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Rock, pigments, and weathering. A preliminary assessment of the challenges and potential of physical and biochemical studies on rock art from southern Ethiopia

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ABSTRACT

Over the past decade, physical and chemical analyses have been widely applied to the study of rock art contexts, particularly to examine the composition of rock art paintings and for direct radiometric dating. Different sampling and analytical methods have been applied to rock art from different parts of the world. However, in Africa these analyses are still at an embryonic stage. The results are often problematic in terms of reliability, mainly as concerns the chronology. This is due to a wide range of fossil and active biodegradation processes affecting rock surfaces and pigments; such processes are still widely underestimated. This paper aims to discuss the state of the art of the physical and chemical analyses undertaken on African rock art contexts, and the urgent need to establish protocols and best practices for sampling and analysis. The preliminary results of a new project in southern Ethiopia are presented here as an example of an integrated study of a rock art context, combining Archaeology and Earth Sciences. Preliminary field observations and SEM-EDS analyses, run on samples from two rock shelters in the Borana area, reveal the presence of a complex set of physical, chemical, and biological weathering processes with manifold effects on the rock art evidence.

1. Introduction

Rock art is one of the most fascinating aspects of global cultural heritage, spanning from at least the Upper Palaeolithic to present-day ethnographic contexts (e.g. Whitley, 2011; McDonald and Veth, 2012; David and McNiven, 2018). Rock art tells us as much about the lifestyle of our ancestors and the landscape they settled in as about their symbolic world. The preservation of rock art is also one of the most challenging issues faced by conservation scientists when studying rock paintings and petroglyphs (e.g. Gibbons, 1984; Hygen, 1996; Walderhaug Saetersdal, 2000; Loubser, 2001; Lambert, 2007). The world's rock art is one of the most endangered types of evidence of the past, due to its direct exposure to atmospheric agents and surface processes. In many cases, it was created under different environmental conditions, and is no longer in equilibrium with the present climate (e.g. Hoerle, 2006; Cremaschi et al., 2008; Bednarik, 2012; Darvill and Batarda Fernandes, 2014; Giesen et al., 2014; Zerboni et al., in press). Aside from natural damage, artworks are all too often threatened by human actions related to economic development programs (e.g. oil exploitation, building, mining, intensive agriculture and sudden intense influxes of tourism), undertaken without awareness of cultural issues, or by deliberate vandalism (e.g. di Lernia et al., 2010; Gallinaro et al., 2018; Taruvinga and Ndoro, 2003). African rock art is a paradigmatic example of these problems. The principal concentrations of African rock art are in arid to sub-arid ecological contexts, often in remote areas that are difficult to control and manage.

Many recent papers have attempted to discuss the properties of the pigments used in African rock art galleries in order to (i) assess the presence of ancient organic matter in binder and pigments, (ii) characterize the properties of organic and, where present, non-organic constituents, and (iii) select the fraction to be subjected to radiocarbon dating. Surveying the recent literature on these topics indicated that detailed characterizations of the state of preservation of pigments and studies of the interaction between the rock substrate and pigments are poorly represented. Yet a more in-depth consideration of the preservation of African rock art raises numerous questions: what happened (or is

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happening) to the pigments? Are they weathered or undergoing any kind of diagenesis? Or, on the contrary, are they stabilised for some reason? What type of processes affect the geological supports of rock art? Aside from climate, how do microorganisms influence these processes? Is there any biogeochemical interaction between pigments and the minerals constituting the rock support?

Starting from our recent work on southern Ethiopian rock art in the Yabelo area, this paper offers a preliminary report on the state of preservation of the local rock art galleries, with a special emphasis on the preservation of the rock substrate and evidence of biogeochemical processes acting at the interface between the pigments and the bedrock. We will not attempt a comprehensive assessment of the preservation of rock art at Yabelo, as analyses are still on-going (e.g. Wu et al., 2020). Rather, we intend: (i) to review the state-of-the-art on analytical approaches to characterizing African rock art – with special attention to those not aimed at radiocarbon dating –, and (ii) to propose a protocol for assessing rock weathering and identifying evidence of interaction between pigments, bedrock minerals, and microorganisms, attempting to elucidate the threat posed by physical, chemical, and biological weathering to the preservation of rock art.

2. Brief review of physical and chemical analyses of Africa rock art

The application of physical and chemical analyses to the study of African rock art started in the late 1980s, with the first attempt at radiocarbon dating in South Africa, by van der Merwe et al. (1987).

In over thirty years, a variety of analyses has been applied to investigate three main issues: (i) direct or indirect dating of paintings and petroglyphs; (ii) characterization of pigments; (iii) investigation of weathering and biodegradation. van der Merwe et al. (1987) was followed by a long series of attempts to date paintings and engravings by direct or indirect methods. These include accelerator mass spectrometry radiocarbon dating (AMS-^{14}C) of organic binders or their organic by-products for paintings (e.g. Mazel and Watchman, 1997; Mori et al., 2006; Bonneau et al., 2011, 2017a; 2017b; Pecchioni et al., 2019), organic matter trapped in rock varnish microlayers covering petroglyphs (Zerboni, 2008; Huyge et al., 2001), or optical stimulated luminescence (OSL) dating of sediments covering engravings (Huyge et al., 2011; Mercier et al., 2012). Dating remains the principal and most ambitious aim of scientific analyses applied to rock art, even in studies focused on pigment characterization and degradation (e.g. Conard et al., 1988; Zerboni, 2008; Gomes et al., 2013; Lofrumento et al., 2012).

A systematic survey of the literature in the main international journals allows us to propose a brief overview of the main trends and areas of research. We considered the principal international publications, using the search tools provided by the SCOPUS and ISI Web of Knowledge databases, as well as the various publishers' websites. The literature survey adopted the methodology described in Gallinaro and Biagetti (2016). To ensure that the results were balanced and comparable between the different research areas, we excluded journals focused on specific areas. Out of a total of 223 papers on African rock art, 16% included physical and chemical analyses (Appendix A). It is interesting to observe that the frequencies by area and by area and topics show the same trend (Fig. 1). We grouped the papers into five main macro-regions, based on geographical location: northern, eastern, central, western, and southern Africa. Southern Africa accounted for the highest percentage of papers on rock art (43%) and the most widespread use of physical and chemical analyses (50%), followed by northern (27% and 28%), and eastern Africa (20% and 17%). These percentages reflect the role played by rock art in the different areas, as recently noted (e.g. Smith, 2013; di Lernia, 2018). The investment in research, conservation projects, and the continuity of research on San rock art is not comparable with any other context in Africa (e.g. Smith, 2013). If we break the data down by topic, southern Africa presents the highest variability, with a significant proportion of analyses focusing on weathering and biodegradation processes affecting rock art (Fig. 2). In particular, the research by Prinsloo (2007) and Prinsloo et al. (2008) represents a sort of cornerstone of physical and chemical research on African rock art. For the first time, the weathering of rock faces hosting rock art is investigated as "a complex mechanism encompassing interdependent mechanical, geological, physical and biological processes" (Prinsloo, 2007: 502). Furthermore, the researchers have since begun to take significant care to reduce the impact of the sampling technique (Prinsloo et al., 2008), followed by the experimental use of non-destructive and non-invasive techniques, such as the *in situ* application of Raman spectroscopy (Tournié et al., 2011). More recently, Bonneau et al. (2011, 2012, 2017a, 2017b) have proposed a multi-technique analysis of rock

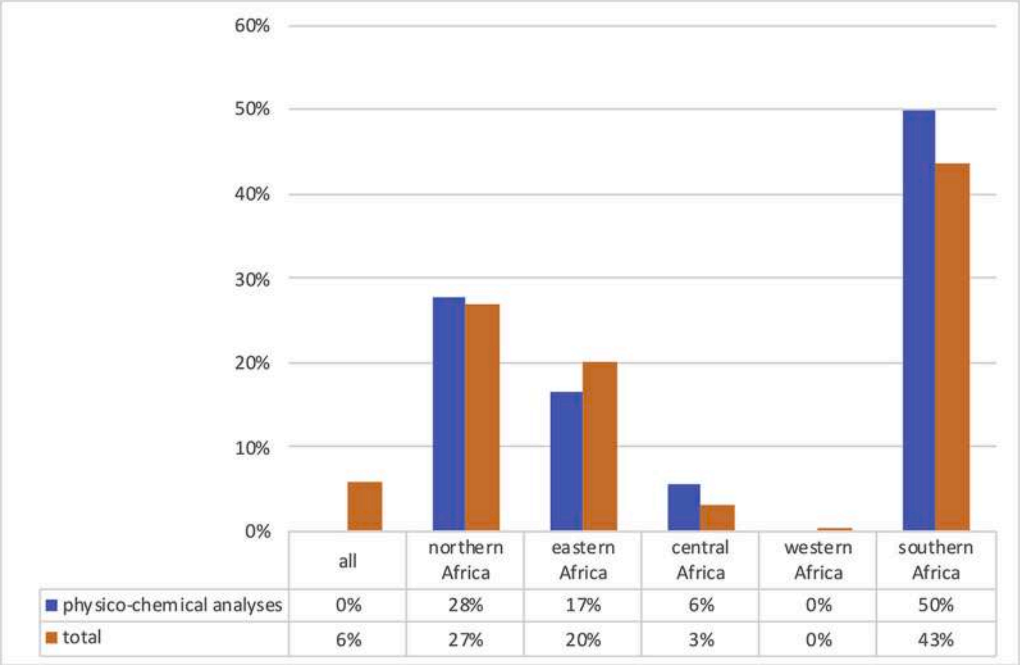
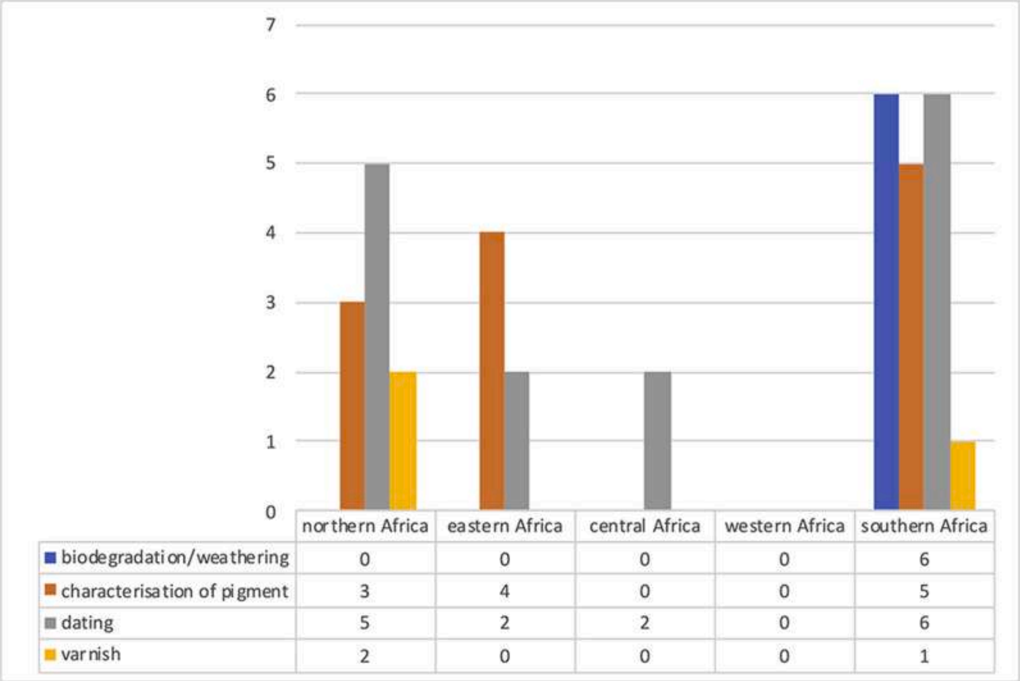


Fig. 1. Distribution of publications on African rock art by area.



	northern Africa	eastern Africa	central Africa	western Africa	southern Africa
🟦 biodegradation/weathering	0	0	0	0	6
🟧 characterisation of pigment	3	4	0	0	5
⬜ dating	5	2	2	0	6
🟨 varnish	2	0	0	0	1

Fig. 2. Distribution of publications with physical and chemical analyses of African rock art by area and sub-topic.

art with a specific sampling procedure, and pre-treatment and analytical protocols aimed at reducing the impact of sampling and isolating the pigment from weathering products (e.g. calcium carbonates, calcium oxalates, or humic acids).

In northern Africa, physical and chemical analyses mainly focused on dating (e.g. Mori et al., 2006; Zerboni, 2012; Huyge et al., 2011; Mercier et al., 2012), and on the characterization of pigments to reconstruct the *chaîne opératoire* in the preparation and use of pigments for parietal rock art (e.g. Darchuk et al., 2011; di Lernia et al., 2016). Only one recent study has approached the problem of the impact of sampling, with the experimental use of Micro-Raman spectroscopy in Western Saharan contexts (Iriarte et al., 2018). This delay is due in part to the political turmoil resulting from the so-called Arab Springs that significantly reduced or completely prevented access to the principal rock art contexts, especially in the Saharan massifs.

Eastern Africa is the third macroarea where physical and chemical analyses have been applied to rock art. Disregarding an initial characterization of pigments on Eritrean samples collected in the 1940s by Graziosi (Zoppi et al., 2002), over the past ten years a few sporadic analyses have been undertaken on single contexts, without a coordinated strategy. They mainly focused on dating and the characterization of pigments, particularly in Ethiopia.

It is clear that a fully integrated approach is far from a standard procedure in rock art studies, and the divide between archaeology, and earth and chemical sciences remains wide.

3. Settings

3.1. Geographic information

The study area is located in the Yabelo woreda, part of the Borana Zone of the Oromia Region, about 600 km south of Addis Ababa (Fig. 3). It lies in a semi-arid ecological zone, with a bi-modal rainfall pattern exhibiting an average annual range of 400–700 mm and a mean annual temperature of c. 19 °C (minimum c. 9 °C and maximum c. 27°), presenting high seasonal variability due in part to the altitude, 450–2500 m above sea level (Coppock, 1994; Sutter, 1995). The past few decades have been characterised by erratic patterns of rainfall and drought, with a strong impact on the availability of natural resources. In the region, the geological bedrock consists of granite intrusions and granitic gneiss, the product of low-grade metamorphism (Clark, 1945; Williams, 2016) belonging to the Adola Belt formations. As a consequence of intense tropical weathering, the local landscape presents an alternation of inselbergs, piles of boulders, tors and large isolated boulders of granite/metagranite. Many rock shelters open into the rocky slopes and at the foot of tors; on investigation, some of these revealed the presence of a human occupation dating from at least the Middle Stone Age (MSA) (Spinapolice et al., 2017; Gallinaro et al., 2018; Carletti et al., in press).

3.2. Background on local rock art

Rock art study in Ethiopia has played a marginal role (e.g. Gallinaro et al., 2018; Negash, 2018) and was substantially ignored in the research area. In 1943, John Desmond Clark rapidly surveyed the area during his military service in East Africa during the Second World War, recording a few very weathered and schematic red paintings (Clark, 1945). Only in the mid-1990s did new studies undertaken by Hundie (2001) locate new rock art sites. However, this evidence remained substantially unpublished and little known until recent years. A new season of research begun in 2016 is revealing an unexpected density of rock art in the area, possibly covering a broad chronological range spanning the last IV millennia BP (e.g. Spinapolice et al., 2017; Gallinaro et al., 2018). The rock art sites recorded in the area during the first two field seasons (2016–2017) consist exclusively of paintings that vary in size, subjects and forms, hosted on the walls of rock shelters or isolated boulders. The recorded artworks present figures and decorative patterns unknown in the area, that are opening up new perspectives for the study of rock art in East Africa and adding significant information on the occupation history of the Middle and Late Holocene. In particular, the presence of potentially different cattle species, both humped and humpless, as in the case of site YAB6, provides important data for the spread of herding in the region. The state of preservation is highly problematic: in some cases the paintings have been damaged by a combination of natural and anthropic processes, whereas at least in the case of site YAB6 the damage seems to result exclusively from natural processes.

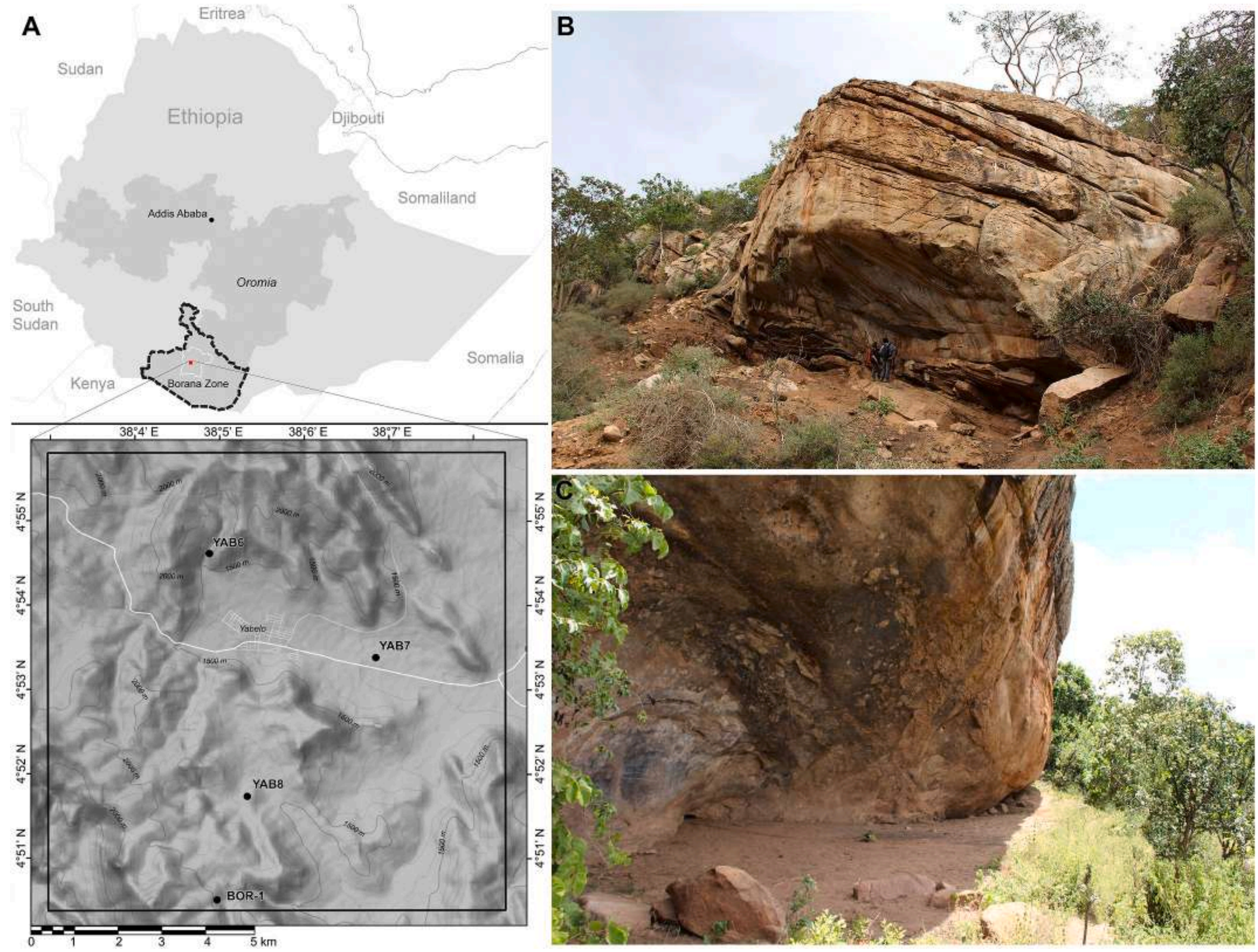


Fig. 3. (A) Map of Ethiopia with the location of rock art sites. (B) View of YAB6 rock shelter. (C) View of BOR-1 rock shelter.

4. Material and methods

To assess the state of preservation of the rock art substrate and its interaction with the pigments we selected two rock shelters, intensively surveyed and recorded: YAB6 and BOR-1 (Fig. 3). YAB6, discovered by Hundie (2001) and known by the local name of Dhaka Kura (Crow's Rock), is located ca. 2 km NW of the town centre of Yabelo. It is the largest of a series of rock shelters opening into an alignment of (meta) granite hills, with a deep cut caused by a stream. The site and the neighbouring area are still intensively frequented by the local communities, including herders and their livestock, thanks to the presence of a well fed by a spring. The site has high potential for archaeological research as well as for conservation and cultural heritage issues (Gallinaro et al., 2018).

The wall and ceiling of the shelter host tens of paintings of differing shape, size, technique and figures. We identified five main panels: three on the main wall and two covering part of the wall and the ceiling. The state of preservation of the panels varies, from figures almost invisible to the naked eye to more visible paintings. The figures are mainly domestic cattle, though wild animals and geometric signs are also present (Fig. 4).

The other site, named BOR-1 by Hundie (2001), is located about 6 km south of Yabelo. The site is a large rock shelter opening at the foot of an inselberg developed on low-grade metamorphic rock. The rock art covers the back wall of the shelter in two main clusters (Fig. 5). Area 1 mainly hosts camels and wild animals (ostriches and giraffes) painted in black; the other large area presents a complex palimpsest of vanished figures and anthropic figures, giraffes and cattle painted in white. In contrast to YAB6, humans have heavily damaged the rock art at BOR-1, and modern graffiti made with charcoal and chalk cover much of the paintings.

We collected very small samples of the rock surface from numerous parts of the shelters and a few pigment samples. To reduce potential damage to the rock art galleries as much as possible, we decided to sample each kind of weathering surface or other damage evident on the rock surface at a distance from the paintings. In a few cases, we collected pigment samples to assess their composition, state of preservation and interaction with the bedrock.

Small samples were removed using a sterile scalpel or small chisel, and preserved in sterile containers. In some cases, we decided to remove weathering products and efflorescence from the rock surface, peeling it off with sterile tape and then preserving it in sterile containers. The same technique was also employed to collect tiny pigment samples. In the laboratory, the samples were subdivided into smaller pieces and observed under the Scanning Electron Microscope (SEM). Subparts of the same samples were preserved for the analysis of the biological fraction using a confocal microscope after selective staining, and (after consolidation) to obtain thin sections for the petrographic optical microscope.

SEM observations employed a Cambridge 360 scanning electron microscope imaging both secondary and back-scattered electrons.

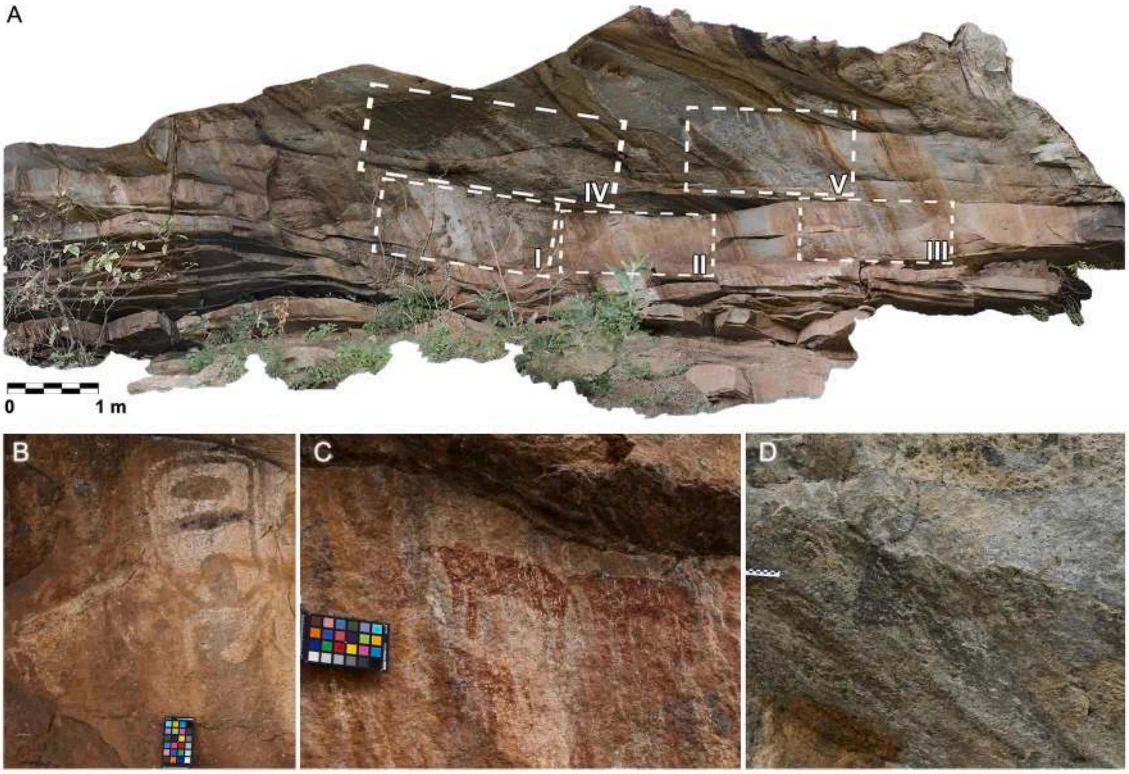


Fig. 4. YAB6 (Dhaka Kura) rock shelter. (A) 3D model of the paintings with the main rock art panels. (B) Detail of panel II with a cow and geometric signs in white. (C) Detail of panel III with red humped cows. (D) Detail of panel IV with a black cow (3D model M. Gallinaro, photos: Italian Archaeological Mission in Southern Ethiopia). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

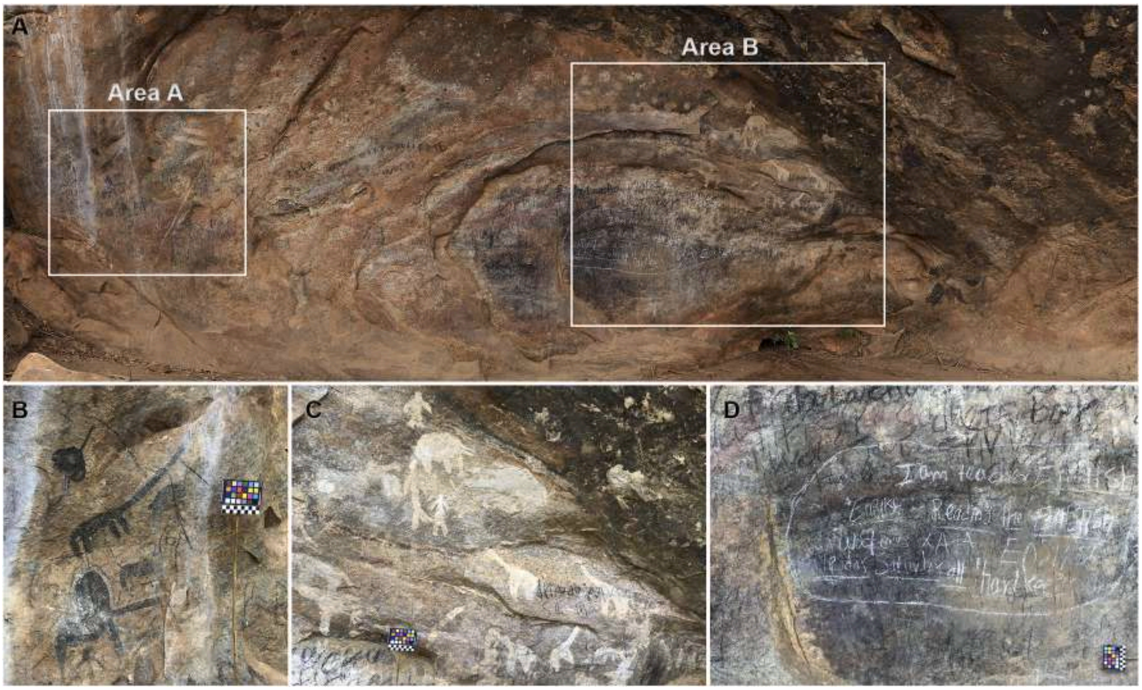


Fig. 5. BOR-1 rock shelter. (A) Panoramic view of the shelter wall with the main painted areas. (B) Detail of Area A with giraffes, ostriches and camels in black. (C) Detail of area B with anthropomorphic figures, giraffes and cattle in white. (D) Modern graffiti. (Photos: Italian Archaeological Mission in Southern Ethiopia).

Energy dispersive X-ray analysis (EDS Link Isis 300) required carbon-coating the samples. Energy dispersive X-ray spectroscopy was done with an accelerating voltage of 20 kV, filament intensity 1.70 A, and probe intensity of 280 pA. Every element analysed was previously standardised using several single element standards (Micro-Analysis Consultants Ltd). Elemental concentrations measured by EDS are reported as oxide weights normalized to 100%. We observed the external and internal parts of samples, and, in some cases, a transverse section.

Peeled pigments and the rock surface were observed after transferring the material removed from the rock surface onto a special carbon-coated tape. All samples were analysed after carbon-coating to allow for EDS measurements, but in specific cases we performed additional observations on gold-covered samples to obtain high-resolution images.

5. Results

5.1. Field observations

The local rock substrate consists of granites and granitic gneiss with a varying degree of metamorphism (Williams, 2016). At both sites, bedrock outcrops display a variety of surface weathering and surface coatings, encompassing almost the entire range of surface processes affecting rocks: physical, chemical, biological weathering and potentially combinations of these.

Generally speaking, weathering processes on crystalline rocks (solutional weathering) are the main factors triggering the formation of the extant landscape. The latter consists of rounded or sub-rounded hills (inselbergs), and residual accumulations of rounded to sub-rounded blocks (jumbles of blocks and tors), partially still covered by weathering products (granitic coarse sand). Rock shelters formed when solutional processes created alcove-type cavities, or due to the accommodation of large, rounded, residual boulders after the removal of weathering products. At the meso-scale, a major difference emerges if we compare the effects of weathering inside and outside rock shelters. The portion of rock shelter outside the drip line appears to be less protected from external agents and displays two different type of weathering resulting in the mechanical disaggregation of minerals. On the one hand, we see granular disaggregation, possibly caused by the local thermal regime and difference in seasonal insolation to rock surface. On the other hand, most rock surfaces outside the rock shelters present a variety of lithobiontic organisms, including epiliths (numerous species of macroscopic lichens), and greenish biofilms in the pore space within the rock (cryptoendoliths). The main effect of epiliths is to enhance granular disaggregation, whereas cryptoendoliths may play a major role in exfoliation.

Surprisingly, inside the drip line of rock shelters the rock surface is more stable, thus permitting the (at least partial) preservation of paintings. Inside the rock shelters, insolation is minimal and the rock walls are almost completely sheltered from rainfall. Locally, humidity is increased by laminar fluxes and percolation along rock cracks and vertical faults. As a consequence, the microclimatic conditions inside rock shelters are less suitable for the growth of lichens. By contrast, in a few cases at YAB6 we noted the presence of weakly developed biofilms related to cryptoendoliths. The internal parts of the rock shelters present evidence of desquamation and exfoliation; these two processes are similar, and a biological contribution to their effectiveness is likely, but the main determinant is the type of rock. Indeed, exfoliation seems to be more intense on granitic gneiss with higher degrees of metamorphism, as at the YAB6 site. Granular disaggregation is less evident inside the rock shelter.

Other processes affect the rock surfaces and are mostly related to the formation of rock coatings and other external disturbances. The latter include the presence of wasps (and other insects) and a whitish efflorescence found at site YAB6. Wasps' nests are built with local soils and in some cases may cover the pigments; their disaggregation leaves semi-cemented daub on the rock walls. The nature of the whitish efflorescence will be discussed in the following section, as field observation did not offer a definitive interpretation. The rock coatings observed consist of whitish, 1–2 mm thick crusts covering large patches of the rock walls, reddish accumulations of Fe-rich oxides along discontinuities and where exfoliation is more intense, and less commonly dark Mn-rich rock varnish evident where there is desquamation (brilliant gray coatings below desquamation flakes). On rock shelves formed along discontinuities, the uppermost surface appears smooth and vitrified as it is covered with glossy precipitates, and leakage of whitish precipitates from the vitrified surfaces can be observed. These are likely related to the presence of rock hyraces (*Procavia capensis*) and are the consequence of urine precipitation as reported elsewhere in Africa (Prinsloo, 2007).

5.2. Preliminary SEM-EDS analyses

Preliminary SEM observations coupled with EDS chemical characterization of compounds suggested the main properties of the weathering products found on and in the rock support of paintings, and showed the complex interaction between bedrock, pigments and microorganisms. Below, we describe the results of analyses on rock fragments taken from the rock wall and on pigments collected after peeling.

A whitish crust covers much of the rock wall and under the SEM it appears as a continuous coating, with an irregular to smooth surface, occasionally organized as tabular, flat bipyramidal or acicular crystals; in many cases, the crystals seem to be smoothed by successive dissolution events. The coating covers the rock surface and fills discontinuities among mineral grains; in some samples, the coating seems to be multilayered as it accreted after successive events. Some organics are trapped within the crusts, including clearly visible fungal hyphae, likely still living. Chemical analyses suggest that gypsum (or anhydride) is one of the main mineral constituents of the crust (Fig. 6); EDS detected a Ca and S content of up to 40% and 55% respectively. Additionally, other chemical elements are well represented, such as concentrations of Cl and K that can be related to the inorganic phases of urine precipitates (KCl), like those identified in western and southern Africa (Prinsloo, 2007; Mazel et al., 2010). A higher concentration of KCl was observed at YAB6 in correspondence with the whitish efflorescence, whose composition is phosphatic. Under the SEM, the efflorescence consists of ca. 10-μm spheroidal objects, initially interpreted as bacteria, but that are most likely urine precipitates (Fig. 6). The latter appear as concentrations of spheroidal precipitates distributed on a continuous phosphatic crust (Fig. 6). In a few samples from YAB6 and BOR-1, the outer parts of the rock walls present a more complex configuration, alternating different mineral coatings and organic remains. Specifically, the SEM-EDS analyses detected a discontinuous gypsum coating alternating with small mineralizations with tabular, acicular, or lamellar crystal aggregates (Fig. 6). In the case of the latter mineralization, chemical analyses detected the presence of Ca, K, and S as the major elements, with smaller amounts of P and Mg. P can be related to organic matter, and the mineral fraction consists of calcium and potassium sulphates, such as syngenite or görgeyite. For instance, syngenite is the sulphate double salt found at San rock art sites in southern Africa (Prinsloo, 2007). The Ca content may also suggest the presence of calcium oxalates. In a few cases, organic remains were detected by imaging on top of or among the mineralizations described above. Fungal hyphae in form of elongated filaments and likely other parts of lichens are the most common organic remains; spores, pollens, and remains of arthropods were also found.

Under the scanning microscope, the internal part of the rock wall of the YAB6 rock shelter revealed a complex assortment of *in situ* weathering of minerals, neoformation of minerals, and organic remains (Fig. 7). Moreover, imaging also revealed a close interaction between the mineral and biological components. In situ weathering is evident on exfoliated samples, and mostly affects feldspar and quartz grains, but in many cases crusts of secondary minerals or organic remains cover its effects. Dissolution pits and micro/nano-runnels are present on single crystals, sometimes in the vicinity of encrusting organic matter (for instance the remains of hyphae), alongside more complex types of dissolution features, likely related to solutional processes triggered by microorganisms (Fig. 7). As is common in the weathering of crystals, its effects are mostly evident according to the orientation of cleavage planes. At YAB6, inside the discontinuities of the rock wall, we detected small concentrations of halite in the form of very small cubic crystals, distributed on the surface of quartz grains, and discontinuous coatings of Mn-rich minerals associated with phosphates (Fig. 8). NaCl and Mn-

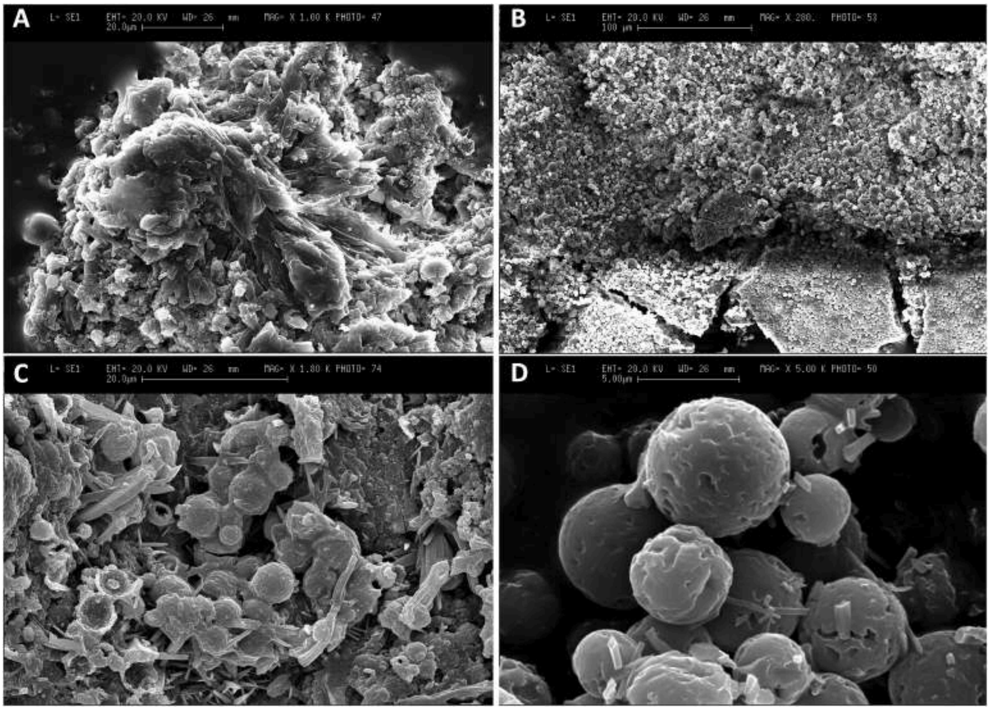


Fig. 6. SEM pictures illustrating crusts formed on the outer surface of the rock wall hosting paintings. (A) Gypsum-rich crust. (B) A carpet of KCl spheroids interpreted as urine precipitates. (C) Urine precipitates embedded in a calcitic and Ca-oxalate crust. (D) Detail of urine precipitates.

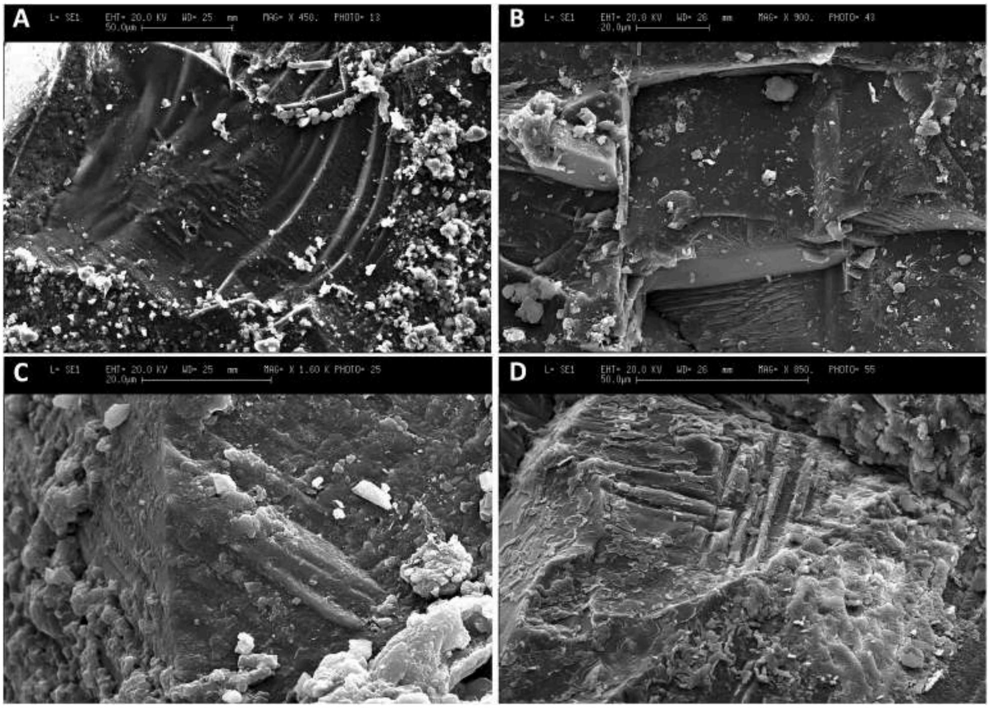


Fig. 7. SEM pictures illustrating the degree of weathering of quartz and feldspar crystals. (A) Solution grooves along the conchoidal feature of a quartz grain. (B) Quartz weathering along fractures. (C–D) Differential etching of feldspar grains forming linear grooves, likely related to lichens (Wilson and Jones, 1983).

bearing crystals are likely mineral neoformations. The most common neoformation of minerals within the rock surface – up to 1 cm inside – consists of flat bipyramidal crystals (Fig. 8) rich in S (24%), Ca (20%), and K (20%), and crusts rich in Ca and S (ca. 40% and 55% respectively) or Ca and P (24% and 15% respectively). The crusts can be interpreted as gypsum (Fig. 8) and phosphate precipitated inside the rock as crystals and possibly weathered onto smoothed crusts. The habit and chemical properties of the bipyramidal crystals (rich in Ca) suggest that they should be attributed to the presence of calcium oxalates. Specifically, the flat bipyramidal and acicular druses have been identified as monohydrate (whewellite) and dihydrate (weddelite) calcium oxalates (Saffo and Lowenstam, 1978; Glasauer et al., 2005; Echigo and Kimata, 2010). Whewellite and weddelite occur extensively in relation to a variety of biomineralization processes, including those driven by fungi and lichens

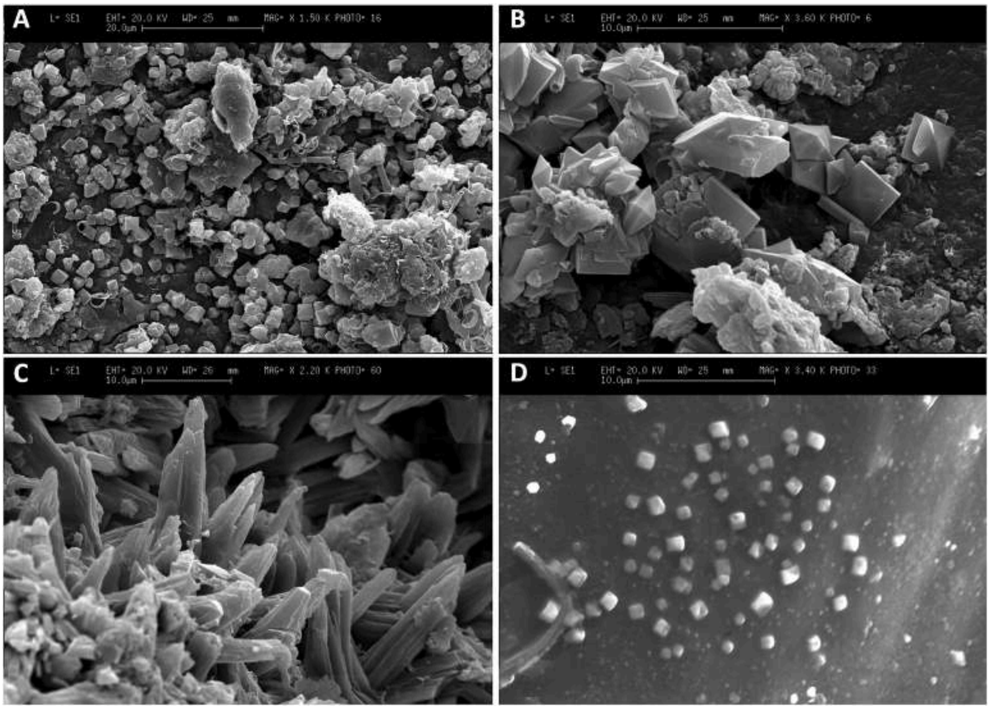


Fig. 8. SEM pictures illustrating mineral neoformation inside the rock surface. (A) A carpet of bipyramidal crystals of calcium oxalate and interspersed plant remains. (B) A detail of well-preserved oxalate crystals. (C) Acicular gypsum crystals. (D) NaCl cubes on the surface of a quartz grain.

as suggested by their interaction with hyphae (Verrecchia et al., 1993; Gadd, 1999), and have also been identified in relation to rock paintings (Watchman, 1993; Russ et al., 1996; Hernanz et al., 2007; Prinsloo, 2007; Bonneau et al., 2012), occasionally associated with gypsum (Russ et al., 1999) as in our case.

The organic matter detected in the inner part of samples mostly consists of the remains of endoliths, and especially fungal hyphae encrusting minerals, tubular and spiral algal structures, and thallus remains (Fig. 9). All remains are closely connected to minerals of the host rocks of newly formed minerals, as in the case of the bipyramidal crystals and surface crusts. The concentration of algae remains is occasionally very high, forming a carpet at the interface between the solid rock and the exfoliation flake (Fig. 9). Smaller organic features such as bacteria are less easy to identify in the samples observed.

Samples peeled from paintings made it possible to remove tiny quantities of pigments for SEM and EDS analyses. At both sites, we collected samples of red and whitish pigments and the underlying rock support or crust. In samples from YAB6 (Fig. 10), for instance, the underlying crust usually dominates and small crystals are detectable only in one case; they are organized into a very fine sheet and chemical analyses detected, beside the dominance of Ca and S due to gypsum and oxalates, a moderate concentration of Si and Fe (Fig. 10). This may suggest that the red pigment is extremely fine and consists of iron oxides; the presence of Si may be related to the presence of quartz and clays, as the local soil is the main source of iron oxides. At YAB6, one of the whitish pigments consists of spheroidal features in a matrix (Fig. 10). The spheroids are very similar to the aforementioned urine precipitates, and chemical analyses detected the presence in the spheroids and the encrusting matrix of dominant Ca. Therefore, we attributed their composition to calcite or at least a mixture of calcite and Ca-oxalates. Calcite, in the form of its polymorph vaterite, is common in the San rock art of southern Africa and may be related to the presence of hyraceum (a mixture of hyrax faeces and urine) (Prinsloo, 2007). As described above, calcium oxalates are by-products of numerous biological processes related to the metabolism of many lithobiontic organisms. In other samples, EDS analysis found abundant phosphates that may have been used in the pigments.

6. Discussion

Fieldwork and laboratory observations revealed a substantial and variegated set of different weathering and bio-chemical actions still active on painted rock surfaces. Based on our experience in the region and in the whole African continent, multiple weathering phenomena affect each site and are the product of the interaction between physical, chemical and biological alteration processes.

At YAB6 and BOR-1 we were able to collect information on many of these processes: on the one hand, bio-physical and bio-chemical weathering of the rock support threatens the stability and preservation of rock art; on the other, the presence of bio-mineralized crusts likely protects the paintings. Processes promoting the physical, chemical, and biological weathering of rock supports are more severe outside the drip line of rock shelters. Inside, insolation and water availability are greater, thus enhancing the intensity of desquamation and disaggregation. The same processes can be observed on a limited scale in the inner part of rock shelters and in general weathering processes are much more evident under the microscope. Likely, the absence of thick organic anthropogenic infilling within the rock shelters prevents or hampers a number of biological processes, which have been identified elsewhere as having a substantial impact on the disaggregation of rock art supports (di Lernia et al., 2016).

The formation of mineral crusts is a further significant feature affecting rock art at YAB6 and BOR-1; the presence of an external crust is evident at both sites, but its role and relationship with the pigments is not completely clear. Indeed, it sometimes seems to cover – and thus protect (?) – the paintings, whereas elsewhere paintings overlap the crust, which appears to form a sort of preparatory layer.

The role of surface processes triggered by microorganisms is likely the most important, but the evidence is evanescent, and its significance can be assessed only under the scanning microscope. SEM observation of rock and pigment samples revealed a very complex interaction between the mineral rock support and microorganisms. The occurrence of

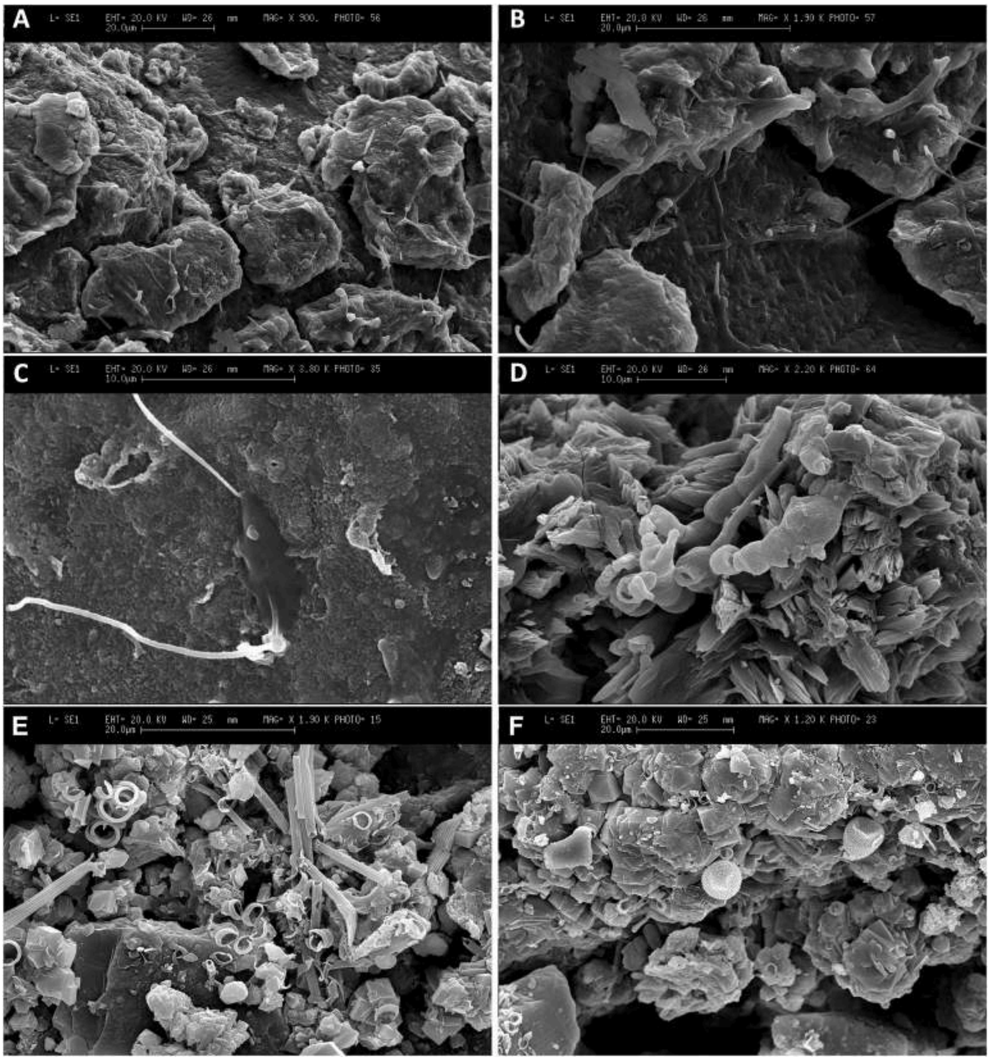


Fig. 9. SEM pictures illustrating biological remains. (A–C) Fungal hyphae growing on crystals; note the presence of mineral precipitates in the vicinity of filaments. (D) Fragment of lichen in gypsum-rich mineral matrix. (E) Algal remains. (F) Pollen grains trapped on the outer part of a Ca-oxalate crust.

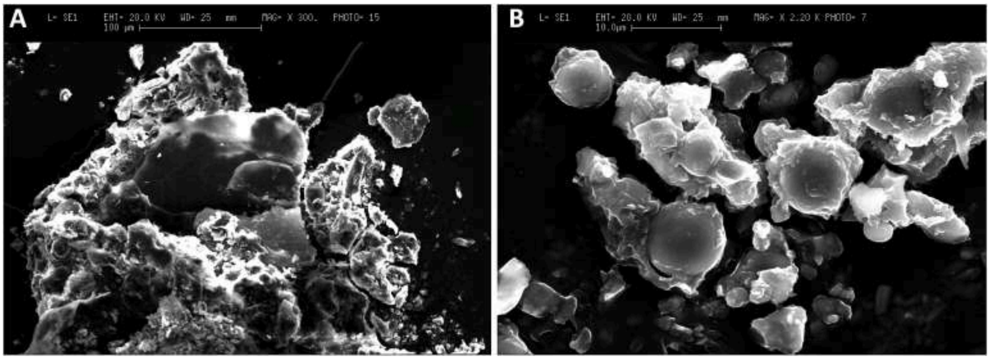


Fig. 10. SEM pictures illustrating examples of small portions of pigments removed with tape. (A) Red pigments consisting of Fe-bearing material. (B) Whitish pigment consisting of a mixture of gypsum and likely hyraceum (note the spheroids similar to those illustrated in figure 6D).

organics is suggested by the presence of a variety of biological remains, the most important of which are fungal hyphae, suggesting that endolithobionts grew here today and/or in the past. Elemental analysis of mineral neoformation from both the sites investigated also confirms the major role played by microorganisms. The systematic presence of Ca-oxalate crystals beneath the rock surface suggests that endolithic lichens and/or fungi actively colonized the walls supporting rock paintings. On the other hand, their existence on the present-day surface may suggest a rejuvenation of the rock surface (for an interpretation of the process see: Mergelov et al., 2012). Further chemical signatures for organic matter are related to peaks in the concentration of P, Ca and S, generally due to the presence of phosphates or P-bearing sulphates (Prinsloo, 2007; Zerboni, 2008), and Cl and K related to the inorganic phases of animal urine precipitates (Prinsloo, 2007; Mazel et al., 2010).

Calcium phosphates associated with oxalates may be related to the presence of endolithic microorganisms, whilst a very interesting observation is the presence of phosphorus sulphates analogous to those identified in San rock art. The presence of these minerals on and within rock supports is likely due to natural processes such as the growth of endolithic communities. Furthermore, the presence of urine precipitates and P-sulphates may be due, as described by Prinsloo (2007), to contamination by the urine and faeces of the rock hyraces (*Procavia capensis*) that still live in the area. The presence of mineral constituents typical of hyraceum detected in the peeled white pigment sample may result from natural contamination, but the occurrence of urine precipitate spheroids interspersed within the Ca-bearing matrix suggests a possible intentional use of hyraceum or other kinds of animal urine as a pigment in rock art, as in the case of San and Dogon rock art (Prinsloo, 2007; Mazel et al., 2010).

These observations raise several fundamental questions that need to be addressed when investigating the role played by biological process in the preservation or deterioration of rock art. What is the principal role of biofilms in rock art conservation? Do biofilms have a negative influence because they degrade pigments and weather the rock support? Or do biomineralized mineral neoformations protect pigments and rock surfaces from severe weathering? How do on-going/fossil biological processes affect our attempts at direct radiocarbon dating of rock art?

To understand the role of biofilms we must consider the presence of extensive biomineralization (oxalates for instance), which has a twofold effect. Oxalates precipitated by endolithic organisms increase the instability of the rock support promoting exfoliation; but once the surface is rejuvenated, they form a surface crust offering protection to the rock surface. Probably, the mineral crusts deriving from hyrax urine and faeces offer the same protection to paintings. From the perspective of radiocarbon dating rock art, our work suggests very intense biological activity within pigments and in the surrounding rock support. As in the case of the biofilms, biological activity may also result in a bidirectional process in terms of organic matter preservation. Microorganisms living in pigments and on/within the rock support may on the one hand decompose pristine organic compounds, but on the other hand, they actively contribute to supplying the system with fresh organic matter. This may result in alternate enrichment or impoverishment of the carbon system that cannot be considered closed and thus reliable for radiocarbon dating. Radiocarbon dating should therefore be preceded by a careful assessment of the quality and quantity of available organics, as suggested for instance by Bonneau et al. (2011). Alternative options for dating Ca-oxalates have been tried (e.g. Watchman, 1993; Mazel and Watchman, 1997 Pecchioni et al., 2019). However, in this case too we need to be aware that the oxalate system is not stable: oxalate crystals can be well preserved or result from multiple episodes of deposition or recrystallized in successive phases. The ^{14}C system within rock art cannot be considered closed without specific investigation of the mineralogy and crystallography of the calcium oxalates.

7. Conclusion

The application of physical and chemical analyses to the study of rock art evidence in Africa is still in an embryonic phase. The primary focus of the analyses performed in different areas of the continent was – and still is – aimed at the chronological issue. However, in recent years a few studies have highlighted the need to change perspective in terms of objectives and sampling procedure, aiming at a multi-analytical investigation of rock art.

Our work on the rock art of southern Ethiopia presents the preliminary results of an integrated approach combining archaeology, geology, biogeomorphological, and paleoenvironmental study, with microscopic, bio-chemical and microbiological analyses. The preliminary results (field observations and SEM-EDS analyses) revealed the complexity and multidirectionality of processes acting on the rock faces hosting rock art and promoting physical, chemical, and biological weathering. Desquamation and disaggregation of the rock supports, the formation of mineral crusts, and microorganisms living in pigments or within the rock support have manifold impacts on rock art, both destructive and protective. Further analyses will make it possible to clarify the role of each process – and its trigger factors – in the current composition of the pigments, as well as on the processes of deterioration or preservation of the artworks.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.quaint.2020.05.056.

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