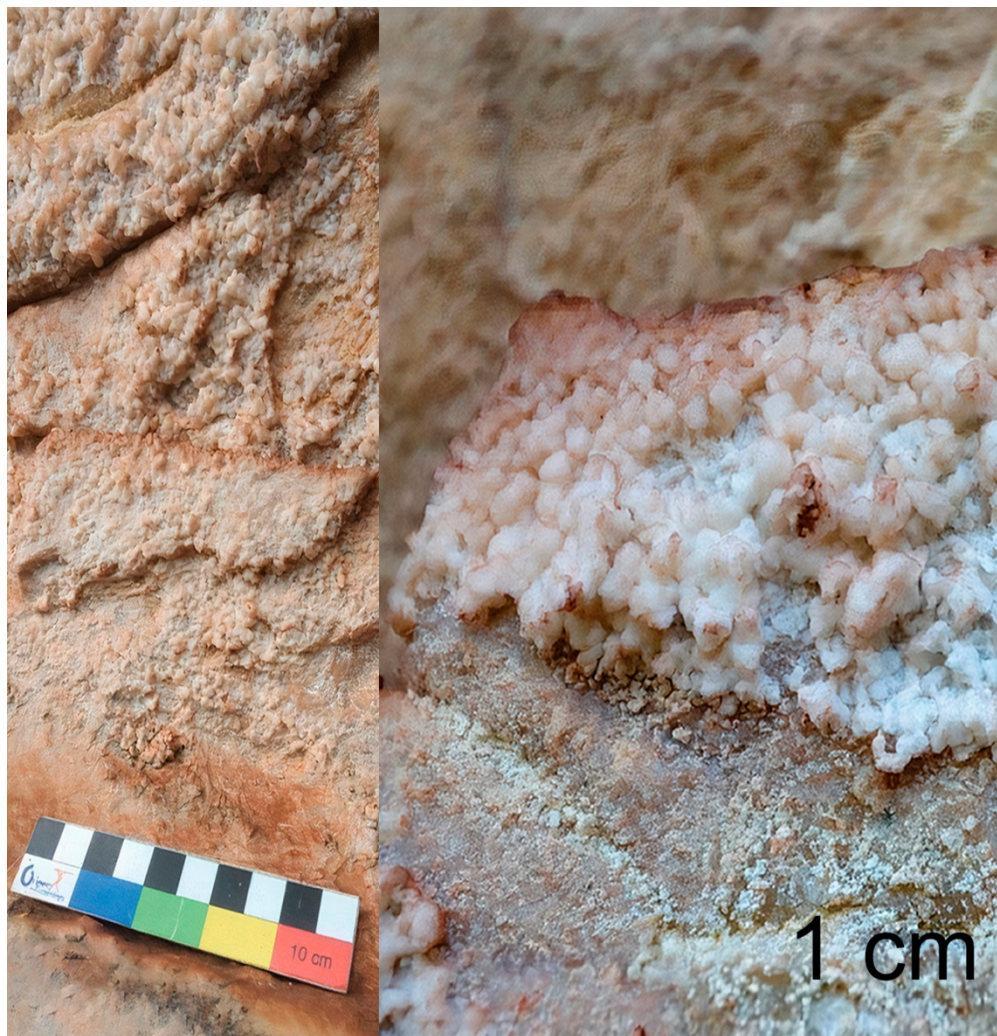


Figure 2 – New mineral detected in the Metamorfose refuge canyon, Piraí do Sul, Paraná

165x170mm (300 x 300 DPI)

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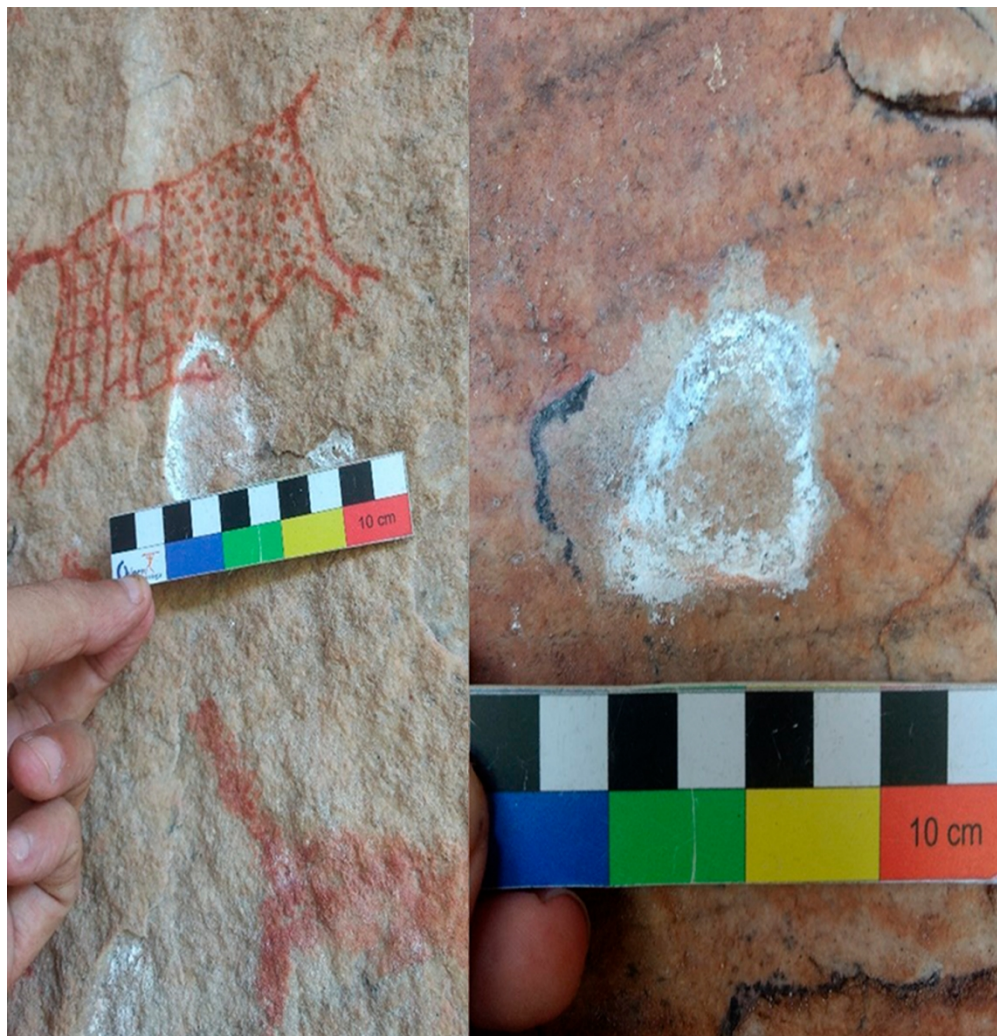


Figure 3 – White mineral on zoomorphic rock painting and on concentric circles in the Metamorfose refuge

165x170mm (300 x 300 DPI)

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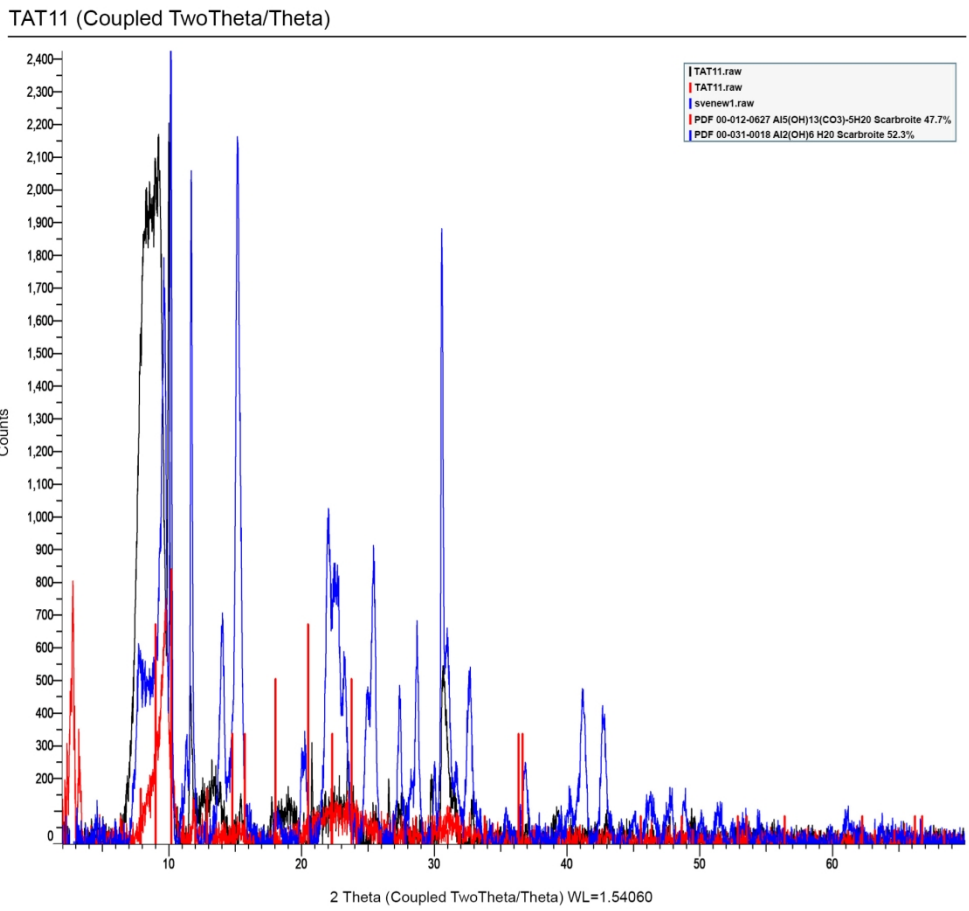


Figure 4 – Identification of a new mineral in XRD in sample 11
165x170mm (300 x 300 DPI)

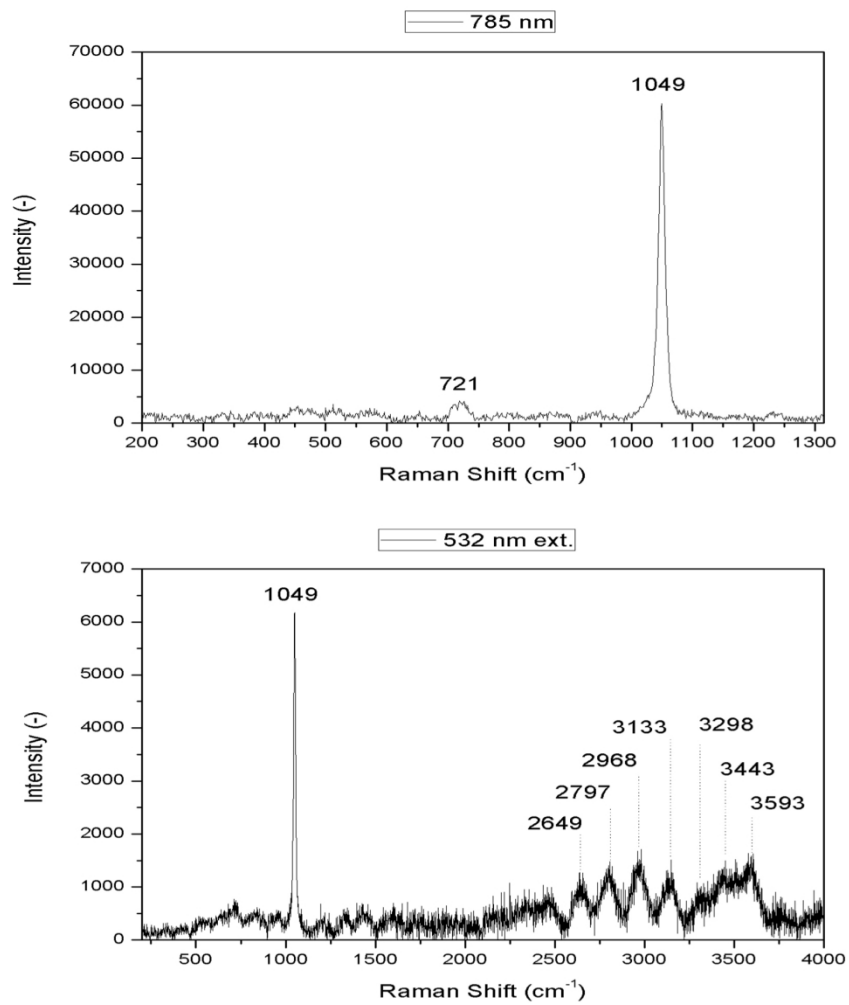


Figure 5 – Detection of the Raman spectrum of the new mineral

165x170mm (300 x 300 DPI)