

1 **Title:**

2 **A critical assessment of the potential and limitations of physicochemical analysis to**
3 **advance knowledge on Levantine rock art.**

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23
24 **Abstract**

25
26 This paper offers an updated review of the variety of physicochemical analysis applied
27 so far to Levantine rock art (Spain) to characterize the composition of the pigments, as
28 well as the substrate and/or the natural coating covering **these particular prehistoric**
29 **paintings. This paper is part of a broader special issue evaluating the real contribution of**
30 **scientific approaches to rock art research, assessing how they have improved our**
31 **understanding of this particular heritage and the new research questions they open. In**
32 **this context, and with a focus on Levantine rock art, our aim is to explore: 1. the guiding**
33 **principles behind the different sorts of analysis conducted and published so far; 2. the**
34 **non-invasive and invasive techniques applied to answer the research questions raised,**
35 **and 3. if the result published as yet have met the expectations of rock art researchers.**
36 **We also reflect on the potential, the limitations and the future developments of this sort**
37 **of studies, as well as on the ethics and desirable protocols of applying invasive**
38 **techniques to this UNESCO World Heritage listed archaeological remain. While the**
39 **focus is Levantine rock art, the discussions raised by this paper and the experiences**
40 **reported in relation to the various techniques used are of global interest, especially when**
41 **dealing with open-air rock art.**

42
43 **Keywords: max. 6 Levantine rock art, prehistoric art, analytical chemistry,**
44 **pigments, binders, crusts**

45
46 **1. Introduction**

47 In the 21st century, archaeometric approaches to rock art are changing the way we
48 understand the materiality of this fragile cultural heritage. The application of analytical
49 chemistry to archaeological research has improved substantially over the last half-
50 century and today it is an essential methodological subfield within archaeological

51 science, becoming a critical part of modern archaeological investigation. Not by chance,
52 archaeology is the study of past human societies through the examination of material
53 remains: it is this focus on material evidence that yields the necessity for scientific
54 approaches to the past (Pollard et al., 2007; Nigra et al., 2015). In rock art research, new
55 approaches to the materialities of art and the analysis of the different stages involved in
56 the process of production or operative sequence (as described by Fiore, 2007), are
57 improving our understanding of what it means to produce art. In the last few decades
58 there has been a growing increase on the use of analytical chemistry to identify pigment
59 procurement practices and sourcing areas (ex. Onoratini, 1985; Couraud, 1988: 22-23;
60 Hameau et al., 1995; Lorblanchet, 1995; Bello and Carrera, 1997; Smith and Pell, 1997;
61 Mooney, Geiss and Smith, 2002; Stafford et al., 2003, Bonneau et al., 2012, Prieto et
62 al., 2016; etc.); the raw materials used, as well as pigment composition, binders and
63 recipes (Watchman, 1990; Montes and Cabrera, 1994; Lorblanchet, 1995: 146; Clottes,
64 1997: 38; Smith et al., 1999; Salomon et al., 2008; Iriarte et al., 2009; Reeves, 2013;
65 Gomes et al., 2013 and 2019, Olivares et al., 2013; Roldan et al., 2013; **Huntley and**
66 **Freeman, 2016**; Brook et al., 2018, **Sepulveda, 2016 and in press**, etc.), technologies of
67 pigment transformation, such as mechanic grinding, heating, shifting, etc. (Bello and
68 Carrera, 1997; Pomies et al., 1999a and b; Guineau et al., 2001: 222; Salomon et al.,
69 2015, etc.) and so forth.

70 Today it is widely accepted that building a systematic knowledge about the
71 materials, instruments and processes involved in rock art production and exploring their
72 continuities and changes over time we can generate knowledge on the technologies and
73 choices of ancient artists and address questions of social dynamics and productive
74 processes not necessarily visible in the more visual characteristics of rock art.
75 Archaeometric approaches to the study of cultural heritage materials, and in this case to
76 rock art, are also important to understand the conservation history of the art (Brunetti et
77 al., 2010; Madariaga, 2015; Mazzeo, 2017), to identify the factors and the taphonomic
78 processes that have facilitated the survival of this ancient legacy to date, as well as those
79 responsible for the degradation threatening the preservation of this heritage. Such an
80 approach is key to anticipate potential risks and to design appropriate preventive
81 measures. In short, they are necessary to secure and improve the future of this
82 vulnerable and singular heritage.

83 In this paper, we explore the use of physicochemical analysis for the study of a
84 particular rock art tradition added to the UNESCO World Heritage list in 1998:
85 Levantine rock art (Fig. 1). This cultural legacy, unique to Mediterranean Iberia, is one
86 of the most singular and fragile artistic phenomena we have inherited from the past in
87 this part of the world, illustrating human practices and behaviours rarely visible in other
88 parts of the archaeological record (Domingo, 2012, 2015). With no other parallels or
89 precedents in Europe, LRA is the only European body of figurative art dominated by
90 narrative scenes, with naturalistic men, women and even children engaged in a wide
91 range of economic, social and cultural activities. They include individual and
92 cooperative hunting of deer, goat, wild boar and bull, as well as battle scenes, marches,
93 dances, representations of pregnancy, birth, maternity, death and so forth. The location
94 in the open air exposes the more than a thousand sites with this particular heritage to the
95 elements and to a wide variety of degrading agents (water, microorganisms, insects,
96 animals and, more damaging, human impacts) (for a recent summary see Rodríguez and
97 Domingo, 2018).

98 This paper aims to provide a general overview on the application of analytical chemistry
99 to archaeological research on this particular art. **Our aim is to** explore to what extent this
100 sort of analyses is contributing to improve our understanding of this rock art tradition,

101 in line with the questions raised in this special issue on the *Impacts of scientific*
102 *approaches on rock art research*. To do so, we summarize the main studies published
103 so far, paying attention to the research questions raised by the authors, the guiding
104 principles behind the different sorts of analysis conducted, the non-invasive and
105 invasive techniques applied to answer the research questions and the results achieved.
106 Finally, we will also discuss other new analytical techniques with potential to contribute
107 to our understanding of the technologies of Levantine rock art.
108 Our final aim is to evaluate to what extent these new interdisciplinary approaches to
109 Levantine rock art are really furthering our knowledge on this particular artistic
110 tradition and if new research questions are opened that we could not even consider
111 before the introduction of these new approaches.

112

113 **2. Analytical chemistry and Levantine rock art: an overview**

114 In the last twenty years, the expanding use of modern analytical techniques applied to
115 Levantine rock art has allowed archaeological research on this particular art to widen
116 the range of knowledge we have so far. Interest on different aspects of the *chaîne*
117 *opératoire* of Levantine rock art (from raw material procurement to techniques and
118 materials involved in rock art production and application) traces its roots back to early
119 studies (Obermaier et al. 1938). However, aside from a few exceptions (Ripoll, 1961;
120 Montes and Cabrera, 1994), during the last century these questions were primarily
121 addressed through experimental archaeology and ethnographic analogy, which were
122 essentially used to suggest potential raw materials and binders, as well as possible tools
123 used for paint application (see a synthesis in Domingo, 2005; Santos da Rosa, 2018).
124 The results of the first physicochemical analysis (Obermaier, 1938; Ripoll, 1961;
125 Montes and Cabrera, 1994) were not very significant or they did not receive the
126 attention deserved at the time. In 1938, Obermaier et al. refer the first spectrographic
127 analysis in the Valltorta-Gasulla complex of sites, one of the most iconic regions
128 containing this rock art tradition. Their only conclusion though was that the colours
129 were fossilised and completely attached to the rock, thus making no progress on our
130 understanding of the pigment nature and composition. Three decades later, in 1961,
131 Ripoll publishes Codina's analysis conducted at la Vacada site (Castellote, Teruel)
132 characterising for the first time the elemental composition of both the pigment (Fe, Al,
133 Mn, traces of Cu and no traces of fatty excipients) and the rock surface (Si, Ca – Sr and
134 Ba-, Mn and Na). More informative was the paper by Montes and Cabrera (1994)
135 identifying for the first time different pigment recipes, the results of which will be
136 further analysed along these lines.

137 A more systematic analytical approach to Levantine rock art occurs as we enter the 21st
138 century. The geographic spread as well as the often remote and difficult location of this
139 rock art tradition certainly constraint the analysis, since non-invasive portable
140 techniques require carrying the instrumentations for on-site operation. They also need a
141 power source, such as a portable generator, thus limiting the type of equipment to be
142 used. The most frequently and effective portable non-invasive spectroscopic methods
143 used so far for the in situ study of Levantine rock art have been energy dispersive X-ray
144 fluorescence (EDXRF) (Roldan et al., 2006, 2007; 2010, 2014; Hernanz et al., 2014;
145 López et al., 2014 and 2017; Pitarch et al., 2014) and micro/Raman spectroscopy
146 (Hernanz et al., 2006, 2007, 2008, 2010, 2014, Mas et al., 2013; Pitarch et al., 2014;
147 Roldán et al., 2014 and 2018; López et al., 2014 and 2017), besides the common use of
148 portable stereoscopic microscope. Energy dispersive X-ray fluorescence (EDXRF)
149 spectrometry is a powerful, compact and commonly used technique for elemental
150 analysis employed on a large variety of materials in the cultural heritage field, offering

151 new opportunities for non-destructive in situ investigations. Roldán et al. were among
152 the first researchers to apply this kind of technique to Levantine paintings (Roldán et al.,
153 2006, 2007 and 2010) (Fig. 2). This technique is appropriate for the qualitative study of
154 high-Z elements in low Z-matrixes, being able to detect chemical elements heavier than
155 Al or Si. However, it also has some limitations. For example, when analyzing
156 multilayer samples, this technique is not able to discriminate between single layers: it
157 detects all chemical elements the X-ray beam encounters on its path without giving
158 information on their distribution across the stratigraphy. Moreover, since it is an
159 elemental technique, other molecular analytical methods have to be used in conjunction
160 if we aim at identifying the nature of the compounds. Assuming the homogeneity of the
161 bedrock, analyses of the Levantine pigments have been based on the comparison
162 between painted and not painted areas in order to highlight differences in the detection
163 of the elements and their relative counts, as well as to characterize the trace elements
164 related only to the paintings (Fig. 3). However, this approach fails when the painting
165 layers are very thin and/or degraded and differences are indistinguishable, as shown by
166 Roldán et al. (2016).

167 Raman spectroscopy is widely used in research on cultural heritage artworks, including
168 both conventional micro-Raman and mobile micro/Raman versions of the technique
169 (Bersani and Lottici, 2016). This vibrational spectroscopic method is fast and non-
170 invasive and it allows the unambiguous identification of a wide range of materials:
171 inorganic and organic pigments, crystalline and amorphous compounds, highly
172 heterogeneous matrixes, thanks to the high space resolution. For these reasons, it is a
173 great tool for the analyses of archaeological objects, and it has been widely used in the
174 study of Levantine rock art, for both the analysis of micro-samples using bench-top
175 setups and on site using portable equipment. The inorganic minerals and pigments
176 composing the bedrocks, pictorial layers, accretions such as calcite, gypsum, hematite,
177 calcium oxalates, etc. of the Levantine paintings are easily identifiable using this
178 vibrational spectroscopy (Burgio and Clark, 2001). Nevertheless, the on site use of
179 micro/Raman portable instrument involves some problems, since Raman spectra
180 collected in situ normally exhibit lower signal-to-noise ratio than the spectra collected
181 in-lab by classical benchtop instruments. In addition, they are also severely affected by
182 sunlight, wind, vibrations, dust, etc. As for sunlight, working at night is not suitable in
183 open-air rock shelters due to the presence of numerous insects over the painted panels.
184 This problem could be potentially solved by covering of the objective head. As an
185 example, Hernanz et al. (2014) suggest the use of an opaque foam rubber tube adapted
186 for their specific micro-Raman portable equipment to solve this issue. Hence, heavy
187 objective lenses, gadgets to cover the external objective, optimizing the focusing, power
188 supply, laser power at the focus position, integration time and the number of spectral
189 accumulations, etc. are some of the factors to be adjusted to eliminate technical
190 limitations and problems involve in on-site working setup. Another complication
191 affecting both on site and benchtop Raman analyses is the presence of crusts and layers
192 of fluorescent materials interstratified with the pigments, since they produce a covering
193 background fluorescence signal that masks the detection of any investigated materials.
194 Moreover, it is important to be careful with laser power when examining micro-samples
195 in which the presence of iron oxides and hydroxides is assumed. It is known the effects
196 of the laser power dependence and associated heating in these kind of compounds (De
197 Faria et al., 1997, Shebanova and Lazor, 2003). Spectral changes and transitions phases
198 between the Fe-oxy/hydroxyes can be produced by increasing the laser power, inducing
199 sample degradation. This fact frequently occurs under intense sample illumination and
200 may lead to misinterpreting the Raman spectra.

201 Portable non-invasive techniques such as these are necessarily the first step of any
202 approach to this fragile cultural heritage, since their non-destructive nature allows the
203 use over extensive surfaces on a virtually infinite number of points, thus providing
204 numerous integrative and representative data. On the contrary, a micro-sample can be
205 representative only of the site where it has been sampled. Furthermore, we have to bear
206 in mind that the number of samples that can be taken is limited, both for ethical and
207 damage reasons (they affect the integrity of the paintings, even when we are now
208 talking about micro-samples). Thus, non-invasive techniques are essential to guide
209 ethically targeted sampling. In addition, when taken, micro-samples should respect the
210 integrity of the motif (sampling from lacunas or borders are preferable) and contribute
211 to deepen the questions arising from previous non-invasive approaches (Fig. 4).
212 Sampling is also necessary to conduct microstratigraphic analysis and identify the
213 different components and layers, which information is of capital importance to better
214 understand and sequencing the paintings and for their protection (Fig. 5). The samples
215 can be investigated in the laboratory using bench-top instrumentations, by
216 non/destructive analytical methods both in micro- and sub-micro scales. Different
217 phases of this ideal approach have been tackled in the study of Levantine rock art and
218 all the analytical methods and methodological procedures used and published so far are
219 reported in Table 1.

220 From this table it is obvious that over the first two decades of this new century,
221 researchers have demonstrated an increasing interest in the study of the pigments and
222 their sources, of use to address questions of mobility and social interaction; the nature of
223 the bedrock surface, raw material transformation and recipes, to identify cultural
224 similarities and differences and potential authors, traditions and schools; the
225 stratigraphic analysis of superimpositions, to identify the order of the paintings events;
226 and the conservation histories and futures of Levantine rock art (table 1). While more
227 pigment analysis than those listed in table 1 have been conducted (for ex. Martínez-
228 Valle, 2002: 200, mentions analysis conducted at la Sarga site, Alcoi; or samples we
229 took at el Carche site, Jalance in 2014), unfortunately many of them are still
230 unpublished.

231 In general terms, while the priority in research on Levantine rock art has been to
232 determine pigment composition, the underlying aims have been to track historical or
233 regional patterns to deduce social and cultural behaviour, and to contribute to better
234 understand the conservation of this art.

235 Two decades later, it is clear that there is no single technique to answer all these
236 questions, so different analytical methods have to be combined. The identification of
237 carbon-based pigment in a black figure is a good example in that regard. The absence of
238 signals related to specific elements of black inorganic pigments such as Mn, Fe, when
239 performing X-ray fluorescence analyses, provides indirect information on the use of an
240 organic-based pigment (as observed by Roldan et al, 2014), the presence of which can
241 be only confirmed by other analytical techniques, among which Raman spectroscopy is
242 one of the most suitable for the identification of these compounds (Coccatto et al, 2015).
243 On the contrary, the latter technique is less efficient for identifying poorly crystallized
244 pigments such as manganese oxides, whose constituent metal is easily detectable by X-
245 ray analysis. This demonstrates that a combination of different techniques may be
246 required to fully understand the processes and materials involved in rock art production
247 and the conservation history of Levantine rock art.

248

249 **3. RESULTS**

250

251 **3.1 The Levantine Palette: Pigments and Binders**

252 The palette of Spanish Levantine artists includes three main colours: red, black and white
253 (Fig. 6). These colours were used to produce mainly monochrome paintings, though a
254 few bichrome paintings (white over red or various red hues) have been also identified
255 (Cabr  1925; Domingo, 2005, 2008 and 2012; Hernanz et al., 2008), **suggesting perhaps**
256 **that this technique was also common but today is underrepresented for conservation**
257 **issues**. While the reasons behind the choice of these nuances are still unknown, whether
258 resulting from specific social rules or from limited access to mineral or organic raw
259 materials, today analytical research has provided a quite complete identification of their
260 components (table 1). Red pigments are mainly composed by iron based oxides or
261 hydroxides, basic compounds of ochers and earths pigments, among which hematite (α -
262 Fe_2O_3) is the most frequently detected in prehistoric Levantine paintings (Table 1). This
263 mineral is an iron (FeIII) oxide present in rocks and soils and it is the principal pigment
264 in red, brown and purple iron oxide-based pigments, known from all cultures usually in
265 the form of hematite-rich earths and/or ochers. Due to its natural abundance, chemical
266 stability and lightfastness, it has been highly employed since prehistoric times as art
267 pigment (Eastaugh et al, 2008). The colour depends on the phase (oxyde, hydroxide...) and
268 crystal size: the hues range from yellowish to red trough several browns.
269 Nanoparticles of hematite lead to red and purple colours or even black for larger crystals
270 (specularite) or for the cementation or the aggregation of very small crystals, as ferricrete
271 dense masses (Schwertmann, 1993).

272 Among the first analytical studies, Montes and Cabrera (1994) investigated the post-
273 Palaeolithic rock art of the Murcia region, carrying out a micro-stratigraphic study of the
274 prehistoric representations. A clay matrix with a composition very similar to an ocher,
275 but more compact and unctuous, as they defined *Bol rojo*, was detected in all the red
276 pigment samples. Moreover, Rold n et al. 2006, 2007, 2010 and 2014 identified *in situ*
277 by portable EDXRF spectrometer the use of various Fe-based pigments (red earths and/or
278 ochres) in the production of the red layers of several figures depicted at *Les Coves de la*
279 *Saltadora* and *Cingle de la Mola Remigia*, both sites belonging to the Valltorta-Gassulla
280 complex of sites (Castell ). The authors concluded that the artists used different raw
281 materials, suggested by the characterization of diverse trace elements found in various
282 red pictograms from the same site. In particular, they detected traces of Mn in some red
283 pigments showing the use of Fe-oxides from different sources as well as the possible
284 intentional addition in one of the figures. Moreover, the identification of traces of As in
285 part of a red deer appeared in agreement with the use of two kinds of red pigments and
286 different phases of execution. On site non-invasive analyses allowed the authors to
287 assume that a complex process of composition lies behind the production of these rock
288 paintings, highlighting possible differences in sources, authors, and execution times.

289 Furthermore, Hernanz et al., 2006, 2008 and 2010 recognized the use of hematite studying
290 several micro-samples belonging to the rock shelters in the Cuenca region. They
291 distinguished three different granular sizes of the mineral (namely, $<1\ \mu\text{m}$ fine, $1\text{--}10\ \mu\text{m}$
292 intermediate and $20\text{--}100\ \mu\text{m}$ gross), evidencing a great technology and ability employed
293 by prehistoric artists during the process of rock art production. Moreover, Raman
294 spectroscopic analyses allowed the authors to achieve structural information regarding
295 the crystallinity of hematite by evaluating the half bandwidth of the Raman bands
296 (Hernanz, 2015). In fact, this spectroscopic technique represents an effective method in
297 the identification of Fe-based pigments (Bersani and Lottici, 2016), narrow Raman bands
298 were observed in well-crystallized hematite (Hernanz et al., 2010), whereas band
299 broadening was observed in impure, amorphous or altered hematite containing other iron
300 oxides and hydroxides (De Faria and Lopes, 2007). These changes in the hematite crystal

301 size could be natural or the result of anthropic manipulation (De Faria and Lopes, 2007).
302 Indeed, it is worth mentioning that hematite is a naturally occurred pigment, but thermal
303 and mechanical processes based on the conversion of hydrated Fe-oxide goethite α -
304 FeOOH (or a goethite containing material such as a yellow ochre) into its crystalline form
305 α -Fe₂O₃, can synthesize it (Cornell and Schwertmann, 2003, González et al., 2000;
306 Cavallo et al., 2018). It has been reported that mechanical dry grinding synthesis produces
307 an important reduction in particle size with respect to thermal treatments (González et al.,
308 2000). Furthermore, hematite can be generated by heating goethite at temperatures below
309 850–900°C, when it undergoes dehydration and crystalization (Pomies et al., 1999;
310 Gialanella et al., 2011). However, heating is not the only agent able to produce hematite
311 since de Faria and Lopes (2007) suggest that biodegradation and weathering can produce
312 the same effect. In addition, the colour changes (from brown-red to deep purple-violet)
313 induced in the hematite by increasing the firing temperature during its thermal synthesis
314 have been attributed to the increase of its grain size; minor colour modifications are
315 observed in natural yellow ochers with high argillaceous content upon firing
316 (Mastrotheodoros, 2010). From an archaeological point of view, the question of whether
317 artists living in prehistoric times have used the red Fe³⁺ oxide in their natural form or after
318 intentional treatments to obtain a desired colour and/or a softer product to be pulverized
319 (Gialanella et al., 2011) is of great interest. Several studies have demonstrated that in most
320 cases, a multi-technical analytical strategy based principally on the use of TEM and XRD
321 techniques can effectively answer these questions (Helwig, 1997, Pomies et al., 1999a
322 and b, Gialanella et al., 2011; Cavallo et al., 2018). As for Levantine rock art, this aspect
323 has not been addressed in depth yet.

324 Again, Hernanz et al. (2008) also identified the presence of apatite in mixture with
325 hematite in the pictorial red layer of some figures from *Sierra de las Cuerdas* (Cuenca).
326 Since phosphates were not detected anywhere in the numerous samples of substrata they
327 analysed and the use of bone implements to grind the pigment does not seemed reasonable
328 to them, considering that Fe-oxide is harder than apatite, the authors hypothesized the use
329 of a specific recipe to prepare the red pigment including powdered hematite and calcined
330 bones as filler. In addition, the authors speculated that such use of an apatite-rich recipe
331 was ritual and the identification of the phosphate compound in some samples belonging
332 to a white painted area of the same site has reinforced this thesis. Moreover, the
333 identification of amorphous carbon mixed with hematite in several red figures also
334 suggested the authors the use of another specific pictorial recipe (Hernanz et al., 2006,
335 2007).

336 Later, Mas et al. 2013 detected concentrations of calcium phosphates in the rock surface
337 besides their identification in the red pigment layer composed by hematite, analysing two
338 micro-samples coming from two red figures from *Minateda* rock shelters (Alpera,
339 Albacete). This finding moved the authors to consider, on the contrary, the presence of
340 apatite as the degradation of shells of invertebrates and fragments of foraminifera,
341 partially replaced by phosphate and not related to any pictorial recipe, rejecting the thesis
342 of a possible ritual. In addition, the authors recognized for the first time the presence of
343 goethite in mixture with hematite from red samples related to Schematic paintings.

344 Another uncommon pigment has been identified at a Levantine shelter, but in the red
345 sample belonging to a schematic figure from *Los Chaparros* shelter (Albalate del
346 Arzobispo, Teruel) by Pitarch et al. (2014). This figure was composed by iron oxides
347 (hematite) in mixture with a Mn- oxide, identified as chalcophanite. This result suggested
348 the authors the use of an intentional pictorial recipe by the schematic artists.

349 Amorphous carbon (charcoal or soot) (Montes and Cabrera, 1994; Hernanz et al., 2010
350 and 2014; Roldán et al., 2014; López et al., 2014 and 2017) and manganese oxides and

351 hydroxides (Roldán et al., 2006; 2007, 2010; Pitarch et al., 2014) are the principal
352 components identified in black Levantine paintings. Carbonaceous matter can be found
353 in nature as geological deposits of graphite and related materials, or can be produced by
354 firing wood (Coccatto et al., 2015). Most natural Mn oxyhydroxides are nanosized and
355 poorly crystalline, especially in soils and sediments, and they exist in various
356 mineralogical forms on the earth's surface (geologists have identified more than 30
357 $Mn_xO_y(OH)_z$). They can be distinguished according to their chemical composition,
358 oxidation degree- Mn^{2+} , Mn^{3+} , Mn^{4+} or mixed- and crystalline structure and some of them
359 are of black shade (Post, 2013). Based on the studies published so far, in Levantine rock
360 art contexts amorphous carbon from vegetal origin occurred more frequently than Mn-
361 based pigments, **contrary to widely held opinions**. This finding appears very interesting
362 from the archaeological point of view: it could be related to a better access to vegetal
363 organic raw material to be burned (Byrne et al., 2013) and to be employed as a black
364 pigment to depict (López et al, 2017). This result also suggests that Levantine prehistoric
365 artists did not use to burn bones in the painting procedures to create black pictograms.
366 López et al. (2017) used an archeobotanical and physicochemical multi-analytical
367 approach to identify very broadly the raw materials used by the prehistoric painters in the
368 production of the black carbon-based pigments, studying several samples coming from
369 the *Les Dogues* shelter (Ares del Maestrat, Castelló). Through the identification of plant
370 cells, they recognized the amorphous carbon belonging to angiosperm (any flowering
371 plants) in one figure and conifer charcoal (including cedars, pines, cypresses, junipers,
372 firs, yews, spruces, among others) in another. While the authors claim that the botanical
373 identification of plants used in the preparation of these black pigments could constitute
374 another effective research line on the understanding of plant resource exploitation by
375 Neolithic communities, their own results (limited identification of very large groups of
376 plants) demonstrated that the grinding process had seriously damaged the charcoal
377 structure, thus “rendering the identification of tissues quite difficult” (López et al.,
378 1917:12/27). At this stage, therefore, the extensive development of this invasive approach
379 should be rejected, unless further experimental approaches demonstrate their potential to
380 go beyond the identification of very large plant groups.

381 Another interesting approach was that of Pitarch et al. (2014) and their analysis of black
382 pigments from Levantine motifs located at *Los Chaparros* shelter (Albalate del
383 Arzobispo, Teruel). They explore the possibility to link the pigments used by the artists
384 with the raw sources available in the surrounding of the rock-shelter. In particular,
385 together with the black sample, they analyzed two additional dark specimens from a black
386 dendrite present in the same rock shelter and another sampled from the *Los Mases de*
387 *Crivillén* mining area, close to *Los Chaparros*. According to the study, the Levantine
388 black figure was composed by Mn oxides/hydroxides whose raw materials corresponded
389 to those identified in the dendrite mineralization of the site. The exact nature of the Mn
390 compound was not identified. The authors highlighted also the analytical difficulties to
391 determinate the specific nature of the Mn oxides/hydroxides by both Raman spectroscopy
392 and X-Ray diffraction when these compounds are a mixture of various poorly crystalline
393 minerals.

394 Finally, to complete the Levantine painting palette, it is interesting to note that
395 descriptions and analysis of white pigments are missing. This colour is not as frequently
396 used as red and black in prehistoric paintings, or at least it is not so well preserved
397 (Beltrán, 1993; Domingo, 2005). In the Levantine context, components like α -quartz,
398 anatase, apatite, muscovite, gypsum and illite were detected in white lines of a bicolour
399 pictographs found in the *Marmalo IV* shelter of *Sierra de las Cuerdas* (Cuenca) by
400 Hernanz et al. (2008). The figure showed many white traces highlighting the perception

401 of the muscles of a red bull. Microstratigraphic investigation showed that the white layer
402 was superimposed on the red pigment. A similar pattern has been previously observed in
403 a couple of sites at Valltorta-Gasulla complex of sites (Civil and Centelles), but in these
404 cases it was used to highlight details and adornments in human figures (Cabr , 1925;
405 Domingo, 2005, 2008 and 2012). In the same red bull, significant amount of amorphous
406 carbon black particles underlying the whitish paints were detected. The authors
407 interpreted them as remains of a previous sketch of the figure made by the artists using
408 charcoal of vegetable origin, as occurred in other prehistoric pictographs in France
409 (Clottes et al., 1990). However, a later work showed that the presence of black-coloured
410 particles could result from the metabolic activities of lichen, fungi, and other
411 microorganisms and could not be exclusively related to an anthropic use as pigment
412 (Darchuk et al., 2009; Mas et al., 2013).

413 Regarding the use and the identification of the binders, not much information is currently
414 available. The common assumption that Levantine pigments were simple
415 solutions/suspensions instead of complex mixtures, since components such as proteins or
416 lipids, which could act as binders, have never been identified, seems no longer appropriate
417 (Montes and Cabrera, 1994). Ethnoarchaeological research has demonstrated that the use
418 of binders plays a significant role in the long-term conservation of the art in the open air,
419 since paintings produced without binders disappear in a few years or decades depending
420 on their exposure (Domingo et al, 2018: 173). Several recent works (Domingo, 2012;
421 L pez et al., 2017; Santos da Rosa, 2018) have shown that prehistoric artists should have
422 used some liquid medium (vehicle) and a binder to suspend inorganic pigments in the
423 creations of their paintings, as well as different kind of brushes to apply such paint
424 mixture to the substrate. Natural carbohydrates, lipids and proteins could have been
425 employed as binding media (from honey, blood, milk, plant resin, etc.), in addition to the
426 potential use of inorganic binders as clay minerals (Hernanz et al., 2008). One of the
427 problems regarding their identification arises by the fact that these organic compounds
428 are actually the basic nutriments of microorganism such as fungi, bacteria, lichens, etc.
429 and they could be fixed into calcium oxalates (Rampazzi, 2019). According to the
430 literature, one of the possible origins of the oxalic acid may be related to the chemical
431 degradation of the organic binding media used for painting due to the feeding and
432 metabolic actions of microorganisms (Spades and Russ, 2005; Mas et al., 2013; Pitarch
433 et al., 2014). Thus, it results doubtful they would have persisted intact on the rock surface
434 since prehistoric times; if any residual amounts are still present, it is often not enough to
435 be detected (Spades and Russ, 2005). Moreover, it has been shown that the presence of
436 metal oxalates can also be correlated directly to the degradation of the lipid media itself,
437 as occurred in extensively deteriorated panels or wall paintings (Salvad  et al., 2013;
438 Sotiropoulou et al. 2015, 2018). They have been considered as final decay product related
439 to the binder degradation mechanism that begins from the auto-oxidation of the fatty
440 content of the binding media, such as egg yolk or drying oil (Sotiropoulou et al. 2018).
441 Thus, it cannot be excluded that the occurrence of Ca-oxalates in proximity of pictorial
442 layer could also be due to aging processes of the binder itself, beyond the action of any
443 microorganisms. Or even more, calcium oxalate could also be produced by the decay of
444 the proteinaceous material of the cell membranes of several microorganisms such as
445 bacteria, fungi, etc. (Rampazzi, 2019). Thus, the presence of calcium (or other metallic)
446 oxalates cannot be directly related with the painting technique.

447 Furthermore, the chemical transformations and aging that the organic residues are
448 expected to have undertaken need to be considered. Generally, lipids of animal and plant
449 origin, as well as plant resins, may survive better than carbohydrates, proteins and
450 nucleotides in archaeological environments due to their lower susceptibility to structural

451 modification and degradation by chemical and microbiological attacks as well as
452 hydrophobicity; degraded lipids in archaeological samples are identified by high
453 concentrations of palmitic (C_{16:0}) and stearic (C_{18:0}) acids (Colombini et al., 2012;
454 Bonaduce et al., 2016). Furthermore, the lack of the organic media detection in the
455 Levantine paint layers can be also related to the limits of the experimental techniques
456 employed for their identification so far. As an example, in situ and laboratory Raman
457 analysis are often frustrated by the fluorescence background signal that frequently occurs
458 during the investigation due to the presence of crusts and layers of fluorescent materials
459 interstratified with the pigments such as naturally fluorescent organic compounds, atomic
460 fluorescence in some minerals, etc. (Smith and Clark, 2004; Hernanz et al, 2014; Bersani
461 and Lottici, 2016). This kind of technical difficulties led the detection of any remaining
462 binders harder. Moreover, among the vibrational spectroscopies, Fourier Transform
463 Infrared spectroscopy (FTIR), both in transmission and reflection configurations,
464 represents an effective and highly suited method in the identification of residual organic
465 matters belonging to the binders, and good results have been also shown elsewhere in
466 rock art micro samples (Rosi et al., 2019; Rosina et al., 2019). Nevertheless, typically
467 liquid/gas chromatographic based-techniques coupled with mass spectrometry, after
468 appropriate sample pre-treatments, represent some of the most commonly and effectively
469 adopted analytical methods in the study of organic materials from archaeological contexts
470 (Pollard et al., 2007; Colombini et al., 2012). Recently, Roldan et al. (2018) have
471 performed a prominent and innovative analytical approach based on the proteomic
472 analyses of some micro-samples belonging to Les Coves de la Saltadora (Coves de
473 Vinromà, Castelló). They used for the first time in Levantine rock art analyses high-
474 throughput sequencing to provide the first description of the bacterial communities
475 colonizing the rock art patina, as well as analyses to determine organic binders. Beyond
476 the identification of the *Firmicutes* bacterial species, that might have a protective effect
477 on the paintings, they also detected casein peptides of animal origin, present both in the
478 pigmented red samples and in one sample taken from a not pigmented area with a reddish
479 patina. The authors conclude that these results could be compatible with the use of animal
480 milk employed as a binding agent in red pigments motifs from *Coves de la Saltadora*. A
481 finding that would be especially significant since, if demonstrated, it would directly relate
482 Levantine rock art to Neolithic populations, closing the debate on the chronology and the
483 lifestyle of the authors. However, they recognize that since it has been also detected in a
484 reddish patina in a not pigmented area, additional and multidisciplinary efforts are needed
485 to confirm whether the casein peptides identified come from modern contaminants or,
486 alternatively, from molecular remains of the binders used. Although they have not still
487 found direct evidence to demonstrate that the discovered casein is not a ubiquitous
488 contemporary contaminant, their results show the potential of the use of proteomics in
489 rock art investigation to contribute to our understanding and knowledge on the technical
490 and socioeconomic aspects of prehistoric Levantine societies.

491

492 **3.2 Bedrock, Crusts and Conservation**

493 A full understanding of the materials used in Levantine rock art paintings is also basic
494 to identify pathologies and conditions not only threatening rock art conservation today
495 but also those that have operated over time to either preserve or destroy this art since it
496 was created. In fact, it is the first step for devising strategies to contribute to the future
497 preservation of this World Heritage. Rock art sites include pigments and binder, but also
498 different sorts of patinas and crusts, usually covering both the painted and not painted
499 surfaces, that we need to understand properly if we aim at progressing in rock art
500 conservation (table1). They are the result of a double process of weathering of the rock

501 substrate and sedimentation due to bioactivity and dust accumulation. If weathering is
502 more active than sedimentation, there is a loss of the surface material and any potential
503 paint would be loss over time. On the contrary, if the biomineralization process is more
504 active than erosion, some new layers of minerals will develop on the paint, protecting
505 them from any erosive process. This is, probably, the main reason explaining how so
506 ancient and fragile layers of paint survived thousands of years in almost open air
507 conditions. Beyond the analysis of the pigments, analytical approaches to rock art also
508 include the analysis of the bedrock, as well as the patinas and alteration products that
509 appear at the rock-pigment-atmosphere interfaces (Roldán, 2013). In fact, rock art
510 located in the open air is constantly threatened by the effect of spontaneous and
511 changeable external environmental conditions (temperature, water, humidity, sunlight,
512 microorganisms, etc.), besides to the aging of its constitutive components. All these
513 factors provoke significant changes in the structure of the bedrock, including physical-
514 mechanical damage in the form of cracks, fractures, loss of cohesion, flaking,
515 pulverizing, etc., that mostly depend on the type of minerals and their intrinsic
516 properties (e.g. mineralogy, texture and structure). Consequently, a comprehensive
517 study of the physicochemical and weathering (from environmental, mechanical,
518 geological and biological causes) phenomena involved in the alteration mechanisms
519 upon which the rock panels are continuously suffering from, allow to monitor and to
520 predict their long-term behaviour. This way, the aim is to minimize and retard their
521 deterioration with the exploration of the most appropriate conservation strategies
522 (Hernanz et al., 2006, 2007, 2008 and 2010, Alloza et al., 2009, del Hollo-Meléndez et
523 al., 2019).

524 The starting point is the examination and characterization of the bedrock used as
525 substrate. While constraint by regional geology, the identification of the constitutive
526 rock minerals and their arrangement (petrography) is important to estimate their
527 deterioration processes and potential pathologies, and it is also crucial in the research of
528 their best conservation measures, as occurs for example when exploring potential
529 consolidating agents and their compatibility with the bedrock (Charola et al., 2007;
530 Otero et al., 2017; Sierra-Fernández et al., 2017; Barreda and Zalbidea, 2019). Three
531 different typologies of bedrock surfaces have been identified in relation to Levantine
532 rock art: limestone (mainly composed by calcite, CaCO_3) (Obermaier, 1938; Roldán et
533 al., 2006, 2007, 2010, 2014; Alloza et al., 2009; Hernanz et al., 2010, López et al., 2014,
534 2017), dolostone (based on dolomite, $(\text{Mg,Ca})\text{CO}_3$) (Montes and Cabrera, 1994), and
535 sandstone (principally constituted of α -quartz, SiO_2) (Ripoll, 1961; Hernanz et al., 2006;
536 2007; 2008). In some shelters, calcite and dolomite were identified together (Mas et al.,
537 2013; Hernanz et al., 2014; Pitarch et al., 2014).

538 Moreover, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and other sulfate salts were identified several times
539 in the pores of the bedrock surfaces as well as of the painting layers of different sites
540 (Hernanz et al., 2006, 2007; 2008; 2010; 2014; Roldán et al., 2006, 2007, 2010; Mas et
541 al., 2013; Pitarch et al., 2014). In particular, their presence was associated with the
542 occurrence of flakes and spallation formations found in various rock shelters, damaging
543 the appreciation both of the painted figures and the rock support. Flake formations are
544 considered as a direct product of the salt weathering processes of the bedrock (Benito et
545 al., 1993; Doehne, 2002; Roldán, 2013). Salts are known to damage porous materials
546 due to the physical stress related to their crystallization in the pores: when water
547 contacts the pore network of a stone, it may carry various salts (Scherer, 2004). Flake
548 accretions were detected both in limestone (Hernanz et al., 2010; 2014) and sandstone
549 (Hernanz et al., 2006, 2007; 2008; 2014) bedrocks in Levantine rock art sites by
550 Hernanz et al. Regardless of the type of substrate, the authors suggested that water from

551 rain, soil moisture, wet areas, etc., dissolves the sulfates, which penetrate into the
552 bedrock due to its porosity. Evaporation in the proximity of the rock surface of the
553 shelters generated gypsum crystals in the pores of the bedrock and close to the surface.
554 The development of flakes can be also produced by the expansion of clay minerals (if
555 they are part of the rock-matrix) when adsorbing water (Vendrell-Saz, M. et al., 1996),
556 even if this aspect has not been explored by the authors. In both cases, humidity–
557 dryness cycles considerably affect bedrock flaking processes. For these reasons, the
558 authors suggested the protection of the painting panels from humidity to preserve and
559 retard the degradation of the rock support from this type of alteration processes. It has
560 been demonstrated that this kind of weathering phenomenon highly depends on the
561 environmental and climate conditions under which the shelters are continuously
562 exposed (temperature, sunlight, moisture, rain etc.) and on the nature of the bedrock
563 itself (mineralogical composition, texture, porosity, capillarity etc.) (Doehne, 2002;
564 Benito et al., 1993). However, it should be reported the option of a contextual biological
565 origin of these sulphate salts (especially in the case of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), baryte
566 (BaSO_4) and celestite (SrSO_4)), as well as superficial carbonates, even such aspect has
567 never been taken into account by the authors. In fact, bio-mineralization could be an
568 effective and further formation path of these superficial inorganic materials, as widely
569 shown in the literature, and the presence of different kinds of microorganisms have been
570 detected in most of the analysed sites (table 1) (Adamo and Violante, 2000; Rodríguez-
571 Navarro et al., 2012; Ngwenya, 2016). It is worth mentioning that limestone and
572 sandstone rocks are both vulnerable to decay, but the synergic effect of both
573 environmental parameters and the specific chemical nature of the rock supports can
574 promote different degradation pathways. As an example, they are both responsive to
575 environmental pollutions even if generally, calcareous stones are more susceptible to
576 deterioration than purely siliceous ones (Sabbioni, 2003; Turkington and Thomas, 2005;
577 Artesani et al., 2020). In particular, any alterations of the chemical equilibrium of the
578 system $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$ in limestones (or any high carbonate content rocks) can induce
579 their dissolution/precipitation. Carbon dioxide dissolves in water with the consequent
580 formation of carbonic acid (H_2CO_3), which is at the base of the dissolution of calcite
581 (CaCO_3). High levels of CO_2 in rainwater promote the dissolution pathways. Moreover,
582 sulphur species contained in the air (dry deposition) or dissolved in rainwater (wet
583 deposition) can affect that equilibrium, leading the subsequent conversion of the calcite
584 to gypsum, $\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$, that often is the responsible of the creation of black crusts
585 (Garcia-Vallès et al., 1998; Sabbioni, 2003; Turkington and Thomas, 2005; Charola et
586 al., 2007; Artesani et al., 2020).

587 For this reason, besides physicochemical analyses, it could be very useful for
588 conservative purposes to constantly monitor the environmental parameters such as
589 moisture, air pollutants, temperature, sunlight, etc. in order to contextualize the
590 analytical results, if possible, also in relation to the climate conditions to which the
591 shelters are subjected. Pitarch et al. (2014), analysing the bedrock surface of the *Los*
592 *Chaparros* shelter (Albalate del Arzobispo, Teruel), constitute by calcite and dolomite,
593 detected also gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and its anhydrous form anhydrite (CaSO_4). Mas et
594 al. (2013) also identified this anhydrous compound on the limestone surface of the
595 bedrock of the *Abrigo del Barranco de la Mortaja*, in *Minateda* rock shelters
596 (Albacete). In both cases, the authors referred the presence of this phase of calcium
597 sulfate to the gypsum dehydration process. According to literature, gypsum and
598 anhydrite are the most abundant sulfate minerals in nature, which solubility and
599 thermodynamic stability are greatly affected by changes in the physical and chemical
600 parameters that occur within common geological environment (Klimchouk, 1996).

601 Thus, a deep knowledge of the rock substrate as well as the environmental conditions
602 under which the rock shelters are exposed could be a key factor to understand the
603 chemical processes that occurred and could be still ongoing on the rock surface.
604 Furthermore, patinas containing calcium oxalates covering open-air rock surfaces were
605 also identified in most of the Levantine sites analysed (Hernanz et al., 2006, 2007, 2008,
606 2010, 2014; Mas et al., 2013; López et al., 2014, 2017; Pitarch et al., 2014¹). Their
607 presence is a widespread decay phenomenon found on stone materials and other
608 substrates (walls, paintings, mortars, glass, etc.), representing one of the most assessed
609 weathering processes (Di Turo et al., 2016; Rampazzi, 2019; Artesani et al., 2020).
610 Calcium oxalates occur in nature in three different crystalline forms: the monohydrate,
611 whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), the dihydrate weddellite ($\text{CaC}_2\text{O}_4 \cdot (2+x)\text{H}_2\text{O}$, $x \leq 0.5$) and
612 the trihydrate, caoxite ($\text{CaC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$). Only the mono/hydrated forms are generally
613 identified in the films. According to literature, the exact variables affecting the
614 prevalence formation of one phase rather than the other are not completely understood:
615 although the most stable form at environmental temperature is the monohydrate, they
616 often are identified together and their distribution is variable and not reproducible
617 (Rampazzi, 2019). Crusts calcium oxalates are recurrently found on the surface of
618 rocks, monuments and buildings and regarding their origin, various possible hypotheses
619 are proposed, as recently summarized by Rampazzi (2019). They could have biological
620 origin, and in this case, the patina is the result of the extensive microorganism
621 colonization due to their metabolic actions; chemical origin, and in this second case the
622 production of the films is considered the final steps of transformation of organic
623 media/binders applied to the stone. Other authors also suggest that the source of oxalic
624 acid derives from the atmosphere, present in the rain (Watchman, 1991), air pollutions
625 (Saiz-Jimenez, 1989), etc.

626 In Levantine rock shelters, both whewellite and weddellite were recognized together in
627 most of the cases (table 1) and their patinas of variable thickness and pigmentation
628 generally cover all the surfaces of the painted figures and bedrocks of the rock panels.
629 They were also detected in the composition of one flake sample, together with gypsum
630 (Hernanz et al., 2006, 2007), belonging to the painting panel of *Cueva del Tío Modesto*
631 shelter, in *Sierra de las Cuerdas* (Cuenca). In addition, in several cases, they were
632 identified interstratified in the painting layers that appear bracketed between two strata
633 of oxalates films (Hernanz et al., 2006, 2007, 2010, 2014; Roldán et al., 2014). In
634 agreement with the analytical investigations, the origin of these accretions of hydrated
635 forms of calcium oxalate on rock surfaces was attributed to the action of
636 microorganisms, as the result of the biological activity of fungi, lichens and bacteria that
637 live and have lived on and within the stone. Fungal hyphae encrusted with small
638 calcium oxalate crystals were recognized by Hernanz et al. using scanning electron
639 microscopy (SEM) in some micro samples from various rock shelters in *Sierra de las*
640 *Cuerdas* (Cuenca) (Hernanz et al., 2006, 2007, 2008), in proximities to which they also
641 detected colonies of the lichen *Verrucaria nigrescens*. The finding of carotenoids
642 (Hernanz et al., 2008), organic compounds characterized by yellowish-orange colour
643 and associated with lichens or bacteria, provided further evidence of the biogenic origin
644 of the crusts. Furthermore, in one sample, the same authors suggested that the fungal
645 hyphae degradation activity is still ongoing since whewellite was recognized up to more
646 than 100 microns inside the rock substratum (Hernanz et al., 2007). Based on the
647 literature, the microorganisms colonize the stone and during their metabolic activities,
648 they could secrete the oxalic acid, a chelating organic acid. This latter in turn reacts and
649 dissolves the Ca-based compounds of the surroundings coming from the bedrock, such
650 as calcite/dolomite, or from the rock surface, like gypsum, leading to fixation of

651 calcium ions in excess and to the precipitation of calcium oxalates (Rampazzi, 2019).
652 When the patinas are associated with the paintings, it cannot be excluded that the
653 occurring calcium oxalates might be also related to the digestion by microorganisms of
654 the organic binder, or to the own degradation process of this latter, independently from
655 their feeding actions (as explained in section 3.1). There is a common assumption that
656 oxalate patinas associated with prehistoric rock art are produced naturally. However,
657 differences of the Ca-oxalates crust characteristics in terms of colour, thickness,
658 location in the rock shelters, could suggest that they might be also formed via various
659 pathways and/or by multiple origins, in which chemical and biological mechanisms
660 could act simultaneously, as occurred on other types of heritage surfaces (Garcia-Vallès
661 et al., 1998). Regardless of their possible origin, from a conservative point of view, the
662 presence of patinas and crusts (that can be formed by calcium oxalates, gypsum, calcite
663 etc.) is strategic. They are characterized by poor solubility in water and high stability
664 against environmental agents and, these factors lead them to be natural protection for
665 the prehistoric paintings, as evidenced also by Hernanz et al. (2007). Although these
666 patinas make the painting pictographs opaque, less visible and appreciable, they have
667 allowed the painting layers to remain quite undamaged over time (fig. 6, middle image).
668 These crusts in fact have resisted to the weathering during thousands of years, as well as
669 in most of the case, they have also been robust to the action of oxalate degrading
670 bacteria that oxidize calcium oxalate into calcium carbonate (Sahin, 2003). This is the
671 case highlighted by Roldan et al, 2018, thanks to the omic analytical approach
672 performed on the patinas of several samples coming from *Les Coves de la Saltadora*,
673 Valltorta-Gassulla Region (Castelló). The analyses showed the presence of different
674 kinds of bacteria: some belonging to the genus of *Bacillus*, producers of oxalic acid,
675 which also generate the calcium oxalates patina on the surfaces. Others from the genus
676 of *Flavobacteria*, known to deteriorate the oxalate patinas as a consequence of calcium
677 carbonates solubilization (Di Bonaventura et al., 1999). From the identification of
678 frequencies and ratios of microbial oxalate producers and degraders that act as
679 protectants or destabilizers, respectively, the authors displayed that in well-preserved
680 samples the ratio *Bacilli: Flavobacteria* was high, suggesting that the bacterial
681 communities in *Coves de la Saltadora* play a predominantly protective role. This kind
682 of analyses have highlighted that microbiome determination can highly contribute to
683 depict informed conservation strategies for Levantine rock art.

684 Another key aspect related to the presence of patinas refers to their occurrence when
685 they are interstratified between the painting layers. Microstratigraphic analyses are
686 essential for this purpose in order to visualize and distinguish the various components of
687 the paints: crusts, depicted pictograms and their possible superimpositions, and
688 bedrocks (fig. 6, middle and bottom images). If two pigment layers are divided by
689 calcium oxalate (or another biogenic patina), a time sequence of events on the rock
690 surface may have occurred. In this way, when achievable, it is possible to delineate a
691 chronological sequence of production of the prehistoric motifs, as suggested by Hernanz
692 et al. for *Cueva del tio Modesto* rock shelter, in *Sierra de la Cuerdas* (Cuenca) (Hernanz
693 et al, 2006, 2007). An initial microorganism's colonization of the surface left the
694 innermost oxalate layer, where the prehistoric artists found the first perfect area to
695 depict. Therefore, a second oxalate layer produced by a new microbial colonization
696 covered the motifs. Subsequent weathering processes can affect the external surface.
697 Furthermore, the layering of carbon-based patinas revealed useful also for dating
698 purposes, using AMS ¹⁴C technique (Ruiz et al, 2006, 2012; Hernanz et al, 2007).
699 Establishing the chronology of open-air rock art still represents one of the main
700 challenges in rock art studies. The paint layer must include some organic matters

701 containing carbon for dating goals. If they were present originally, organic materials
702 must be available and persisted nowadays without exchanging carbon. Moreover,
703 ethical consideration based on the size of samples required to carry out AMS ^{14}C dating
704 may be prohibitive under the present experimental requirements. To overcome these
705 limitations, based on the stratigraphic relationship between painted figures and
706 accretions, patinas have been used as an alternative to pigments for radiocarbon dating,
707 requiring no organic material be present in the paintings, in order to obtain *ante quem*
708 and *post quem* dating values of these layers between which the painted motifs are
709 sandwiched. However, this method is not exempt from questions and issues (Bednarik,
710 2002; Cole and Watchman, 2005; Domingo, 2008: 29; Ruiz et al, 2012). It is based on
711 the presumption that all of the mineralized carbon was derived contemporaneously from
712 the atmosphere by biological processes and that it did not fractionate or change the
713 relative abundances of the three-carbon isotopes (in particular ^{14}C) between the
714 atmosphere and the patina. Moreover, the relationship between the measured age of
715 formation of the crusts and the painting layer event is indirect and it presumes that
716 patinas have formed at regular intervals over a long interval (Cole and Watchman,
717 2005). Furthermore, once deposited, the calcium-rich patinas are not necessarily closed
718 carbon systems, but they may be involved in further alteration processes: rejuvenation
719 through deposition of younger solute, accumulation of organic material from different
720 sources and isotopic exchange or fractionation (Bednarik, 2002). Additional issues are
721 also related to the difficulties occurred during the sampling process in order to sample
722 selectively the layers interested in avoiding any contamination due to other layers
723 and/or components present in them.

724

725 **4. Conclusions**

726 Analytical approaches to Levantine rock art are changing the way we understand the
727 materials, instruments and processes involved in rock art production and preservation,
728 and their change over time, through multidisciplinary research. To rock art this means
729 moving from traditional descriptive analysis of the motifs to reconstruct the creative
730 process or operative sequence (from raw material procurement to rock art production
731 and past and present consumption), as well as to understand how it has survived over
732 millennia.

733 While literature on analytical methods used in **this particular rock art tradition** is still
734 scarce when compared to European Palaeolithic art (ex. Onoratini, 1985; Lorblanchet,
735 1995; Clottes, 1997; Pomies et al., 1999; Smith et al., 1999; Guineau et al., 2001;
736 Salomon et al., 2008 and 2015; Iriarte et al., 2009; Olivares et al., 2013; Roldán et al,
737 2013, etc.), when globally evaluated the analysis conducted so far (including both non-
738 invasive and invasive techniques) are starting to provide interesting results to
739 understand the palette and the practices of Levantine artists. Any stage of the process of
740 production involves socio-cultural decisions and therefore is stylistic in itself (Domingo
741 and Fiore, 2014). Local procurement practices have been detected at *Los Chaparros* site
742 by identifying the pigment sources (Pitarch et al., 2014). The use of different sources
743 has been also deduced through the presence of different trace elements (Mn, As, Pb) at
744 *Coves de la Saltadora* site (Roldán et al. 2007 and 2010) and *Cingle de la Mola*
745 *Remigia* (Roldán et al., 2014), suggesting the participation of different authors, different
746 painting events and even potential diachronic retouching, and thus complex processes of
747 composition. We now know that hematite is the most used material to produce red
748 paintings, while black paintings are produced either from black charcoal or manganese
749 oxides. However, information on white pigments is still missing. We also know that
750 Levantine pigments show different degrees of grain size maybe related to different

751 processing practices, though this aspect requires further analysis to advance knowledge
752 on the technologies of Levantine rock art production. Different pigment recipes are
753 beginning to be identified (Roldán et al. 2010; Hernanz et al., 2008), while
754 unquestionable information on binders and instruments is still missing. With the
755 available data we observe that the variety of mixtures identified in Palaeolithic rock art,
756 seems to disappear in LRA, despite differences in colour hues. Moreover, it is not
757 possible to link yet specific raw materials or recipes to specific styles or regions.
758 Considering the fragility of this cultural legacy and the distinction as both Bien de
759 Interés Cultural by the Spanish Heritage Act and World Heritage by UNESCO, the
760 utilization of non-invasive techniques should be prioritized as a first step. Here after the
761 synergistic and combined use of several analytical methods is the best strategy to study
762 highly heterogeneous matrices, such as those found in rock paintings. The results
763 achieved using portable instrumentations will be necessary to guide sampling that is still
764 required since microstratigraphic studies represent another essential step to advance
765 knowledge on this tradition. Importantly, sampling should be always guided by ethical
766 principles and as such it should only be conducted if research questions cannot be
767 answer with any other methods. As summarized in this paper analytical approaches are
768 also important for conservation purposes: to identify crusts, degradation,
769 microorganisms, and so forth, and ensure compatibility of any introduced materials for
770 rock art conservation. These conservation practices should be guided by policies
771 securing a balance between preservation of scientific and heritage values, giving careful
772 consideration to the fact that any materials introduced (pigments and consolidating
773 materials) or removed (crusts) could impact archaeological approaches to past
774 technologies and practices. Thus, multitechnical, multidisciplinary and collaborative
775 approaches are the key to advance knowledge on rock art production and conservation
776 minimizing impacts on the different values of this and other rock art traditions
777 worldwide.

778

779

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