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Case Report

Pyrite Decay of Large Fossils: The Case Study of the Hall of Palms in Padova, Italy

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Abstract: Pyrite decay is arguably the major problem in geological and palaeontological conservation, as it can cause total destruction in valuable specimens. Various methods have been devised since the 19th century to treat and prevent it with different degrees of success. Nevertheless, the conservation of large fossils at risk of pyrite decay remains an unsolved issue, because a feasible method for maintaining them in a controlled microclimate that is suitable for specimens on public display has remained elusive. This paper describes the study carried out to investigate the alterations that developed in a large fossil palm of the collection of the Museum of Geology and Palaeontology in Padova (Italy), already treated for pyrite decay several years before. Results of X-ray powder diffraction and Raman spectroscopy performed on samples collected from that fossil palm confirmed that the alterations were due to pyrite decay. The microclimate indoors (inside showcases and in the Hall itself) and outdoors was monitored for one year to investigate its possible relation with the damage observed. The measured thermo-hygrometric conditions exceeded the recommended thresholds for the prevention of pyrite oxidation and indicated the fossils were at high risk of damage from that process. This study demonstrates that treatment alone is not sufficient for the conservation of fossils at risk of pyrite decay and that it can be ineffective without a proper management of the microclimatic conditions under which the fossils are preserved.

Keywords: pyrite decay; fossil palm; paleontological collection; microclimate; preventive conservation

1. Introduction

1.1. Pyrite and Pyrite Decay

Iron disulphide (FeS_2) is widespread in sedimentary rocks; it commonly occurs as isometric pyrite or, less frequently, as its dimorphic, orthorhombic marcasite [1,2]. It can be microcrystalline and finely disseminated, or framboidal, or it can form a variety of larger crystals, often inside pores and cavities, or massive nodules. Pyrite can often replace or coat fossils [1–5]. The formation of sedimentary pyrite depends on several factors, such as the burial rate and the availability of organic material, sulphate and iron. The deposition is usually mediated by microbial activity and may start very early during the sedimentation [1,4,6–8], at the point that pyrite is recorded forming even in living animals, namely around the shells of mollusk [9] and 'pyritization' has been attempted in laboratory experiments [8].

The presence of pyrite is documented also in archeological items, e.g., in stone [3,10] and wood artifacts. Well known examples are the ships sank in the 15th–17th centuries, such as the celebrated

Swedish Vasa, the Dutch Batavia and the Henry VIII's vessel Mary Rose [11]. Garcia-Guinea et al. [12] reported the presence of framboidal pyrite in antique books.

Both pyrite and marcasite can be affected by oxidation, a phenomenon known as 'pyrite decay', 'pyrite disease' or 'pyrite rot' [2,3,13]. Although not all fossils containing pyrite undergo oxidation, pyrite decay is one of the most serious problems faced in geological and palaeontological conservation, and the chemistry of pyrite and marcasite oxidation has been investigated in both mining and museum collections for decades [3,14]. Oxidation products of pyrite consist of sulphuric acid, various hydrated iron sulphates ($Fe^{2+}(SO_4){\cdot}nH_2O$: szomolnokite, rozenite and so on) and also calcium sulphates ($Ca(SO_4){\cdot}2H_2O$ gypsum), depending on the composition of the fossil and of the embedding matrix [2,3,13,15]. Usually they appear as yellowish or grey/white powder, commonly smell of sulphur and cover the surface of the specimen. The transformation from sulphide to sulphate induces a significant volume increase, which may cause the specimen to break down and crack. The damage is irreversible, and pyritised fossils often break down very quickly, even to the point of complete destruction. The sulphuric acid produced by the oxidation and hydration may also degrade labels, storage cardboard boxes and even wooden furniture [2,14,16,17].

Due to the irreversibility of pyrite decay and the damage it produces on specimens, preventive conservation is extremely important to properly manage collections of pyritic materials.

A number of factors are known to contribute to the activation and rate of pyrite decay: temperature, relative humidity (i.e., water availability), oxygen concentration, pH, light, exposed surface (grain size), presence of bacteria and trace elements. However, some factors are known to require conditions that are unlikely in a museum setting and so they are probably inapplicable to preventive conservation of museum collections, such as the role of bacteria like *Thiobacillus* in the initiation and acceleration of pyrite decay, which usually occurs above 95% humidity [2,3,17]. The most important factors of decay are considered to be high relative humidity (which is linked strongly to temperature) and oxidising conditions. In particular, controlling relative humidity (RH) seems to be fundamental in museum environments [1–3,14,16]. Howie [3] stated that 60% RH represents the critical level above which damage starts for most specimens, but some pyritised fossils might start decaying if exposed even for only a few days over 60% RH [2]. According to Howie [3] and Fellowes and Hagan [14], a maximum 30% RH is considered safe. On the other hand, Newman [15] and Larkin [2] suggested that 40%–45% RH is a more realistic threshold, because it could be more easily reached and kept stable. In addition, this value is more compatible with the requirements of other materials stored together with the pyritic specimens. Low levels of RH can be achieved using dehumidification systems, maintaining the building and using special packaging. The latter consists of microclimatic enclosures [18,19] created by sealing the specimens in boxes or purpose-built bags together with silica gel, or Art-Sorb®, to reduce the humidity level. Further inhibition of the decay reaction can be obtained by dropping the oxygen concentration in the environment around the specimens by including oxygen scavengers in the enclosure [2,18,19]. Usually, such enclosures are used for small items kept in storage rooms and are not feasible for specimens that are large and/or on display. In the past, various protective coatings have been applied to pyritised specimens as a barrier to humidity and oxygen, however success was limited [1,2].

In the last decades, conservators have developed a numbers of treatments to deal with pyrite decay in fossils, especially to remove oxidation products, neutralise acidic substances and stabilise iron compounds. Currently, the most effective conservation treatments are the exposure to ammonia gas [5,20] and the use of ethanolamine thioglicollate [1,21]. The first method consists of creating a 'gas chamber' in which the specimens to treat are exposed to vapours from a solution (10% volume to weight) of ammonium hydroxide in polyethylene glycol (PEG); the ammonium hydroxide evaporates, saturating the chamber and reacting with the iron compounds, turning them from yellow (or grey) to rust coloured. Finally, the specimens are cleaned with alcohol and left to dry. The use of a non-aqueous solvent is fundamental in limiting the presence of water, which may lead to further decay [20]. For a detailed description of this technique see also Andrew [5] and Larkin [2]. The use of ethanolamine thioglicollate was experimented with for the first time by Cornish and Doyle [21] and subsequently improved by Cornish [22] and Cornish et al. [23]. Its aim is to neutralise and remove the soluble and insoluble iron compounds from specimens. This is achieved by placing them in a solution of 2%–5% ethanolamine thioglicollate in ethanol or isopropanol. Alternatively, it is possible to apply an ethanolamine thioglicollate poultice thickened with sepiolite to the oxidised areas [22]. For further details of these techniques see also Shinya and Bergwall [13] and Larkin [2].

Both the ammonia gas and ethanolamine thioglicollate methods are effective and each is best suited to different circumstances [2,5]. Ammonia gas is usually more appropriate for small and fragile specimens, although Andrew [5] reported the use of this method for in-situ treatment of wall-mounted specimens of large Jurassic reptiles. More frequently, large specimens, especially if on display, are treated with ethanolamine thioglicollate poultice.

Fellowes and Hagan [14] compared the state of preservation of specimens in the National History Museum in London treated against pyrite oxidation with one of the above described methods, or a combination of both. After treatment, the specimens were stored for 15 years between 40% and 50% RH. According to these authors the ammonia gas seems to be the most effective treatment.

Regardless the performance of the treatment used, pyrite decay is not arrested in the treated fossils if they are maintained under the same conditions that caused the damage: further oxidation will be very likely to occur and could proceed very quickly, so in the end, preventive conservation remains the only way to control and avoid the process of degradation [2,13].

Within the framework of an environmental risk assessment and a preventive conservation strategy, the analysis of the microclimate [24,25] is fundamental to identify the main damage processes [26,27] and to assess the suitability of an environment respect to the conservation requirements [27,28].

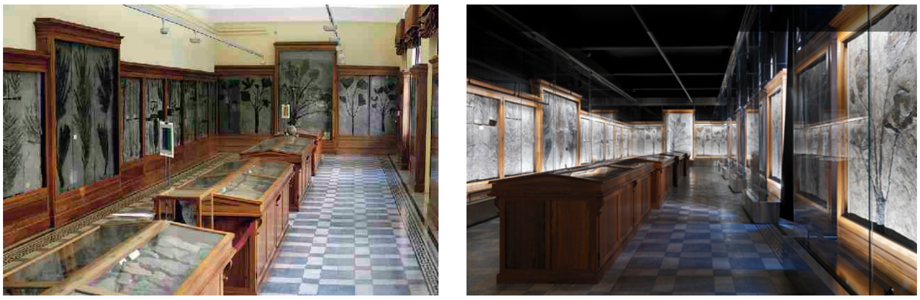
1.2. The Hall of Palms

The Museum of Geology and Palaeontology of Padova University houses an important historical palaeobotanical collection consisting of about 5000 specimens (leaves, part of trunks, seeds, and so forth) acquired by the museum at different times since its establishment. The most spectacular fossils are the remains of coconut-like fruits, leaves and complete palm trees: about 160 of these specimens are wall-mounted for display in the hall. Among them is the impressive *Latanites maximiliani*, over three metres tall. This unique exhibition, put up in the 1930s, gave the name to the room: 'Hall of Palms' in English or 'Sala delle Palme' in Italian (Figure 1).

Some of these fossil palms were collected from the lignite and tuffaceous beds, outcropping at famous sites such as Purga di Bolca, Praticini and Vegroni near Bolca (Verona, Italy) and date back to middle Eocene (about 40 Ma) [29]. None of these outcrops is currently accessible. Other important early Oligocene (about 30 Ma) specimens came from the Chiavon-Salcedo hills near Marostica (Vicenza, Italy) [30]. These fossils are preserved as thin carbon films in different rock matrices, namely marls, marly limestones and volcanic sandstones interbedded with basalts flows. In some cases, trunks are also preserved, although very deformed.

Most of the palms were collected in the 19th century, and they were prepared according to the practices and the style of exhibition typical of the period. A number of fossil fragments were generally assembled together to build a regular-shaped slab, and gaps were filled with plaster or other fillers of various compositions. Occasionally the missing parts of the fossil were reconstructed with plaster. All of the integrated materials were painted to disguise them; in some cases, the embedding matrix was also painted to achieve a uniform background colour and the fossil was coated with an unidentified consolidant [31].

In the 2000s some specimens housed in showcases showed the typical damage related to pyrite decay, i.e., spots of sulphur-scented grey-yellowish powder. In addition, an obvious yellowish nodule appeared on the trunk of one of the largest and most complete palm, a specimen of *Latanites* sp. [31]. Other fossils had developed cracks and fractures during the years, probably related to the different thermo-hygrometric behavior of the fossils, the embedding matrix and the various materials used for restoration. The conservation issues in the Hall of Palms were similar to those described by Cornish et al. [23] for the Jurassic marine reptiles exhibited in the Gallery 30 in the Natural History Museum London.



(**a**) (**b**)

Figure 1. Internal view of the Hall of Palms (**a**) before and (**b**) after renovation.

In 2007, three of the fossil palm trees were restored (including *Latanites* sp.), with pyrite decay treated using ethanolamine thioglicollate. On that occasion, X-Ray powder diffraction (XRPD) analysis performed on the alterations revealed the presence of iron sulphate and calcium sulphate in all the three palms, and of two ammonium sulphates (in two of the three palms, *Latanites* sp. excluded). The presence of ammonium sulphates indicated that in the past these two palms had been treated with ammonia to neutralise the pyrite decay [31]. At the same time, a major refurbishment of the room was carried out and completed in 2009. New glass and steel cabinets surrounded and enclosed the old wooden cases, after the removal of their original panes of glass. Some of the new cabinets form a very large structure, covering almost completely three walls of the room (Figure 1).

Until February 2009, there was neither heating nor air-conditioning in the Hall of Palms, and the lighting was produced by a few chandeliers with traditional bulb lamps. The refurbishment also included the installation of a new LED lighting system, as well as a heating and air conditioning system. This last system should have allowed the separate management of the thermo-hygrometric conditions in the room and inside the showcases, keeping these latter in compliance to the recommended values of temperature (T) and relative humidity (RH) for an optimal preservation of the fossils, reported in Table 1 [16,32,33].

Table 1. Thermo-hygrometric recommended values for the conservation of fossils.

Season	Hall T (°C)	Hall RH (%)	Showcases T (°C)	Showcases RH (%)
Summer	24–25	50–55	20–22	<40
Winter	18–20	50–55	18–20	<40

Short-term hygrometric fluctuations should have been avoided as they are responsible for dimensional changes in particular in the case of hygroscopic minerals, such as clay materials, and sub-fossil bones [34]. The maximum daily variation suggested is 4%–5% [35].

In May 2014, one of the palms previously treated for pyrite decay, *Latanites* sp., showed new small alterations in the same area where oxidation products were removed in 2007 [31]. Therefore, a multidisciplinary study was carried out to: (i) identify the nature of the alterations; (ii) investigate the possible factors responsible for damage. Four samples were collected from different areas of the *Latanites* sp. fossil palm, and their chemical composition was characterised by means of XRPD and Raman spectroscopy. In November 2015 the Padova University Museum Centre, the Department of Geosciences of the Padova University and the Institute of Atmospheric Sciences and Climate of the National Research Council signed a cooperative agreement aimed at the microclimatic monitoring of the Hall of Palms, which started in December of the same year. The main aim of the monitoring program was to measure the thermo-hygrometric conditions inside the showcases of the Hall of Palms, to compare them to the values recommended for the proper conservation of the fossils, and thus to evaluate the suitability of the climatic control system installed in the room. At the same time, the evolution of damage to that palm was followed by regular visual inspections and documented by taking pictures during the entire program.

2. Materials and Methods

2.1. Sampling and Analytical Techniques

About 500 milligrams of material were gently removed from four different areas of the *Latanites* sp. fossil palm: (1) the powder yellow-grey efflorescence; (2) the palm trunk; (3) the base of the trunk; (4) a palm leaf (Figure 2). Sampling was performed using a sharp scalpel and collected material for the analysis was placed into a small plastic capsule.

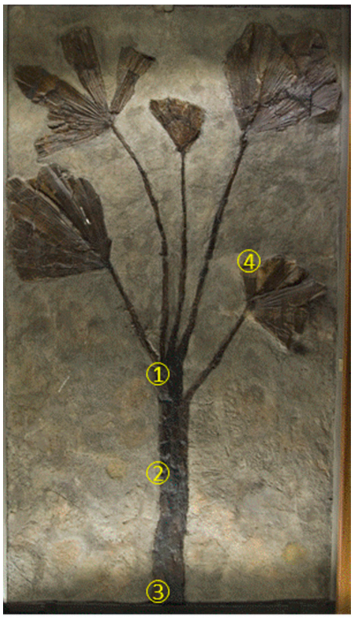


Figure 2. Picture of the *Latanites* sp. fossil palm with the indication of the sampling points.

XRPD and Raman spectroscopy were performed on the scratched samples to identify the main compounds.

XRPD was recorded on a PANalytical θ-θ diffractometer (Cu radiation) (ASD Inc., PANalytical NIR Excellence Center, Longmont, CO, USA) equipped with long fine focus Cu X-ray tube operating at 40 kV and 40 mA, capillary spinner and a solid state detector (PIXCel), at the Department of Geosciences of the Padova University.

Raman spectra were collected at the Department of Chemical Sciences of the Padova University using a Raman DXR (ThermoFisher Scientific, Waltham, MA, USA) with laser wavelength of 532 cm^{-1} (power 8 mW).

2.2. On Field Investigations: Microclimatic Monitoring and Visual Inspections

The microclimatic monitoring of the Hall of Palms was performed with ten automatic data loggers (HOBO® U12-012, Onset Computer Corporation, Bourne, MA, USA) equipped with sensors for the measurement of air temperature T (°C) and relative humidity RH (%).

Thermo-hygrometric conditions were measured continuously inside the room and outside of the museum for more than one year, with a sampling time interval of 15 min.

The software (HOBOware) supplied with the data loggers was used for setup, graphing and analysis.

To verify and improve their accuracy, all the sensors were previously calibrated in climatic chamber for T and RH measurements. The accuracy declared in the datasheets was respectively, ±0.35 °C for air temperature in the range 0–50 °C and ±2.5% for relative humidity in the range 10%–90%. The instrumental set-up used for calibration included:

- Climatic chamber VC3 4034 (Vötsch Industrietechnik, Balingen-Frommern, Germany);
- Selelogic sPRT—450 Smart Thermometer (Selelogic Instruments, Webresults advanced solutions, Bergamo, Italy), range T (−196 °C; 420 °C), accuracy 0.01 °C (−196 °C; 250 °C) and 0.02 °C (250 °C; 420 °C);
- Optidew High Performance Optical Dew Point transmitter (Michell Instruments, Michell Italia s.r.l, Milan, Italy), range RH (<0.5; 100%), accuracy ±0.2 °C dew point.

The calibration of the T sensors was performed in the range 0–60 °C with steps of 10 °C. The calibration of the RH sensors was performed in the range 25%–90% RH with steps of 10%, keeping temperature at 25 °C.

The thermo-hygrometric values measured by HOBO data loggers were compared with the values measured by the sensors used as references for accurate measurements, respectively Selelogic for T and Optidew for RH, and the best fitting line was found for temperature and relative humidity, after having previously checked the linearity of the sensors. The absolute error in T and RH that characterised each data logger was calculated as the difference between the T and RH values measured with the high accuracy sensors (real value) and the ones calculated with the linear fit. The relative error was calculated by dividing the absolute error with the real value; for RH it was expressed as percentage. The highest relative errors for the data loggers used indoors were 0.01 °C for temperature in the range 10–40 °C and up to 2% for relative humidity in the range 30%–100%. The sensor installed outside was characterised by an error on temperature of one order of magnitude higher (i.e., 0.4 °C), as the operating range was wider (−5°C; 40 °C). The thermo-hygrometric operating ranges were selected in accordance to the expected indoor and outdoor climate in Padova and they were verified a posteriori.

The data collection points are listed in Table 2, and their positions are indicated in the map in Figure 3.

Table 2. Data collection points.

Identification Number/Name	Location	Showcase Dimensions	Height from the Floor
1	Inside showcase	5.87 × 3.75 × 0.64 [1]	1.5 m
2	Inside showcase	5.87 × 3.75 × 0.64 [1]	1.5 and 2.6 m
3	Inside showcase	22.85 × 3.75 × 0.64 [2]	1.5 m
4	Inside showcase	3.5 × 0.5 × 0.11	1.5 m
5	Inside room		2.5 m
6	Inside showcase	22.85 × 3.75 × 0.64 [2]	1.5 m
7	Inside showcase	3.23 × 2.67 × 0.20	1.5 m
8	Inside room		2.5 m
9	Inside showcase	1.67 × 3.75 × 0.64	1.5 m
10	Inside showcase	4.00 × 3.76 × 0.63	1.5 m
out	Outside		7 m

[1,2] These two showcases are connected with one another.

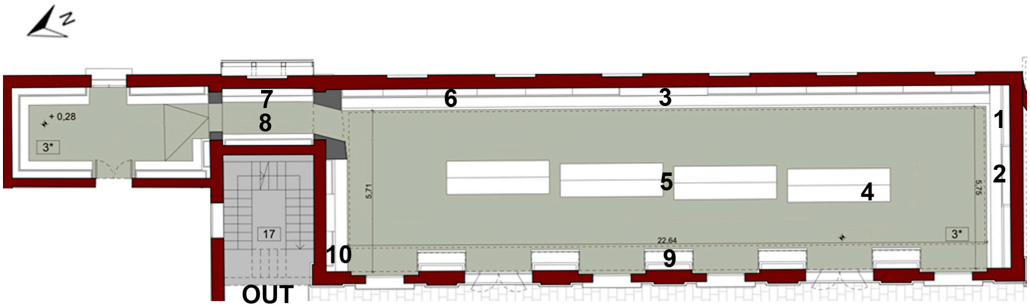


Figure 3. Map of the Hall of Palms with the positions of the sensors (courtesy of Arch. G. Mar).

Concerning the indoor locations, the data loggers were placed inside the selected showcases, but also outside them even in the room to study exchanges between the atmosphere in/out the showcases (see Table 2, Figures 3 and 4). The selection of the showcases included the ones containing fossils with conservation problems and showcases of different sizes, two of which (points 9 and 10) were added in the last period of the monitoring program for comparison. The sensors were installed in such a way to minimise any aesthetic impact that might detract from the experience of visitors to the gallery.

Figure 4. Some monitoring points inside the Hall of Palms.

When monitoring a museum environment, it is always necessary to also study the climate outside, to assess the influence of the external climate on the internal conditions. Because the data taken from the meteorological station closest to the study site may not have accurately represented the climatic conditions at the location of the museum, a data logger was placed outside, protected from direct rain and solar radiation, as close as possible to the Hall of Palms.

At the beginning of the monitoring program, the *Latanites* sp. palm (point 1) already showed an evident whitish nodule, hence during the entire period of investigation, photos of the whitish nodule were taken monthly with a Canon Powershot G6 digital camera to control the progress of the damage.

3. Results and Discussion

3.1. XRPD and Raman

Raman spectroscopy and X-ray powder diffraction allowed for the identification of the main compounds of the samples collected and the characterization of several mineral phases.

XRPD of sample 1 (Figure 5) revealed that the yellow-grey efflorescence was mainly composed of rozenite, hydrate iron sulphate [$Fe^{2+}(SO_4)\cdot 4H_2O$], gypsum, hydrate calcium sulphate [$Ca(SO_4)\cdot 2H_2O$] and ammoniojarosite, potassium iron hydroxyl-sulphate [$KFe^{3+}{}_3(SO_4)_2(OH)_6$]. Sample 2 was a fragment of the fossil palm tree embedded into a greyish matrix composed of calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$], montmorillonite, a clay mineral [$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$], and quartz [$SiO_2$]. The matrix contained as well amounts of brownmillerite [$Ca_2Fe^{3+}AlO_5$] and larnite [Ca_2SiO_4], two calcium-bearing compounds. Sample 3, taken from the base of the trunk, was mainly composed by organic compounds that were not identified due to their amorphous structural characters. Other mineral phases in lesser quantities that were identified, were goethite, an iron hydroxide [$FeO(OH)$], calcite and montmorillonite. Finally, sample 4, a fragment of the palm leaf, was mainly composed of calcite and a clay mineral, probably saponite, belonging to the smectite group; baryte, barium sulphate and anatase, titanium oxide were also identified in lesser amounts.

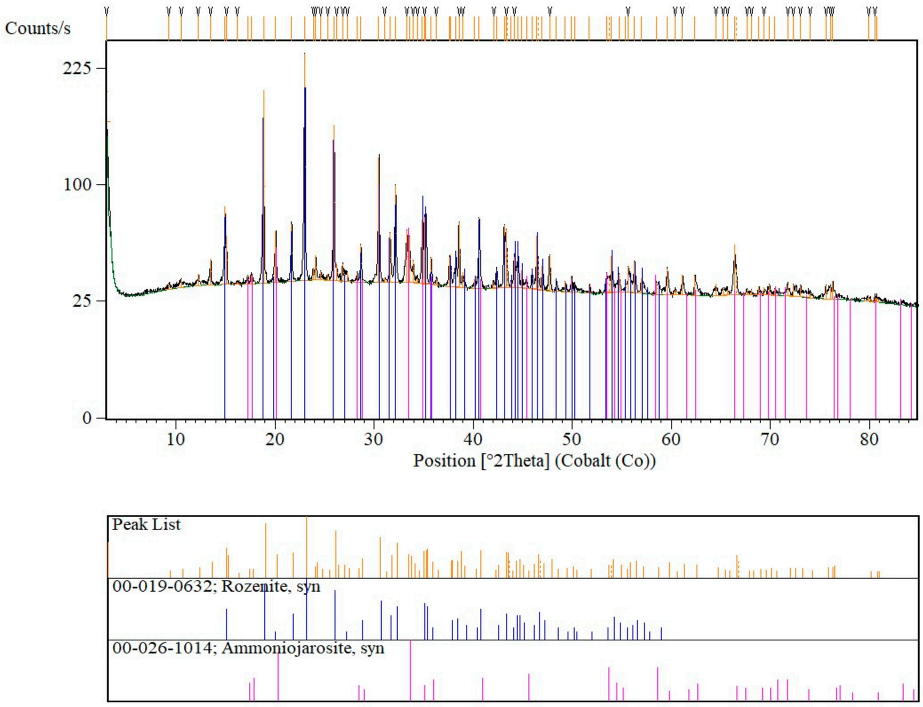


Figure 5. X-Ray powder diffraction diffractogram of sample 1: rozenite and ammoniojarosite have been clearly identified.

Raman spectroscopy on the samples confirmed the presence of the main mineral phases previously identified by XRPD, such as gypsum, rozenite, calcite, dolomite, quartz, baryte and anatase. The absence of characteristic peaks in the Raman spectra did not allow for the differentiation of any of the organic compounds related to their amorphous structural characters. Indeed, the Raman spectroscopy of sample 1 revealed presence of NH_4 probably related to ammoniojarosite, a mineral containing ammonium molecular groups in its structure.

The results of the analyses confirmed that the yellow-grey efflorescence (sample 1) developed in the *Latanites* sp. fossil palm was the result of pyrite decay, as the minerals found, i.e., sulphates (rozenite and gypsum) and iron hydroxide (goethite), usually develop after pyrite and marcasite oxidation processes.

The fossil palm leaf (sample 2) contained larnite and brownmillerite, two mineralogical phases usually associated with cement mixtures, while the trunk (sample 3) was characterised by significant amounts of baryte and anatase. These latter are not rock-forming minerals of sedimentary rocks, but probably relics of inorganic compounds used as additives in previous restorations. In the past, anatase and baryte were also utilised as pigments due their high refractive index.

Smectite group minerals (montmorillonite and saponite) calcite, dolomite and quartz are rock-forming minerals of marls and claystones and they occurred in all the samples analyzed.

Neither pyrite nor any other iron disulphide were detected in any sample.

3.2. Thermo-Hygrometric Conditions

Padova, located in the north of Italy, in the easternmost part of the river Po Plain, is characterised by a humid temperate climate ('Cfa' climate, according to Köppen classification), with hot summers, mild to cold winters, the most humid period between autumn and winter, and rainfall concentrated in spring and autumn. Analysis of climate in Padova from the time the fossils were restored in 2007 showed that the winter and spring of 2014 were particularly humid and rainy. In May of that year signs of alteration in the *Latanites* sp. palm were first detected, suggesting the specimen had been affected by these external climatic conditions despite being conserved in a climatically controlled showcase.

During the monitoring period, the measured values of air temperature and relative humidity outdoors were in accordance with the typical humid temperate climate of Padova. As expected, air temperature indoors followed the time trend of the external one, but with different average values and amplitude of the variations: the averages were higher inside than outside in autumn and winter, more similar during the rest of the year, and the variations inside were reduced in amplitude during the entire year.

The monthly averages of air temperature recorded in the monitoring points inside the Hall of Palms were not fully in compliance with the recommended values (Table 1), in particular in summer, when the temperatures were slightly higher than threshold maximum, especially inside the showcases (Figure 6). In any case, it is notable that the average T values were very similar at all monitoring points, indicating air exchange between the showcase and room environments. This behaviour was confirmed by the direct comparison of the T at the monitoring points 1, inside the showcase, and 5, inside the room but outside the showcase, that showed the same monthly average and maximum temperatures (Figure 7). Among the locations investigated, point 8 recorded the highest monthly average temperature in winter (Figure 8), due to its location in a narrow corridor that connects the Hall of Palms to another part of the Museum characterised by higher temperatures.

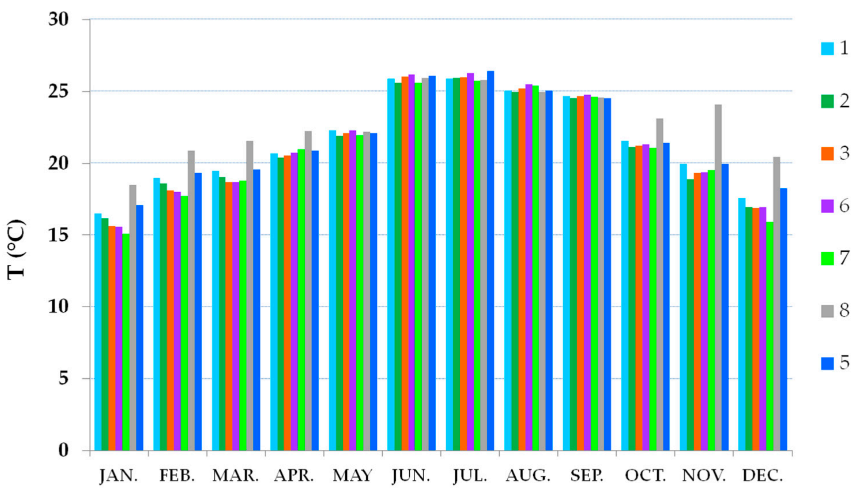


Figure 6. Monthly average temperature values recorded at the monitoring points.

Like air temperature, relative humidity indoors also followed the time trend of the external RH, but with variations reduced in amplitude and lower average values inside than outside in the autumn and the winter (as relative humidity stands in inverse proportion to air temperature). The average hygrometric level inside the Hall of Palms in winter was lower than recommended, because of the heating system. At the same time, for nearly the entire year the RH monthly average inside the showcases exceeded the threshold of 40% (Figure 8). In fact, analysis of the RH distribution inside the showcases indicates that for most of the time (60%–80%), RH was higher than 40% in all the showcases under study (Figure 9a). In particular, the most critical months for pyrite decay were from April to October (Figure 9b).

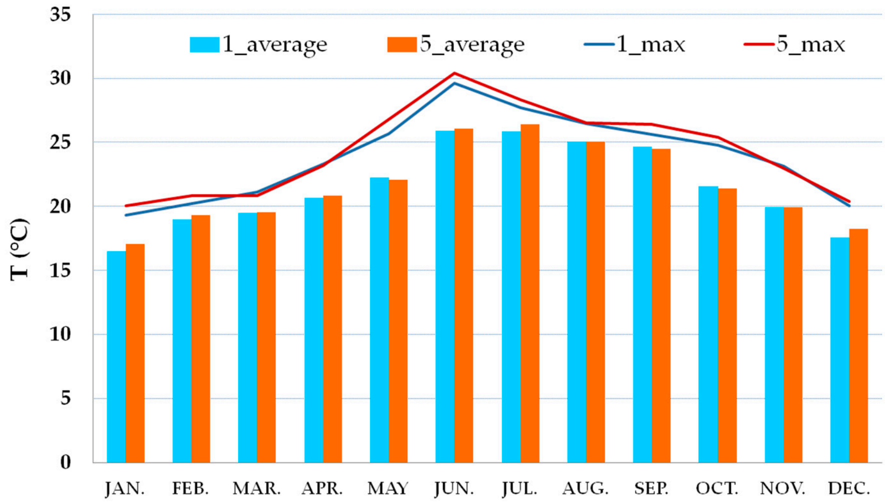


Figure 7. Monthly average and maximum temperature values measured at points 1 (inside showcase) and 5 (in the room).

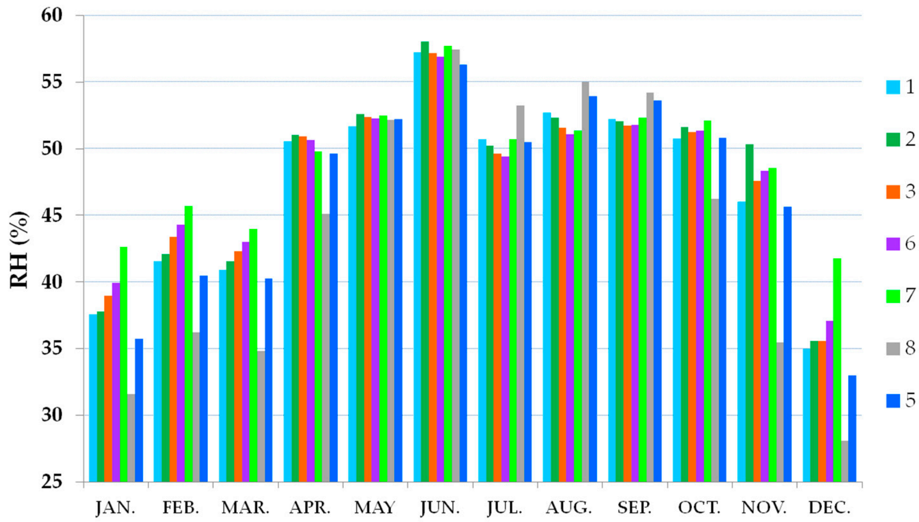


Figure 8. Monthly relative humidity (RH) averages recorded at the monitoring points.

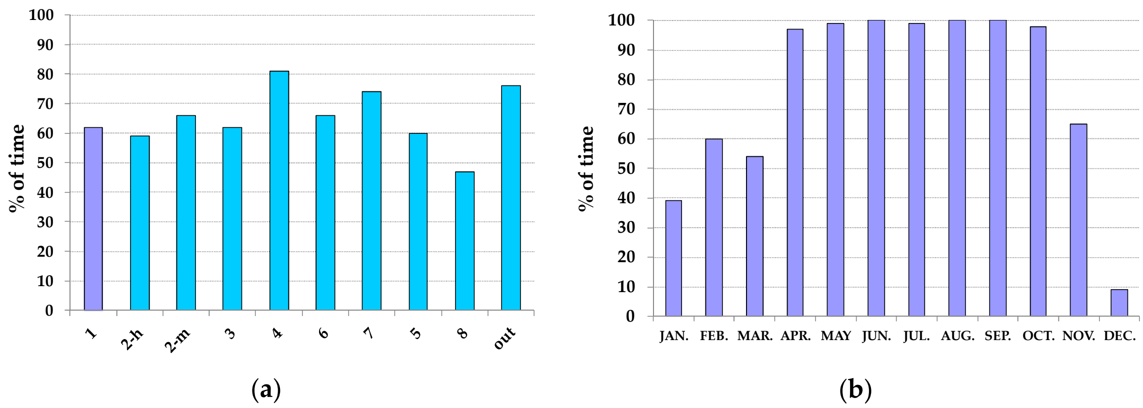


Figure 9. (**a**) Percentage of total time when RH was higher than 40%; (**b**) Percentage of monthly time when RH was higher than 40% at the monitoring point 1.

Inside all the investigated showcases, the maximum daily RH variation (ΔRH) exceeded the threshold (4%–5%) reaching up to 25% (Figure 10). These maxima were all recorded on the same day (28 November 2016), which was also characterised by a strong decrease in RH outdoors. A comparison of the hygrometric time trends indoors and outdoors on that day further confirms that the microclimate inside the showcases was strongly influenced by the outdoor conditions (Figure 11).

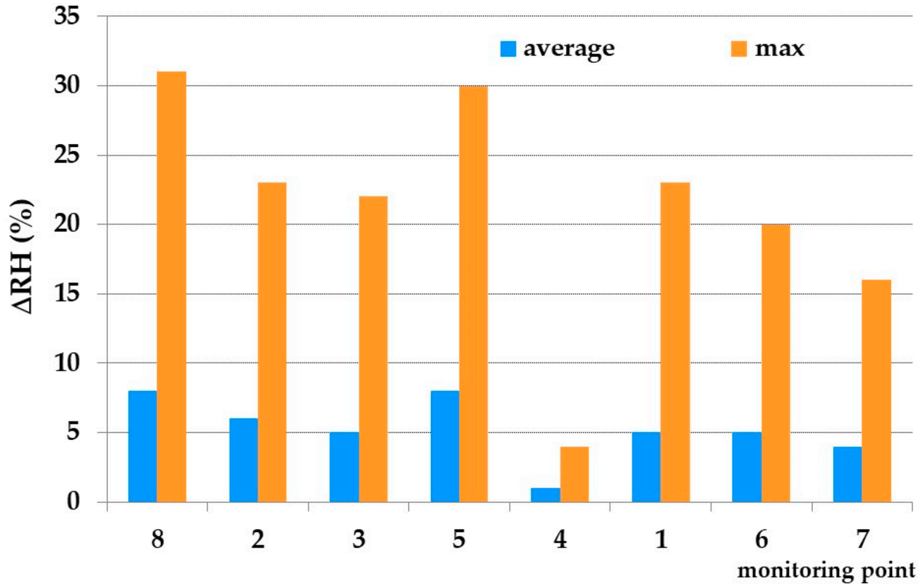


Figure 10. Average and highest RH daily variation (for point 2 only one value was reported, as the values measured at the two heights were the same).

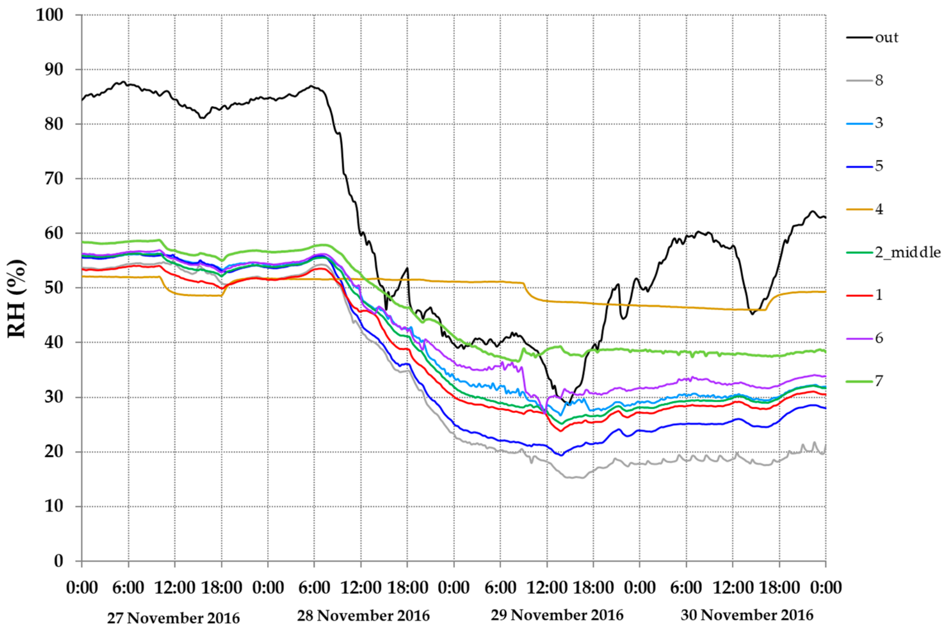


Figure 11. RH trend at the end of November 2016 outside, inside the Hall of Palms and inside the showcases (2_high point was very similar to 2_middle and is not reported).

At the start of the monitoring program the yellowish nodule in the *Latanites* sp. palm was clearly larger in size with respect to the period in which it appeared, i.e., May 2014. The regular visual inspection and photographic documentation during the monitoring period didn't show any notable change in the outline of the nodule, except for a small area to the right that, in March 2017, appeared yellowish (Figure 12b), while four months before was unaltered (Figure 12A), indicating that the decay process was evolving in that period.

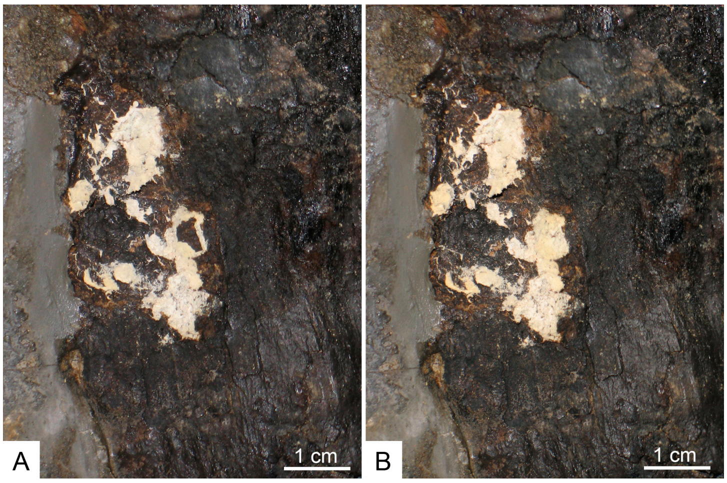


Figure 12. Evolution of efflorescence due to pyrite decay in the *Latanites* sp. palm in (**A**) November 2016; (**B**) March 2017.

4. Conclusions

The results of the analysis performed on the samples collected from the *Latanites* sp. fossil palm that showed signs of alteration confirmed the occurrence of the by-products of pyrite oxidation (pyrite decay). At the same time, the microclimatic monitoring clearly indicated that the thermo-hygrometric conditions measured inside the showcases were not in compliance with those recommended for the proper conservation of fossils. In particular, the relative humidity exceeded the threshold value of 40% and this is likely the reason of the pyrite decay observed in the *Latanites* sp., as well as of the partial failure of the chemical treatment performed in 2007. In fact, any restoration treatment is useless if it is not followed by preventive conservation measures. In particular, as the treatment with ethanolamine thioglicollate does not remove pyrite, but only by-products, it is strongly recommended to create microclimatic conditions such as to prevent further oxidation of pyrite.

Therefore, it is extremely important to undertake mitigating actions in the museum to create and maintain thermo-hygrometric conditions in compliance with those recommended, by improving the efficiency of the air conditioning and heating systems, as well as by enhancing the insulation between the showcases and the room environments. In addition, the possibility to create separate, insulated compartments for those fossils in which the pyrite decay has occurred will be considered, despite the problems caused by their large size. Moreover, this solution would allow for installing inside the compartments materials and/or technologies to reduce the internal relative humidity, making it as close as possible to the recommended threshold. The research for the most feasible solution is underway.

In any case, permanent microclimatic monitoring of the museum (inside and outside of the showcases) is strongly recommended, as well as the regular check on the good working order of the active systems (air conditioning, heating, etc.) and the periodical visual inspection of the fossils.

Finally, to prevent the occurrence of pyrite decay, more needs to be known about the conditions in which it can develop and about the interplay of the different variables involved.

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