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Weathering Processes on Sandstone Painting and Carving Surfaces at Prehistoric Rock Sites in Southern Spain

Juan Carlos Cañaveras 1,*, Enrique Sanz-Rubio 2 and Sergio Sánchez-Moral 30

- Department of Environmental and Earth Sciences, University of Alicante, Campus San Vicente del Raspeig, E-03690 Alicante, Spain
- GEOMNIA Natural Resources SLNE, C/Cea Bermúdez, 14, E-28003 Madrid, Spain; esanz@geomnia.es
- Department of Geology, National Museum of Natural Sciences, MNCN, CSIC, C/José Gutiérrez Abascal, 2, E-28006 Madrid, Spain; ssmilk@mncn.csic.es
- * Correspondence: jc.canaveras@ua.es

Abstract: The sandstones which constitute the host rock for the prehistoric artwork in the Rock Groups of Tajo de las Figuras and Peñas de Cabrera (southern Spain) show a serious degree of alteration, due both to natural processes and those related to anthropogenic and animal activity. A detailed study was carried out on the petrological and compositional characteristics of the sandstones (fresh and altered rock) in both rock groups, and on the geological and climatological characteristics of the area in which they are located. The sandstones have very similar petrological and compositional characteristics in both areas. This likeness causes the nature of the natural weathering processes to be similar in the rock areas studied. These processes can be divided in terms of the predominant mechanisms of alteration into three inter-related categories: mechanical weathering, chemical weathering, and bio-induced alteration processes. However, the different climatic conditions of the areas in which the two rock areas are located directly influences the intensity of these processes. The precipitation and the range of temperature variation with heavy winter frosts in the area of El Tajo de las Figuras are significantly higher than in the area of Peñas de Cabrera; this translates into a higher rate of weathering at El Tajo de las Figuras. Regarding the anthropogenic action, two types of influence on the deterioration can be distinguished: a direct one, which consists of scouring and wetting of the walls in order to increase the chromatic contrast; and an indirect one, which is the extraction of blocks of sandstone in the upper part of rock shelters, which in turn encourages the development of the chemical weathering processes.

Keywords: sandstone weathering; chemical weathering; rock shelter; rock art



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1. Introduction

Rock materials have been employed as a host rock and/or frame for artistic representations, paintings, sculpture, and architecture since prehistoric times. In the last decades, great progress has been made in investigating the processes of alteration in rock used for architectural monuments ([1–11], among others). However, works on to the state of alteration of the host rock for artistic representations located in natural rock outcroppings, both karstic cavities and rock shelters, are much less common. Recent works address this problem in art representations executed in natural rock shelters. Campbell (1991) [12] classified the intensity of the weathering which has affected the sandstone host rock for the historic carvings in the Writing-on-Stone Park in Canada. Pentecost (1991) [13] studied the rate of weathering of the Cretaceous Ardingly Sandstone in the Weald (England) where there are abundant pictorial representations. Benito et al. (1993) [14] analysed the state of conservation of the paintings and carvings in different rock groups in NE Spain together with the processes of weathering in their sandstone host rock. Sjöberg (1994) [15] carried out a study on the alteration of surfaces with carvings from the Bronze Age in southwestern Sweden. Hall et al. (2007) [16] and Meiklejohn et al. (2009) [17] suggested that rock moisture

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and thermal regimes exert the most damaging influence on indigenous rock art painted on porous sandstones in southern Africa. Díez-Herrero et al. (2009) [18] studied the influence of direct insolation in the weathering of cave paintings on Triassic sandstones at Central Spain. More recently, Peña-Monné et al. (2022) [19] highlighted the role of hydroclastic and haloclastic processes on weathering processes of the sandstones in the painted rock shelters of Cerro Colorado (Argentina).

Paintings and carvings on rock surfaces become closely linked with the natural evolution of the host rock from the moment that they are executed. Because of this, and in order to carry out an extensive study of the state of conservation of these artistic and cultural features, it is first necessary to establish the processes and mechanisms by which the rock has been altered. The purpose of the present work is to establish the alteration processes which affect the sandstones that constitute host rocks for the paintings and carvings of the so-called Rock Groups of Tajo de las Figuras (Cádiz) and Peñas de Cabrera (Málaga), southern Spain.

2. Study Area

The Rock Group of Tajo de las Figuras is located within the municipal boundaries of Benalup (Cádiz province, southwestern Spain) (Figure 1A), in the extreme southeast of the Sierra Momia, at an altitude which ranges between 110 and 170 m above sea level. These sierras, which have little relief, are formed of siliceous sandstone belonging to the Aljibe Formation (lower Miocene) that grades downwards into reddish clays which range in age from Oligocene to Aquitanian. The Aljibe Fm., a 1500 to 2000 m thick succession, consists of meter thick planar-tabular or cross-stratified beds of medium to coarse-grained, pale orange to yellowish brown sandstones. The quartzose sandstones of Aljibe Fm. are strongly tectonized, the basic directions of the diaclase network being E–W. Its structure is in the form of piled up thrust sheets which provides important relief in the form of sierras with an average altitude of 400 to 500 m. It also has an abundance of structures due to tectonic instability, such as landslides and sand dykes [20]. The Rock Group of Tajo de las Figuras includes a total of seven natural rock shelters, mainly facing the south, termed Cueva del Tajo de las Figuras, Cueva del Arco, Cueva Cimera, Cueva Negra, Cueva Alta, Cueva del Tesoro, and Cueva de los Pilones. These host a set of engravings which can be attributed to the upper Palaeolithic and post-Palaeolithic (Neolithic-Chalcolithic-Bronze Age) [21]. These paintings are of zoomorphic and anthropomorphic motives and signs [22] and form their own artistic style within the so-called "schematic" style, which can be differentiated from the rest of the artistic rock works in the Iberian Peninsula [23,24].

The Rock Group of Peñas de Cabrera is located within the municipal boundary of Casabermeja, in the interior of the Málaga province (southern Spain) (Figure 1A). Most rock shelters are sited on the northern flank of a thick succession of sandstones which ends in a small hill (570-620 m above sea level) which is located on the southern side of the Lower Miocene Colmenar Depression. The sandstones are arranged in meter-thick beds which generally are folded with dips that slightly exceed 30°. However, at some points, such as where rock shelters with paintings are found, sandstones appear as blocks with chaotic distribution, being arranged vertically and even seem to be inverted with some frequency. The degree of tectonic fracturing of sandstones is very high, showing a dense network of faults and diaclases with preferential N260°E and N orientation. Given their affinity with the Germanic facies and the lack of fauna in the study area, the Permo-Triassic age has been assigned to these sandstone beds [25]; thus placing them in the Andalusian domain precisely in contact with the flysch of the Colmenar Unit. The Rock Group of Peñas de Cabrera is formed of a total of 23 well-known rock shelters of smaller dimensions facing N, NW, and W. It contains a series of post-Palaeolithic paintings (Chalcolithic) which can also be assigned to the "schematic" style, with an abundance of anthropomorphic and idiomorphic representations, idols, tectiforms, and arboriforms [26].

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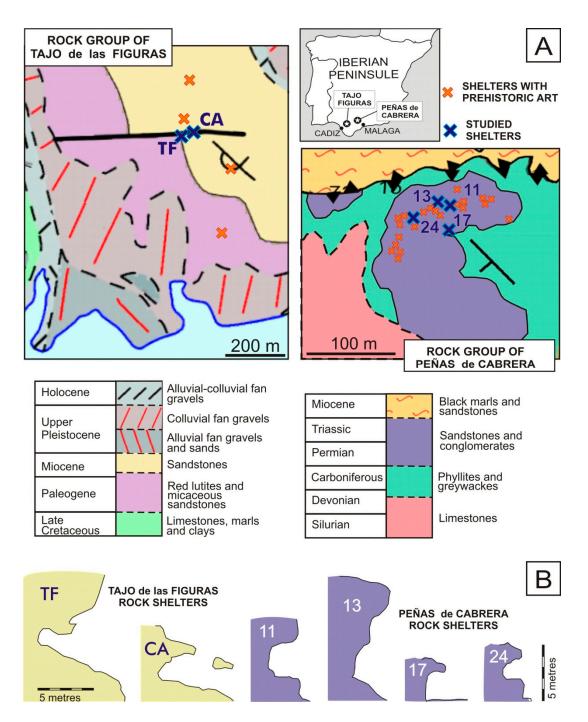


Figure 1. (A) Location map. Small crosses indicate locations of rock shelters with prehistoric paintings and engravings. Large crosses indicate locations of the studied rock shelters: Cueva del Tajo de las Figuras (TF), Cueva del Arco (CA), Shelter nº 11, Shelter nº 13, Shelter nº 17, and Shelter nº 24. (B) Cross-sections of the studied rock-shelters.

Both Rock Groups (Tajo de las Figuras and Peñas de Cabrera) show a high degree of deterioration, both of natural and anthropic origin, which has promoted various actions aimed at their protection by the relevant authorities, including their temporary closure to tourism [27,28].

As the climatic conditions have a determining role in the development of rock weathering processes [29], the main climatic parameters of the study areas were collected for the period 1995–2014 from data supplied by the Antequera meteorological station (Z = 408, 370146 N, 044454 W) for Peñas de Cabrera and the Grazalema station (Z = 913, 364538 N,

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052227 W) for Tajo de las Figuras. Regarding temperatures, both areas have a mesothermal to hot climate, but with a greater seasonal contrast in the area in which Tajo de las Figuras is located with relatively frequent frosts in December, January, and February, and a greater annual thermal fluctuation can be observed. The mean annual temperature values for both Tajo de las Figuras and Peñas de Cabrera areas range from 15.2 to 17.3 °C, and from 14.7 to 16.5 °C, respectively. In the case of precipitations, the differences between the two areas are of much more importance; Grazalema (Tajo de las Figuras) shows indices of very high rainfall with mean annual ranging from 1800 to 2200 mm, which are considerably greater than that in Málaga (Peñas de Cabrera), with mean annual precipitation values ranging from 3310 to 660 mm. The average annual wind speed in Grazalema is 13.86 km/h with gusts of over 130 km/h. In Antequera, the average annual value of the wind speed is slightly lower, 11.99 km/h with some gusts exceeding 80 km/h. At both areas the climate is Csa (hot summer Mediterranean climate) according to the Köppen-Geiger classification [30].

3. Materials and Methods

The geomorphological disposition of the sandstone beds which act as host rock for paintings and carvings was determined through a photo-geological study of the area, a revision of the existing geological cartographies, and field work in which structural and textural data were collected. The study concentrated on six representative rock shelters from the two archaeological groups (Figure 1). Two shelters belong to the Rock Group of Tajo de las Figuras (Cueva del Tajo de las Figuras and Cueva del Arco) and four to the Rock Group of Peñas de Cabrera (rock shelters 11, 13, 17 and 24), as these are the ones that have the largest number of artistic representations. To assess the deterioration phenomena, detailed and comprehensive in situ visual analyses were performed before the sampling campaigns. The ICOMOS ICS glossary (2008) [31] was used for weathering form terminology. A total of 80 samples were taken from these six rock shelters in order to carry out a petrological, mineralogical, and geochemical characterization of alteration processes which affect the sites. These samples correspond both to fresh rock and to altered rock (flaking, filling with joints, oxide patinas, detritus of alveoli, and concretions). Analytical procedures were performed at Museo Nacional de Ciencias Naturales (MNCN-CSIC, Madrid) laboratories. Optical microscopy and SEM techniques were used for the petrographic study. Qualitative and semi-quantitative data were obtained on the chemical composition of the different mineral components present in the sample using an EDS analyser. The mineralogical analyses were performed using X-ray diffractometry, with quartz as the internal standard. The geochemical composition of the host rock and of the alteration products were determined using standard procedures with an X-ray fluorescence spectrometer.

4. Geological Characteristics of Rock Shelters

4.1. Morphology

The general morphological characteristics of the six rock shelters studied are provided below. The main alteration products, whose mechanisms of formation are explained later, are schematically indicated:

The Cueva del Tajo de las Figuras is a rock shelter opening towards the south, 5.8 m in height, 4.2 m wide, and 8 m deep (Figure 1B). It is located on a vertical incision corresponding to a fault plane with an E–W direction (Figure 2A). It has alveolar structures formed by one centimetre to decimetre-width alveoli with a spherical to ellipsoidal section particularly located in the back wall and the ceiling of the shelter. Holes are used by animals (wasps and birds) for their nests. Patinas of reddish to blackish tones are abundant on the walls and ceiling. Whitish patinas on the external part of the shelter are also present. These stains are closely related to the colonisation of plants and the defecation of animals. The floor of the shelter has a smooth, polished, shining surface. Fallen rock flakes are abundant, particularly in the more external part of the shelter;

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- The Cueva del Arco is a rock shelter with a domed roof and an overhanging rock ledge that has partially collapsed. Consequently, a large arch with an elliptical section has been formed at the entrance of the cavity (Figure 2B). Its approximate dimensions are 2.3 m in height, 10 m wide, and 7.5 m deep (Figure 1B). Alveolar surfaces throughout the stratification are abundant on the walls and ceiling. The alveoli are one centimetre in width and have an ellipsoidal shape. Both the walls and the ceiling and floor show patinas of reddish and orange tones and an abundant colony of fungus, lichens, and other plants. Remains of fallen rock flakes are numerous;

- Shelter 11 (Peñas de Cabrera) is morphologically similar to the Cueva del Tajo de las Figuras, but not as deep, with approximate dimensions of 5 m in height, 4 m in width, and 2.5 m deep (Figure 1B). This shelter is orientated to the north and has developed on a practically vertical E–W fracture plane. Alveolar structures similar to those previously described can be seen on the ceiling and upper part of the walls of the shelter (Figure 2C). The floor is covered with a patina of an intense red colour, with bright and dark areas. The red tones of the floor appear to be related to the traces of Neolithic pictorial activity. A well-defined surface blackening can also be observed on walls and ceilings;
- Shelter 13 (Peñas de Cabrera) faces the north according to fracture planes in a N100°E direction and a dip of 50–60° S (Figure 2D), with the development of one meter-width tafone morphologies on its back wall (Figure 2E). This is a shelter with little depth (less than 3 m) and a maximum height of 8 m (Figure 1B). Honeycomb structures formed by alveoli of the order of one millimetre can be seen on the back wall of the shelter together with brownish orange patinas, fallen rock flakes, and white marks from the defecation of animals. Traces of biological communities, such us fungi or lichen, on the inner walls of the shelter are practically absent;
- Shelter 17 (Peñas de Cabrera) is 2.5 m in height, 6 m wide, and 1.8 m maximum in depth (Figure 1B). It faces north and is located very near ground level, thus making a very clear ground-level ledge. This shelter is almost masked by abundant vegetation. Reddish patinas and signs of fallen flakes are very abundant. The lower part of the shelter, up to a height of 50 cm, does not show alteration patinas and is completely devoid of flakes (Figure 2F);
- Shelter 24 (Peñas de Cabrera) faces west and is small (1.8 m high by 4 m wide and a maximum depth of 1.5 m) (Figure 1B). This shelter has a great development of alveolar morphologies in the interior, particularly towards the ceiling. Colonisation of fungi, lichens and other plants is abundant. The walls of the shelter have a very extensive blackish patina.

The degree of tectonic fracturing of the sandstone host rock in both rock groups is very high as they have been affected both by faults and a dense network of joints (Figure 2A,D). There are older recrystallized, hardened, and patinated fractures in the diaclase systems which are more resistant to weathering than the sandstone itself. The fracture network stands out inside the shelters; the sandstone is compartmentalized into patina-encased rock masses. The most recent fractures, on the other hand, are in a period of enlargement. It must be taken into account that this is a tectonically active area [20,25] and therefore the more recent joints must have originated through neo-tectonic activity.

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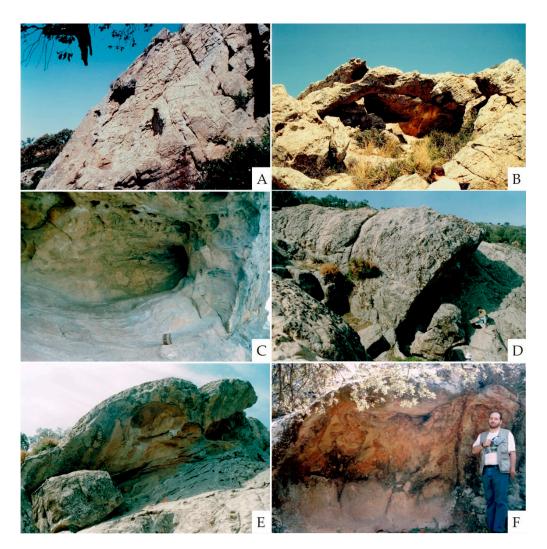


Figure 2. Morphological features of the studied rock-shelters (see text for explanation). (**A,B**) Rock Group of Tajo de las Figuras. (**C-F**) Rock Group of Peñas de Cabrera. (**A**) View of the entrance of the Cueva del Tajo de las Figuras, which is located in a fault plane; note the high number of fissures and fractures affecting the host rock. (**B**) General view of the Cueva del Arco. (**C**) View of the interior of the shelter 11; honeycomb weathering is developed on walls and ceiling. (**D**) Lateral view of shelter 13, which is developed on a fault plane. (**E**) Frontal view of shelter 13; decimetre-width tafone are developed in the uppermost part of the shelter wall. (**F**) Frontal view of shelter 17; selective weathering due to proximity to ground level is observed.

4.2. Petrology and Geochemistry

The sandstone host rock of the Tajo de las Figuras site is mainly composed of medium to coarse-grained, poorly sorted sub-arkoses. The framework grains show a relatively high degree of roundness (Figure 3A). It is mainly composed of: quartz (80–90%); feldspar (0–15%), with a predominance of plagioclase; mica (<5%), mainly muscovite; tourmaline (<2%); and opaque minerals (<2%). The matrix is very scarce (<5%) and mainly consists of kaolinite masses (to a lesser extent illite). Syntaxial siliceous cements, ferruginous rims and kaolinite pore-linings and pore-fillings were observed. The chemical composition of the Tajo de la Figuras fresh rock samples (Table 1) is characterised by the high content of SiO₂ (>95%) and low content of Al₂O₃ (<1.8%) and other elements. In most of the samples, the MgO and MnO content was below the sensitivity limit of the analytical technique employed (XRF). This fact appears to be related to the low proportion of phyllosilicates observed in the petrographic study.

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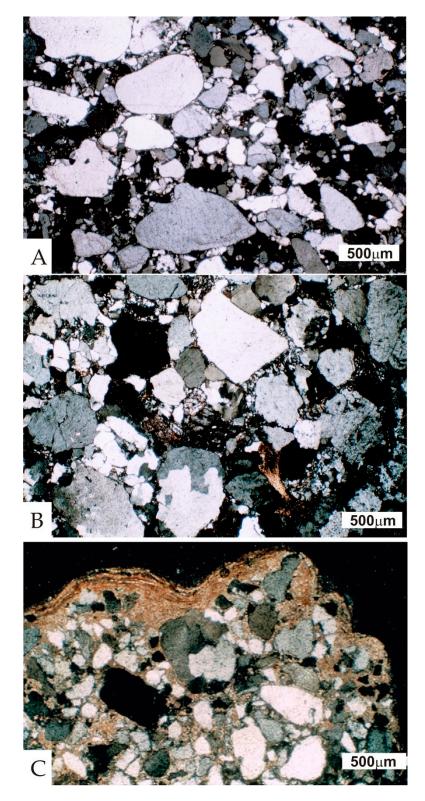


Figure 3. Thin section photomicrographs. **(A)** Poorly sorted sub-arkose showing clast-supported fabric and grains with high degree of roundness (Cueva del Arco). **(B)** Sub-arkose with feldspar and biotite grains showing fine-grained alteration and pore-filling kaolinite cement (Shelter 13, Peñas de Cabrera). **(C)** Stromatolite-like crust surrounding sandstone surface (Cueva del Tajo de las Figuras). Calcite cements filling intergranular pores and partially replacing both siliceous framework grains and cements. All photographs were taken under cross polarized light.

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Table 1. Average chemical composition (in weight %) of fresh sandstone host rocks.

	Tajo de las Figuras	Peñas de Cabrera
SiO ₂	96.3	91.53
Al_2O_3	1.4	5.5
$FeO + Fe_2O_3$	0.5	0.45
TiO ₂	0.25	0.28
MgO	0.10	0.13
CaO	0.07	0.04
MnO	<0.01	<0.01
Na ₂ O	0.1	0.04
K ₂ O	0.3	0.98
P ₂ O ₅	0.06	0.1
L.O.I.	0.99	0.90

Peñas de Cabrera sandstones are very similar to those of Tajo de las Figuras. They are medium to coarse-grained, poorly sorted quartz-rich sandstones with grains showing a moderate to high degree of roundness and sphericity. The sandstone is composed mainly of: quartz (80–90%); mica (5–20%); feldspar (mainly plagioclase) (0–15%); and metamorphic rock fragments (0–10%). The matrix is scarce (<5%) and consists of masses of illites and kaolinites. The cements, although scarce, are mainly siliceous and ferruginous. Most of these sandstones can be classified as sub-arkoses, although locally, sub-lithoarenites are relatively abundant (Figure 3B). The chemical composition is also similar to Tajo de las Figuras sandstones (Table 1). The main difference is clearly the greater concentration of Al_2O_3 and K_2O due to the presence of phyllosilicates (mainly mica and illites).

The superficial alteration rinds on the shelters' walls and of the fallen flakes are formed by a compact mass, which is not very porous and has reddish tones. The chemical analysis for these alteration rinds in the two rock groups indicate a marked enrichment in FeO + Fe₂O₃ (4.9% \pm 0.5%), MgO (0.42% \pm 0.17%), and in the loss on ignition (L.O.I.) (1.8% \pm 0.3%). This fact is consistent with the petrographic observations made and the mineralogical analyses performed. Framework components show weathering features such as: (1) strongly altered feldspars and biotites; (2) masses of authigenic kaolinites; (3) quartz grains with signs of dissolution and syntaxial overgrowth; (4) and muscovites fragmented into flakes. Fe and Mn oxides/hydroxides in the form of amorphous masses, which commonly appear to be fragmented and re-cemented, are relatively abundant. Traces of biological activity, such as lichen thalli, fungal hyphae, and the remains of insect skeletons were also recognised.

Micrometre to millimetre-thick laminar carbonate crusts (Figures 3C and 4A) formed by 5 to 50 μ m-thick layers mainly composed of calcite crystals (micrite and microsparite) also occur. Lenticular gypsum crystals (Figure 4B), Fe and/or Mn oxides/hydroxides grains, clays, and organic elements (biofilms, algae, fungi, and spores) were also recognised. In the areas where these crusts are developed, it was observed that the calcium carbonate crystals penetrated the sandstone replacing and/or disintegrating both the framework components and the matrix/cements (Figure 3C).

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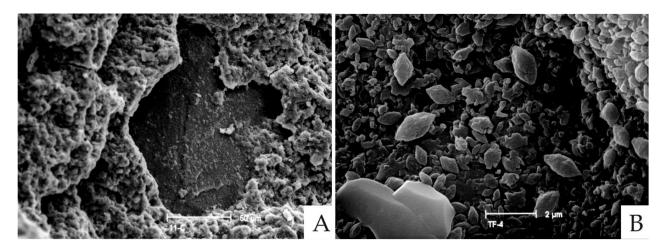


Figure 4. SEM micrographs. **(A)** Detail of stromatolitic calcite layers enveloping grain surfaces (Shelter 11, Peñas de Cabrera). **(B)** Small lenticular gypsum crystals within the stromatolite crust (Cueva del Tajo de las Figuras).

5. Weathering Processes

A simple visual examination of the shelters which form the two rock groups denotes the major effectiveness of weathering processes in the Tajo de las Figuras Group, as is revealed by a major development of alteration rinds, oxide-rich patinas, falling of flakes, etc. A detailed field and laboratory examination of the alteration products and forms allowed us to differentiate between natural weathering processes and those induced by human activity.

5.1. Natural Weathering Processes

The natural weathering processes, observed with different intensity in each of the studied sites, can be divided in terms of the predominant alteration mechanisms in three inter-related groups: mechanical weathering, chemical weathering processes, and bioinduced alteration.

5.1.1. Chemical Weathering Processes

Petrological and geochemical analyses of rock samples from the weathered surface of the walls of the shelters indicate the existence of chemical alteration processes which include dissolution and/or transformation of minerals and the redistribution of ionic substances. The main effect observed was the formation of hardened superficial layers. These layers are enriched in Fe and/or Mn oxides, clays, and silica. This process has been widely referred in the literature as case hardening (e.g., [32–34]). The driving mechanisms for case hardening on sandstones are the hydrolysis and carbo-hydrolysis reactions which affect the aluminosilicate minerals. The carbo-hydrolysis phenomenon constitutes the mechanism whose action has the greatest effectiveness, in a coherent manner, with warm and humid climatic conditions. These conditions favour the adsorption of water and a chemical attack on the rock components through the action of meteoric water which is slightly acidic due to the dissolved $\rm CO_2$. The $\rm CO_2$ source may be atmospheric or organic (vegetable covering and soils rich in organic material in the upper area of the shelters). Next is detailed the geochemical expression that summarises feldspar alteration and clay authigenesis:

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\begin{array}{lll} 6KAlSi_3O_8 + 4CO_2 + 4H_2O \rightarrow K_2Al_4(Al_2Si_6O_{20})(OH)_4 + 4K^+ + 12SiO_2 + 4HCO_3^- \\ K-feldspar & Illite \\ 2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 4SiO_2 + 8H_2O \\ K-feldspar & Kaolinite \\ 2CaAlSi_3O_8 + 11H_2O + 2CO_2 \rightarrow Al_2Si_2O_5(OH)_4 + 2Ca^{2+} + 2HCO_3^- + 4H_4SiO_4 \\ Anorthite & Kaolinite \end{array}
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An example of this phenomenon can be observed in Figure 5A,B, with feldspar crystals altered by carbo-hydrolysis and kaolinite crystals neoformed as the result of the alteration. It is precisely the abundant presence of kaolinite (Figure 5C) in the Tajo de las Figuras samples which corresponds to the high humidity level in this location since this authigenic mineral has been commonly employed as an indicator of wet climates [35]. The availability of water is very important in the development of the chemical weathering processes [36], since the solubility of the feldspars is very low (e.g., 3×10^{-7} mol for the K-feldspar and 6×10^{-7} mol/L for the Na-feldspar) [37] its saturation is reached rapidly and the dissolution of feldspars needs a continuous renewal of under-saturated water.

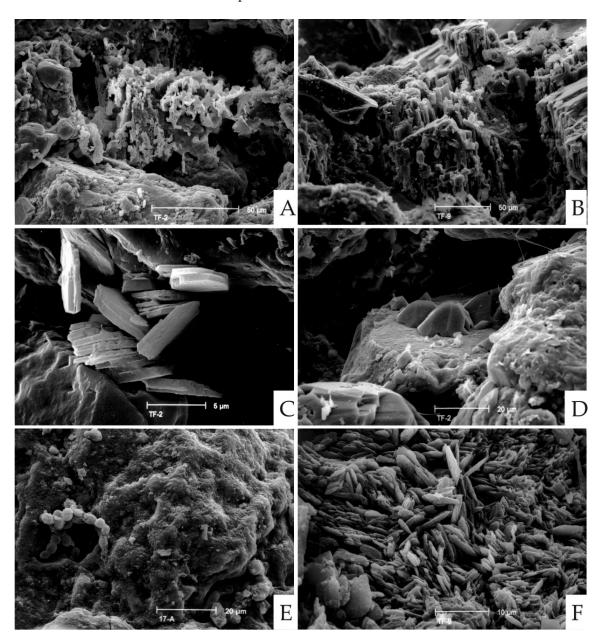


Figure 5. SEM micrographs. **(A)** Altered Na-feldspar crystal; on right, authigenic kaolinite cement. **(B)** Altered K-feldspar; note the development of intracrystalline fractures and etching features on crystal surfaces. **(C)** Detail of authigenic kaolinite aggregates showing booklet morphology. **(D)** Siliceous overgrowth on quartz crystal. **(E)** Organic biofilm coating quartz grain surfaces. **(F)** Brucite aggregates.

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The silica released (initially as H_4SiO_4) migrates to the exterior of the rock according to the preferential directions of water flow and starts to form the superficial hardened rinds and fillings in the system of joints and fractures (Figure 5D). A similar chemical attack, even more rapid and efficient, is produced simultaneously on the micaceous ferromagnesian minerals, such as biotite ($2K(Mg,Fe,Mn)_3AlSi_3O_{10}(OH)_2$)). The products are the neoformation of kaolinite, the release of Fe-oxides (limonite and haematite by oxidation) (Figure 5E) and, in smaller proportions, of Mg-oxides (brucite) (Figure 5F) and Mn-oxides (pyrolusite, manganite). These oxides migrate to the outer layers of the rock in a similar manner to the silica and, together, form alteration rinds with reddish tones, which are common in all the studied shelters. EDS chemical analyses clearly show the Fe and Mn enrichment of these alteration rinds. The simple dissolution of quartz and feldspar along their crystalline edges may be added to the processes, favouring the redistribution of cations in the superficial parts of the rock.

The formation of these hardened surfaces inhibits the progress of superficial alteration processes since these have low permeability and prevent the ingress of water to the rock interior. A crumbly area of mineral impoverishment developed below these hardened rinds. Flakes detachment takes place in favour of these areas (Figure 6A). When a detaching of part of the alteration rinds is produced in the form of flakes, it can be seen that the migration of the silica continues to progress and takes the preferred route between the contact and discontinuity areas, i.e., between these rinds and the fresh rock. Once a piece of hardened rind is broken or separated, the heterogeneity favours the development of microclimatological differences, which numerous authors have evoked as the cause of cavernous weathering features (e.g., [38–40]). Case hardening, simultaneous with the removal of sand grains by dissolution or salt weathering are the responsible for the formation of alveoli and honeycomb patterns on rock surfaces [41].

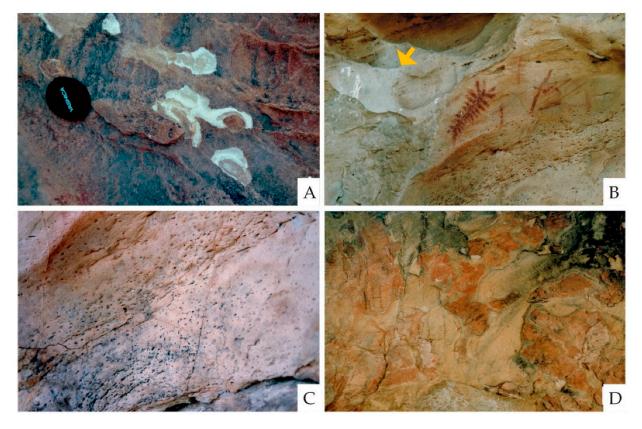


Figure 6. Weathering products. **(A)** Flaking processes and bleaching; Cueva del Arco. **(B)** Incipient alveolar weathering affecting schematic Palaeolithic rock paintings; on top left, bird droppings (arrows); Shelter 13. **(C)** Detail of alveolar weathering; Shelter 13. **(D)** Flaking; Shelter 17.

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These chemical alteration processes can favour the development of mechanical weathering processes, whose main effect is granular disintegration through the superficial dissolution of the grains [34,42] or by the effect of increasing the volume and the pressure between crystals/grains through the alteration of biotites and feldspars [32].

5.1.2. Mechanical Weathering Processes

In the two cases studied, two different but inter-related mechanisms were observed:

- (a) Thermal weathering due to the effect of changes in temperature suffered by rocks, both seasonally and in night-day cycles. This temperature variation may lead to the development of a thermal gradient between the surface and the interior of the rock, given its low thermal conductivity, the effect being their final breaking [17,43–46]. This process is clearly seen in the case of the Peñas de Cabrera shelters, where the metamorphic rock grains, with dark tones, can become relatively abundant (10%) in some parts of the shelters. Given their colouring and their textural characteristics, these components have higher specific heat and expansion coefficients than quartz and feldspar (majority components in the host rock). This leads to differential expansion processes and, therefore, variations in greater magnitude through dilatation-retraction phenomena, which in the long term cause their separation. As a consequence, on many occasions, lines of holes were observed in the rock. These alignments, which originally corresponded to laminations enriched in slaty grains, produce incipient alveolar surfaces (Figure 6B,C). In the studied cases, the heating agent is the sunshine, for which reason the term 'insolation weathering' can be used [47]. Effects of thermal expansion due to fire [48] have not been recognised. The effects of lighting fires have only been translated into the formation of blackish patinas with abundant sooty particles;
- (b) Frost weathering as a consequence of successive freeze-thaw cycles. The water present in the rock, whether through the infiltration of meteoric water or through the nocturnal condensation phenomena, is introduced in the rock through weakness planes (fractures, joints, and bedding planes) and may freeze in the winter periods. In many instances, these weakness planes constitute the contact between the superficial alteration rinds and the fresh rock. In this case, the effectiveness of the weathering phenomena is increased by its simultaneous action with chemical and biological weathering processes. The final result is the detaching of large superficial rock flakes (Figure 6D) and the granular disintegration of the rock. Structural (fractures, joints) and textural (laminations, abundance of phyllosilicates) features of the host rock have an effect on its frost resistance and its response to other weathering processes such as salt weathering [49,50]. In the two studied rock groups it was possible to check that the phenomena of formation and shedding of flakes are very common and intense. Nevertheless, it must be stressed that in the Tajo de las Figuras site a greater effectiveness was appreciated as a consequence of the greater thermal oscillation.

5.1.3. Bio-Induced Alteration Processes

The structure of the natural shelters studied favours the colonisation of the surface part of the rock by diverse biological communities, including various colonies of mosses, nitrophilous lichens and blue-green algae, particularly associated with fissures and cracks. The walls with paintings are not much affected. Small black stains observed in the Peñas de Cabrera shelters can be attributed to the activity of fungi [51]. In Tajo de las Figuras shelters a greater profusion of nitrophilous lichens, fungi, and crypto-endolithic cyanobacteria were recognised, particularly in the Cueva del Arco, given the major incidence of direct light on the walls of this shelter. The influence of these organisms on the alteration processes of host rock is much contrasted [52–54]. Previous information has been obtained on the action of lichens both in biochemical alteration processes [55–57] and in the biophysical processes [58,59] of fungi [60,61] and crypto-endolithic cyanobacteria [3,62,63]. The action of micro-organisms on Fe-rich rinds [64] has also been recognised. These biological communities facilitate water adsorption and the maintenance of a certain level of humidity

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and they produce CO₂ and organic compounds which are soluble in water. These waters can accelerate the chemical alteration processes and induce the precipitation of CaCO₃ in the form of thin crusts. In the Tajo de las Figuras site, these lining alteration crusts show great development, which is significantly higher than in the Peñas de Cabrera site. This fact can be related to the high indices of rainfall in the location area with its own more closed shelter structure and possibly with the higher deterioration through anthropic actions (paintings getting wet) presented in this rock group. These crusts have different types of action: (1) covering the rock surface, including the areas where the paintings are present; (2) favouring the retention of oxides from the chemical alteration processes; and (3) favouring the precipitation of salts, such as gypsum, whose crystallization pressure in many cases causes mechanical tensions which aid the flaking of these crusts (haloclasty).

5.2. Human and Aninal-Induced Deterioration Processes

The previous paragraphs focus on the main natural weathering processes detected in the host sandstones. Nevertheless, it is important to emphasise the influence of anthropogenic action on the state of conservation of the paintings. Both in the Tajo de las Figuras and Peñas de Cabrera sites, the signs left by visitors when wetting and rubbing the paintings in order to bring up the chromatic contrasts in the artistic features are evident. This action considerably increases the effect of the wetting-drying cycles of the host rock. The effect produced by the continuous rubbing of the walls and floors is unquestionable; this is particularly noticeable in the floor of the Cueva del Tajo de las Figuras [26–28]. Other deterioration effects resulting from human activity are: (1) fires lit in the shelters, which have caused the rock surfaces to become black; and (2) removal of blocks of sandstone (Figure 7A), which has left despoiled areas where the water accumulates and where organic soils are produced. These actions can considerably favour the natural processes of rock alteration (e.g., shelter 13, Peñas de Cabrera). Animal activity has also caused deterioration both in the host rock and in the paintings. The presence of wasps' nests (Figure 7B) and the influence of birds, bats, goats, and deer is evident with defecations in the interiors of the shelters (Figure 6B) and rubbing against the walls.

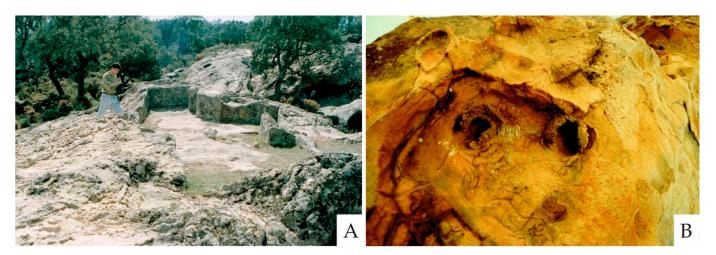


Figure 7. Human and animal-induced deterioration. (**A**) Sandstone excavation near the top of shelters 11 and 13; the floors of these artificial depressions commonly dam water, and the development of organic soils is favoured. (**B**) Wasp nests on the ceiling of the Cueva del Tajo de las Figuras.

6. Discussion and Conclusions

The results of field work and the laboratory analyses showed that the most common mechanisms of alteration in the study area are: carbo-hydrolysis (chemical weathering), frost weathering (mechanical weathering) and bio-induced encrustation (biotic weathering). Other mechanisms such as haloclasty, abrasion, or slaking are considered to be of lesser importance. Haloclasty, combined with other mechanisms, has been interpreted as being

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the most important in coastal environments ([33,34,41,65], among others) and even desert areas [66]. However, in our case study, it is not easy to evoke a source of airborne salts in the form of an aerosol [67,68] because of the long distance to marine waters and industrial centres [69]. The very scarce gypsum crystals in the alteration rind and in the bio-induced crust are due to interstitial fluids which migrate outwards controlled by environmental conditions [67,70]. This is consistent with the existence of levels of gypsum in the underlying facies below sandstones beds [20,25]. Hydro-aeolian abrasion processes participate mainly in the removal of weathering debris in tafoni and alveoli [14,19,40]. Both windblown and water-driven deposits, including organic matter remains and salts, partially cover the shelter surfaces and/or infiltrate through the porous host rock. The slaking phenomena must have more influence on some shelters (e.g., shelter 17), where repeated cycles of wetting and drying facilitate extensive flaking by means of ordered-water molecular pressure mechanisms [47,71].

The similar structural and lithological characteristics of the studied sandstones mean that, qualitatively, the alteration processes that affect them are similar. In this sense, this has only been observed as the presence of a greater proportion of slaty grains in the Peñas de Cabrera sandstones and their separation by thermal weathering processes causes the formation of lines of small alveoli which was not observed in Tajo de las Figuras. However, it was proved that the different climatic conditions in the location of both rock groups directly influence the intensity of physicochemical weathering of sandstones. The Tajo de las Figuras area shows a rainfall index three times higher than in the Peñas de Cabrera area. In addition, the Tajo de las Figuras area has a greater seasonal contrast, with a wider thermal oscillation range and frequent frosts during the winter months. These differences in the climatic features cause the recognised alteration processes and the interaction between them to be more effective in the Tajo de las Figuras rock group, since:

- The greater availability of water leads to greater intensity in the chemical alteration processes. The most obvious effects of which are: (1) a higher degree of alteration in the feldspars, with kaolinite neoformation; (2) a greater development in case hardening processes with the formation of superficial alteration rinds, which are enriched in silica, Al and Fe, and Mg and Mn oxides;
- This hardened rind, a priori, inhibits the development of mechanical erosion processes but favours the retention of the water infiltrated in the new rock-rind contact area. When cracking or flaking occurs, the existence of a discontinuous rind produces differences in the distribution of permeability, humidity, etc., favouring the alteration processes. This is particularly noticeable in the discontinuity planes which constitute the contact areas between the superficial alteration rind and the underlying rock. The latter is generally bleached, relatively poor in cations, such as Si, Al, Fe, and Mn, and is crumbly. These discontinuity planes act similar to preferential water accumulation areas, in such a way that the action of the winter freeze-thaw cycles becomes more effective and the flakes formation and separation phenomena are more common;
- At the same time, the splitting away of the flakes leaves areas of fresh rock once more exposed to chemical alteration;
- The releasing of Ca²⁺ and HCO₃⁻ by the feldspars carbo-hydrolysis favours a greater development of the bio-induced carbonate crusts. This in turn has an incrusting effect and favours the physical and chemical attack processes towards the interior of the rock.

With respect to the rates of weathering, the preservation of rock paintings denotes low rates of weathering, at least in the immediate host rock. Although no data are available in the form of old photographs, for example to quantify the alteration, the existence of hardened rinds lining a large part of the walls of the shelters of alveolar structures on the walls and ceilings of same and biological colonisation are indicative of slow rates of alteration in the shelters [13,36,72]. The rates of alteration would vary as a function of the climatic and geographical contexts and the lithological and geomorphic characteristics of the host rock, generally ranging from microns to a few millimetres a year [13,72–74].

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In the present case, considering both art sites, climate is the most important controlling factor in the rates of alteration as indicated previously. However, considering each shelter separately, the major influence of other local factors can be observed, both in the types and rates of alteration. In this way, it may be stated that in shelters 24 (facing W) and the Cueva del Arco, given that they have a greater effect of natural light, the rates of alteration (in particular, biotic) are relatively greater. On the other hand, in the case of the Cueva del Tajo de las Figuras, the biotic alteration through micro-organisms is restricted, given its nature of a more enclosed shelter. For shelter 17, its closeness to floor level causes the alteration in the lower part to accelerate with regard to the rest of the shelter due to the greater degree of humidity [32].

It is necessary to note that these relatively low rates of alteration correspond to the more recent evolution of the shelters, at least that which is clearly later than the time that the paintings were executed (Epi-Palaeolithic-Neolithic). The genesis of rock shelters probably dates from the humid and glacial cold stages of the Quaternary, when mechanical alteration processes (freeze-thaw cycles) were predominant and the rates of alteration were considerably greater.

The alteration features found in the different shelters mainly correspond to natural physical and chemical phenomena. For this reason, corrective measures are difficult to apply without producing unforeseen consequences. Presently, the state of conservation of the paintings is not bad. Natural weathering processes can be considerably accelerated by both anthropic and animal activity. Anthropic action can be direct (wetting and rubbing against the paintings, lighting of fires) or indirect (removal of blocks of sandstone from the ceilings of the shelters). Large animals can produce alteration by different actions (rubbing, defecation, building of nests, etc.) which are particularly harmful for this type of artwork.

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References

- 1. Chowdhury, A.N.; Punuru, A.R.; Gauri, K.L. Weathering of limestone beds at the Great Sphinx. *Environ. Geol. Water Sci.* **1990**, *15*, 217–223. [CrossRef]
- 2. Saíz-Jiménez, C.; García-Rowe, J.; García del Cura, M.A.; Ortega-Calvo, J.J.; Roekens, E.; Van Grieken, R. Endolithic cyanobacteria in Maastricht limestone. *Sci. Total Environ.* **1990**, *94*, 209–220. [CrossRef]
- 3. Ortega-Calvo, J.J.; Ariño, X.; Hernández-Marine, M.; Saíz-Jiménez, C. Factors affecting the weathering and colonization of monuments by phototrophic microorganisms. *Sci. Total Environ.* **1995**, *167*, 329–341. [CrossRef]
- 4. Zezza, F. Marine spray and polluted atmosphere as factors of damage to monuments in the Mediterranean coastal environment. In Proceedings of the 3th International Symposium on the Conservation of Monuments in the Mediterranean, Venice, Italy, 22–25 June 1994; pp. 269–273.
- 5. Heinrichs, K.; Fitzner, B. Deterioration of rock monuments in Petra/Jordan. In Proceedings of the 9th International Congress of the Deterioration and Conservation of Stone, Amsterdam, The Netherlands, 19–24 June 2000; Volume 2, pp. 53–61.
- Paradise, T.R. Sandstone weathering and aspect in Petra, Jordan. Z. Geomorphol. 2002, 46, 1–17. [CrossRef]

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7. Sánchez-Moral, S.; Luque, L.; Cuezva, S.; Soler, V.; Benavente, D.; Laiz, L.; Gonzalez, J.M.; Saiz-Jimenez, C. Deterioration of building materials in Roman catacombs: The influence of visitors. *Sci. Total Environ.* **2005**, 349, 260–276. [CrossRef] [PubMed]

- 8. Sánchez-Moral, S.; Cañaveras, J.C.; Benavente, D.; Fernández-Cortés, A.; Cuezva, S.; Elez, J.; Jurado, V.; Rogerio-Candelaria, M.A.; Saiz-Jiménez, C. A study on the state of conservation of the Roman Necropolis of Carmona (Sevilla, Spain). *J. Cult. Herit.* **2018**, *34*, 185–197. [CrossRef]
- 9. André, M.F.; Etienne, S.; Mercier, D.; Vautier, F.; Voldoire, O. Assessment of sandstone deterioration at Ta Keo temple (Angkor): First results and future prospects. *Environ. Geol.* **2008**, *56*, 677–688. [CrossRef]
- 10. André, M.F.; Voldoire, O.; Roussel, E.; Vautier, F.; Phalip, B.; Peou, H. Contrasting weathering and climate regimes in forested and cleared sandstone temples of the Angkor region. *Earth Surf. Process. Landf.* **2012**, *27*, 519–532. [CrossRef]
- 11. Zhang, J.; Huang, J.; Liu, J.; Jiang, S.; Li, L.; Shao, M. Surface weathering characteristics and degree of Niche of Sakyamuni Entering Nirvana at Dazu Rock Carvings, China. *Bull. Eng. Geol. Environ.* **2019**, *78*, 3891–3899. [CrossRef]
- 12. Campbell, I.A. Classification of rock weathering at Writing-on-Stone Provincial Park, Alberta, Canada. *Earth Surf. Process. Landf.* **1991**, *16*, 701–711. [CrossRef]
- 13. Pentecost, A. The weathering rates of some sandstone cliffs, central Weald, England. *Earth Surf. Process. Landf.* **1991**, *16*, 83–91. [CrossRef]
- 14. Benito, G.; Machado, M.J.; Sancho, C. Sandstone weathering processes damaging prehistoric paintings at the Albarracín Cultural Park, NE Spain. *Environ. Geol.* **1993**, 22, 71–79. [CrossRef]
- 15. Sjöberg, R. Diagnosis of weathering on rock carving surfaces in northern Bohuslän, Southwest Sweden. In *Rock Weathering and Landform Evolution*; Robinson, D.A., Williams, R.B.G., Eds.; Wiley: Chichester, UK, 1994; pp. 223–241.
- 16. Hall, K.; Meiklejohn, I.; Arocena, J. The thermal responses of rock art pigments: Implications for rock art weathering in southern Africa. *Geomorphology* **2007**, *91*, 132–145. [CrossRef]
- 17. Meiklejohn, K.I.; Hall, K.; Davis, J.K. Weathering of rock art at two sites in the KwaZulu-Natal Drakensberg, southern Africa. *J. Archaeol. Sci.* **2009**, *36*, 973–979. [CrossRef]
- 18. Díez-Herrero, A.; Gutiérrez-Pérez, I.; Lario, J.; Cañaveras, J.C.; Benavente, D.; Sánchez-Moral, S.; Alonso-Azcárate, J. Analysis of potential direct insolation as a degradation factor of cave paintings in Villar del Humo, Cuenca, Central Spain. *Geoarchaeology* **2009**, *24*, 450–465. [CrossRef]
- 19. Peña-Monné, J.L.; Sampietro-Vattuone, M.M.; Ariel Báez, W.; García-Giménez, R.; Matía Stábile, F.; Martínez Satgnaro, S.Y.; Tissera, L.E. Sandstone weathering processes in the painted rock shelters of Cerro Colorado (Córdoba, Argentina). *Geoarchaeology* **2022**, *37*, 332–349. [CrossRef]
- 20. Ménanteau, L.; Vanney, J.R.; Zazo, C. Belo et son environnement (Détroit de Gibraltar). Étude physique d'un site antique. Belo II. *Archéologie* **1983**, *4*, 39–221.
- 21. Ripoll, S.; Mas, M.; Torra, G. Grabados paleolíticos en la Cueva del Tajo de las Figuras (Benalup, Cádiz). *Espac. Tiempo y Forma* **1991**, *4*, 111–126. [CrossRef]
- Cabré, J.; Hernández-Pacheco, E. Avance al estudio de las pinturas prehistóricas del extremo sur de España (laguna de Janda),
 Trabajos de la Comisión de Investigaciones Paleontológicas y Prehistóricas. Mus. Nac. Cienc. Nat. 1914, 3, 35.
- 23. Baldellou, V. "II Reunión de Prehistoria Aragonesa": La terminología en el arte rupestre Post-Paleolítico. In *Bolskan Revista de Arqueología Oscense*; Instituto de Estudios Altoaragonenes: Huesca, Spain, 1989; Volume 6, pp. 5–14.
- 24. Breuil, H.; Burkitt, M.C. Rock Paintings of Southern Andalusia. A Description of a Neolithic and Copper Age Art Group; Clarendon Press: Oxford, UK, 1929.
- 25. Barba, A.; Martín, A.; Piles, E. *Memoria del Mapa Geológico de España 1:50,000 de la Hoja nº 1039 de Colmenar*; Instituto Geológico y Minero de España: Madrid, Spain, 1979; p. 88.
- 26. Barroso, C.; Medina, F. El conjunto rupestre de arte post-paleolítico de Peñas Cabreras (Casabermeja, Málaga). *Anu. Arqueol. Andal.* **1989**, *II*, 333–345.
- 27. Rodríguez Guzman, S.; Santana, I.; Martínez, J. La gestión del arte rupestre en Andalucia. Actuaciones en materia de protección y conservación. *Panel Rev. Arte Rupestre* **2001**, *1*, 32–43.
- 28. Mas, M. La Cueva del Tajo de las Figuras (Cádiz); UNED: Madrid, Spain, 2005; 256p.
- 29. Peltier, C. The geographic cycle in periglacial regions as it is related to climatic geomorphology. *Ann. Assoc. Am. Geogr.* **1950**, *40*, 214–236. [CrossRef]
- 30. Geiger, R. Classificação climática de Köppen-Geiger, Great. In *Commons Attribution-ShareAlike 3.0 Unported*; 1936. Available online: https://creativecommons.org (accessed on 12 January 2020).
- 31. ICOMOS-ICS. Illustrated Glossary on Stone Deterioration Pattern. 2008. Available online: http://international.icomos.org/publications/monuments_and_sites/15/pdf/Monuments_and_Sites_15_ISCS_Glossary_Stone.pdf (accessed on 12 January 2020).
- 32. Dragovich, D. The origin of cavernous surfaces (tafoni) in granitic rocks of southern south Australia. *Z. Geomorphol.* **1969**, *13*, 163–181
- 33. Mustoe, G.E. The origin of honeycomb weathering. Geol. Soc. Am. Bull. 1982, 93, 108–115. [CrossRef]
- 34. Mottershead, D.N.; Pye, K. Tafoni on coastal slopes, South Devon, U.K. Earth Surf. Process. Landf. 1994, 19, 543–563. [CrossRef]
- 35. Drever, J.L. The Geochemistry of Natural Waters; Prentice-Hall: Englewood Cliffs, NJ, USA, 1982; 388p.
- 36. Friedmann, E.I. Endolithic microorganisms in the Antartic cold desert. Science 1982, 215, 1045–1053. [CrossRef]
- 37. Berner, R.A. Rate controls of mineral dissolution under earth surface conditions. Am. J. Sci. 1978, 278, 1235–1252. [CrossRef]

Appl. Sci. 2022, 12, 5330 17 of 18

- 38. Martini, I.P. Tafoni weathering, with examples from Tuscany, Italy. Z. Geomorphol. 1978, 22, 4-67.
- 39. Conca, J.L.; Astor, N.M. Capillary moisture flow and the origin of cavernous weathering in dolerite of Bull Pass, Antartica. *J. Geol.* **1987**, *15*, 151–154. [CrossRef]
- 40. Sancho, C.; Benito, G. Factors controlling tafoni weathering in the Ebro Basin (NE Spain). *Z. Geomorphol.* **1990**, 34, 165–177. [CrossRef]
- 41. McBride, E.F.; Picard, D. Origin of honeycombs and related weathering forms in Oligocene Macgno Sandstone, Tuscan coast near Liborno, Italy. *Earth Surf. Process. Landf.* **2004**, *29*, 713–735. [CrossRef]
- 42. Wray, R.A.L.; Sauro, F. An updated global review of solutional weathering processes and forms in quartz sandstones and quartzites. *Earth-Sci. Rev.* **2017**, *171*, 520–557. [CrossRef]
- 43. Ollier, C. Weathering, 2nd ed.; Longman: London, UK, 1984; 270p.
- 44. Warke, P.A.; Smith, B.J. Short-term rock temperature fluctuations under simulated hot desert conditions: Some preliminary data. In *Rock Weathering and Landform Evolution*; Robinson, D.A., Williams, R.B.G., Eds.; Wiley: Chichester, UK, 1994; pp. 57–70.
- 45. Hoerlé, S.; Salmon, A. Microclimatic data and rock art conservation at Game Pass Shelter in the Kamberg Nature Reserve, KwaZulu-Natal. S. Afr. J. Sci. 2004, 100, 340–341.
- 46. Hoerlé, S. Rock temperatures as an indicator of weathering processes affecting rock art. *Earth Surf. Process. Landf.* **2006**, 31, 383–389. [CrossRef]
- 47. Ollier, C.; Pain, C. Regolith, Soils and Landforms; John Wiley & Sons: Hoboken, NJ, USA, 1996; 316p.
- 48. Allison, R.J.; Goudie, A.S. The effects of fire on rock weathering: An experimental study. In *Rock Weathering and Landform Evolution*; Robinson, D.A., Williams, R.B.G., Eds.; Wiley: Chichester, UK, 1994; pp. 1–56.
- 49. Jiménez-González, I.; Rodríguez-Navarro, C.; Scherer, G.W. Role of clay minerals in the physicomechanical deterioration of sandstone. *J. Geophys. Res.* **2008**, *113*, F02021. [CrossRef]
- 50. Cnudde, V.; De Boever, W.; Dewanckele, J.; De Kock, T.; Boone, M.; Boone, M.N.; Silversmit, G.; Vincze, L.; Van Ranst, E.; Derluyn, H.; et al. Multi-disciplinary characterization and monitoring of sandstone (Kandla Grey) under different external conditions. Q. J. Eng. Geol. Hydrogeol. 2013, 46, 95–106. [CrossRef]
- 51. Saíz-Jiménez, C.; Ortega-Calvo, J.J.; de Leeuw, J.W. The chemical structure of fungal melanins and their possible contribution to black stains in stone monuments. *Sci. Total Environ.* **1995**, *167*, 305–314. [CrossRef]
- 52. Saiz-Jimenez, C. Biogeochemistry of weathering processes in monuments. Geomicrobiol. J. 1999, 16, 27–37. [CrossRef]
- 53. Warscheid, T.; Braams, J. Biodeterioration of stone: A review. Int. Biodeterior. Biodegrad. 2000, 46, 343–368. [CrossRef]
- 54. Miller, A.Z.; Sanmartin, P.; Pereira-Pardo, L.; Dionisio, A.; Saiz-Jimenez, C.; Macedo, M.F.; Prieto, B. Bioreceptivity of building stones: A review. *Sci. Total Environ.* **2012**, 426, 1–12. [CrossRef]
- 55. Galván, J.; Rodriguez, C.; Ascaso, C. The pedogenic action of lichens in metamorphic rocks. Pedobiologia 1981, 21, 60-73.
- 56. Cooks, J.; Otto, E. The weathering effects of the lichen *Lecidea aff. sarcogynoides* (Koerb.) on Magaliesburg quartzite. *Earth Surf. Process. Landf.* **1990**, *15*, 491–500. [CrossRef]
- 57. Ariño, X.; Ortega-Calvo, J.J.; Gómez-Bolea, A.; Sáiz-Jiménez, C. Lichen colonization of the Roman pavement at Baelo Claudia (Cádiz, Spain): Biodeterioration vs. bioprotection. *Sci. Total Environ.* **1995**, *167*, 353–363. [CrossRef]
- 58. Moses, C.A.; Smith, B.J. A note on the role of the lichen *Collema auriforma* in solution basin development on a carboniferous limestone. *Earth Surf. Process. Landf.* **1993**, *18*, 363–368. [CrossRef]
- 59. McCarroll, D.; Viles, H.A. Rock-weathering by the lichen *Lecidea auriculata* in an artic alpine environment. *Earth Surf. Process. Landf.* **1995**, 20, 199–206. [CrossRef]
- 60. Friedman, G.M.; Sanders, J.E.; Kopaska-Merkel, D.C. *Principles of Sedimentary Deposits*; McMillan Publishing Company: New York, NY, USA, 1992; 717p.
- 61. Petersen, K.; Kuroczkin, J.; Strzelczyk, A.B.; Krumbein, W.E. Distribution and effects of fungi on and in sandstones. In *Biodeterioration*; Houghton, D.R., Smith, R.N., Eggins, H.O.W., Eds.; Elsevier: London, UK, 1988; Volume 7, pp. 123–128.
- 62. Bell, R.A.; Athey, P.V.; Sommerfeld, M.R. Crytoendolithic algae communities of the Colorado Plateau. *J. Phycol.* **1986**, 22, 429–435. [CrossRef]
- 63. Wu, F.; Zhang, Y.; He, D.; Gu, J.-D.; Guo, Q.; Liu, X.; Duan, Y.; Zhao, J.; Wang, W.; Feng, H. Community structures of bacteria and archaea associated with the biodeterioration of sandstone sculptures at the Beishiku Temple. *Int. Biodeterior. Biodegrad.* **2021**, 164, 105290. [CrossRef]
- 64. Adams, J.B.; Palmer, F.; Staley, J.T. Rock weathering in deserts: Mobilization and concentration of ferric iron by microorganisms. *Geomicrobiol. J.* **1992**, *10*, 99–114. [CrossRef]
- 65. McGreevy, J.P. A preliminary scanning electron microscope study of honeycomb weathering of sandstone in a coastal environment. *Earth Surf. Process. Landf.* **1985**, *10*, 509–518. [CrossRef]
- 66. Mustoe, G.E. Cavernous weathering in the Capitol Reef Desert, Utah. Earth Surf. Process. Landf. 1983, 8, 517–526. [CrossRef]
- 67. Brierly, W.B. Atmospheric sea salts design criteria areas. J. Environ. Sci. 1965, 8, 15–23.
- 68. Skarveit, A. Wet scavenning of sea salts and acid compounds in a rainy coastal area. *Atmos. Environ.* 1982, 16, 2715–2724. [CrossRef]
- 69. Malloch, A.J.C. Salt-spray deposition on the maritime cliffs of the Lizard peninsula. J. Ecol. 1972, 60, 103–112. [CrossRef]
- 70. Winkler, E.M. Stone: Properties, Durability in Man's Environment, 2nd ed.; Springer: New York, NY, USA, 1975; 230p.

Appl. Sci. 2022, 12, 5330 18 of 18

71. Weiss, T.; Siegesmund, S.; Kirchner, D.; Sippel, J. Insolation weathering and hygric dilatation: Two competitive factors in stone degradation. *Environ. Geol.* **2004**, *46*, 402–413. [CrossRef]

- 72. Turkingnton, A.V.; Paradise, T.R. Sandstone weathering: A century of research and innovation. *Geomorphology* **2005**, *67*, 229–253. [CrossRef]
- 73. Gill, E.D. Rapid honeycomb weathering (tafoni formation) in greywacke, S.E. Australia. *Earth Surf. Process. Landf.* **1981**, *6*, 81–83. [CrossRef]
- 74. Matsukura, Y.; Matsuoka, N. Rates of tafoni weathering on uplifted shore platforms in Nijima-Zaki, Boso Peninsula, Japan. *Earth Surf. Process. Landf.* **1991**, *16*, 51–56. [CrossRef]