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RESEARCH ARTICLE

Patinas developed in environmental burial conditions: the Neolithic steles of Reguers de Seró (Lleida, Spain)

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Abstract
Background, aim and scope Weathering patinas in rocks are the result of interaction processes between rock surfaces and atmosphere, biosphere and soil. Therefore, their textural and mineral composition is strongly related to environmental and bioactivity conditions. Whereas the development of weathering patinas in atmospheric conditions is well documented (e.g. typical Mediterranean patina), only very few studies focus on their formation in a burial environment. Our study of patinas developed on the tumular structure of Reguers de Seró deals with the knowledge of burial patinas from a textural and mineralogical point of view. The aims of this study include: (1) the characterisation of the rock used in this megalithic monument as well as inferences regarding the origin of the raw material; (2) the evaluation of the patinas developed on the surface of the carved steles; and (3) the discussion of the environmental conditions (atmospheric or burial) that favoured the development of the patinas.
Materials and methods Whole rock and related patinas (powdered samples and small single pieces) were carefully sampled in five of the seven Neolithic steles discovered during a municipal excavation. Some whole rock samples from the surrounding outcrops were also collected in order to correlate them with the stone forming the megalith. Samples were analysed macroscopically, using a glass binocular, and microscopically, by means of a polarising light microscope and a scanning electron microscope (SEM-EDAX). The mineralogical composition was determined by X-ray diffraction, and a colorimetric analysis was also carried out in all the sampled patinas.
Results The obtained results evidence a strong textural and mineralogical correlation between the whole rock of the megalith and the collected samples of the nearby outcrops; both are classified as calcarenite. A uniformly distributed beige–orange patina (35–100 μm thick) covering the surface of the steles modifies their aspect. A layer of calcite (micrite) with granular texture was detected in all the sampled patinas, being the main mineral compositions (~60–90%). In contrast, a discontinuous external layer (25–50 μm thick) of botryoidally gypsum occurs on only a few patinas. SEM-EDAX analyses evidenced that Ca is related to several processes, including inorganic processes, as well as to minor bioactivity.
Discussion The textural and mineralogical characteristics of the Reguers patinas differ from typical Mediterranean patina sequences, suggesting different environmental conditions for their formation. Several arguments supporting the formation of the Reguers patinas in a burial environment include: (1) patinas cover the entire surface of the steles, iconograhic motifs and fractures. The uniform colour, texture and composition of the patinas throughout the steles suggests their development after the construction of the megalithic tomb during a period in which the

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archaeological site was buried and sealed by the products of the Senill ravine; (2) the absence of heavy metals mainly contained in flying ashes and other depositions from atmospheric dust and pollutants in the micritic patina; (3) non-appearance of minerals directly formed by biological activity (i.e. oxalates and phosphates); (4) the absence of a well-defined textural sequence (typically of the Mediterranean area) already defined for patinas developed in an atmospheric environment; and (5) the discontinuous occurrence of an external gypsum layer (only present in a few samples) without the presence of the typical spherules related to atmospheric particulate matter.

Conclusions and recommendations The petrographic characteristics of the Neolithic steles of Reguers de Seró show that the raw material came from a nearby outcrop. The formation of beige–orange patinas is related to a burial environment attending their textural and mineralogical features. The protective role played by these patinas indicates that no previous treatment of such steles would be necessary on an eventual exhibition in atmospheric conditions. Further in-depth studies, similar to those that already exist for patinas developed in atmospheric conditions, are recommended in order to better define the petrographic characteristics and mechanisms on the formation of patinas in burial environments.

Keywords Weathering patinas · Gravestones · Calcite · Gypsum · Beige–orange crust

1 Background, aim and scope

Interaction between atmosphere–rock, biosphere–rock and soil processes can modify the aspect of rock surface and sometimes its physical behaviour. Such processes occur on monuments, glass and on natural rocks including outcrops and abandoned quarries (Garcia-Valles et al. 1997, 2000, 2002; Urzì and Realini 1998; Urzì et al. 1999; Silvestri et al. 2005; Aulinas et al. 2009). Although in most cases there is only a superficial alteration of the rock, sometimes deeper modifications are present which affect the internal structure of the stones. This new surface is called patina. Generally, in the Mediterranean basin, patina has a sequence type that is formed, from the outer to the inner zone, by recent or present bioactivity and/or biological remains; the gypsum level and calcitic are brown to orange, with silicates and calcium oxalates (Garcia-Valles et al. 1998; Rampazzi et al. 2004). Depending on the original mineral phases, the rock texture, as well as environmental and bioactivity factors, new minerals can be formed. The natural or monumental rocks exposed to atmospheric conditions can also be affected by biological activity (Garcia-Valles et al. 1997, 2002, 2003; Gorbushina and Krumbein 2000; Hoffland et al. 2004). The distinction between physical, chemical and biological mechanisms is not always obvious since the bioactivity can be listed among the general inorganic processes occurring simultaneously with the chemical and physical–chemical reactions. Occasionally, patinas are also attributed to man-made ancient treatments which were applied for protection (e.g. Lazzarini and Salvadori 1989; Martín-Gil et al. 2005; Campos-Suñol et al. 2008).

In nature, the alteration of rocks is the result of different chemical, physical and biological factors and leads to the production of (bio)-mineral (deposition) and/or to erosive processes (i.e. biodeterioration and dissolution), constituting constructive or destructive phenomena, respectively. In both cases, they can have mineral processes (transforming and neoformed mineral phases). Biodeterioration can be considered as adverse changes in the properties or aspects of a material related to the vital activities of living organisms. The effects of these changes on stone or other substrates vary according to mineral composition and crystallographic structure. Dissolution processes have been described in marbles and other carbonate stones. The effect of dissolution is the formation of sulphate and gypsum reaction products, being in many cases accompanied by volume expansions which contribute to the stone deterioration. In most of the cases, such processes have been related to acid rain in urban atmospheres, being less evident in other environmental conditions (Fedema and Meierding 1987; Turkington et al. 2003, André et al. 2008; Toniolo et al. 2009, among others).

Weathering mechanisms and decay of stone surfaces exposed to underground environments have not been studied systematically. However, the action of leaching and/or dissolution processes in buried stones with subsequent recrystallisation seems to play an important role on the generation of weathering patinas in indoor conditions. According to Polikreti and Christofides (2009), for surfaces buried since the antiquity, calcite dissolution affects several crystal layers and reprecipitation forms rather thick secondary calcite layers.

Neoformed phases can develop layers with variable texture and characteristics. In this process, organisms play important roles. In the Mediterranean areas, significant changes in the ecological dynamics of microorganisms colonising rock surfaces occur due to seasonal and environmental variations, and they contribute to mineral deposition. Garcia-Valles et al. (2000) and Garcia-Valles and Vendrell (2002) found that this rate can be correlated with atmospheric climatic changes and that patina developed on the rock surfaces can be used as a possible paleoclimatic parameter.

However, whereas interaction processes between atmosphere and rock are systematically analysed, studies focusing on the development of patinas in burial conditions are still scarce. Most work deals with the weathering characteristics of burial marble surfaces, in which case, the typical burial patina mainly consists of quartz, iron oxides, clay minerals, calcite and dolomite. Moreover, a micritic calcite layer is always present resulting from the dissolution of the outer layer marble crystals in soil water and successive precipitation of secondary calcite (Margolis and Showers 1988; Polikreti 2007; Polikreti and Christofides 2009). Only very few studies deal with the development of patinas in other rock types (e.g. Ilani et al. 2002, 2008).

The tumular structure of Reguers de Seró was discovered by chance in 2007 during the construction of a public infrastructure. The top of the tumulus was buried at a depth of approx. 3 m from the present-day surface (the base at approx. 4 m). The 4-m paleosol mainly consists of claystones, sandstones and gravelstones whose origin is related to an anomalous filling of the Senill Valley, the consequence of an exceptional high energy outflow of the Senill ravine.

The cist, which was constructed around a sepulchral room, has an oval plant of 9 m long and 6 m wide. An apparent random distribution of tombstones used for its building is recognised. However, the northern and eastern parts of the monument show an accurate arrangement with small gravestones used as a paving of the tumular structure with the largest ones piled up vertically or horizontally.

From an archaeological point of view, the tumular cist of Reguers de Seró is a unique and interesting archaeological site contributing to the knowledge of the Iberian Peninsula and European megalithic art. Its cultural identity has no similar referent in the Iberian Peninsula or in the rest of Europe. During the first half of the third millennium BC, it was used as a megalithic tomb (Fig. 1). This chronology is confirmed by the cultural elements observed in the outcropping (bell-shaped ceramics, "V" drilling button, arrow and peduncles, etc.) as well as by C14 dating (López et al. 2010), giving the tumular structure an age of Beta-230406, 4150±50 BP. The exceptionality of this megalith is the presence of carved steles (Fig. 1) whose provenance is related to a previous Neolithic monument. These steles are comparables to European Neolithic and Chalcolithic end age (e.g. Petit-Chasseur, Valais, Switzerland; Saint-Martin-de-Corleans, Aosta, Italy; Arco Trento, Italy; and Rouergue, Aveyron, France). Moreover, the iconograhic motifs observed on the steles (e.g. schematic representations of clothing) allow us to presuppose the existence of a specific cultural group in the zone of Artesa de Segre (Pre-Pyrenees area UTM 343991 4638706). This megalithic monument is located at the Ponts-Calaf anticline (Molassa de Solsona Formation, Oligocene), in the Catalan Central Depression, mainly consisting of marls and limonitic calcareous clays interlayered with sandstones and conglomerates.

According to archaeological studies (López et al. 2010), during the Neolithic period, the steles were exposed to atmosphere conditions with the exception of the parts used to sustain them, which were buried. Just before 4150±50 BP, the steles were reused for the construction of the tumular cist. Some of the steles were modified by "sawing" and repositioning some pieces. The tumulus (and thus the steles) was probably exposed to environmental conditions until the arrival of the high-energy transport of the Senill ravine which buried and sealed the archaeological site until its recent discovery. Therefore, the exposure of the Reguers steles to atmospheric conditions would have been continuous (with the exception of the parts buried to sustain the monuments) until an undated period (<4150 BP), coinciding with the filling of the Senill Valley.

The aims of this study include: (1) the characterisation of the rock used in this megalithic monument as well as the inference on the origin of the raw material; (2) an evaluation of the patinas developed on the surface of the carved steles; and (3) a discussion of the environmental conditions (atmospheric or burial) which favoured the development of the patinas.

2 Materials and methods

2.1 Materials and sampling

The Neolithic carved steles of Reguers de Seró consist of eight rectangular tombstones with rounded spines ranging from 1.1 to 2.3 m in height, 1 to 1.6 m in width and approx. 25 cm thick (Fig. 2a, b). Each stele was fully decorated (front and back sides as well as spine) with iconograhic motifs. Nowadays, such motifs are observable in the inner parts of the steles which were located at the interior of the tumular cist structure. The rest has been strongly eroded, probably as a consequence of environmental conditions. Two of the steles were modified during the construction of the tumular cist as evidenced by the clean cuts on their bases.

In this study, a total of 27 samples were collected from five of the seven carved steles forming the tumular cist of Reguers de Seró. Twenty-three correspond to patinas developed on the surface and four to stone fragments. Three whole rock samples were collected from the surrounding outcrop in order to infer on the origin of the steles (Table 1).

2.2 Methods

Rock description (mineral composition and microtextures of steles and surrounding outcrops) was carried out using a magnifying glass binocular (Nikon SMZ-500) and polar-

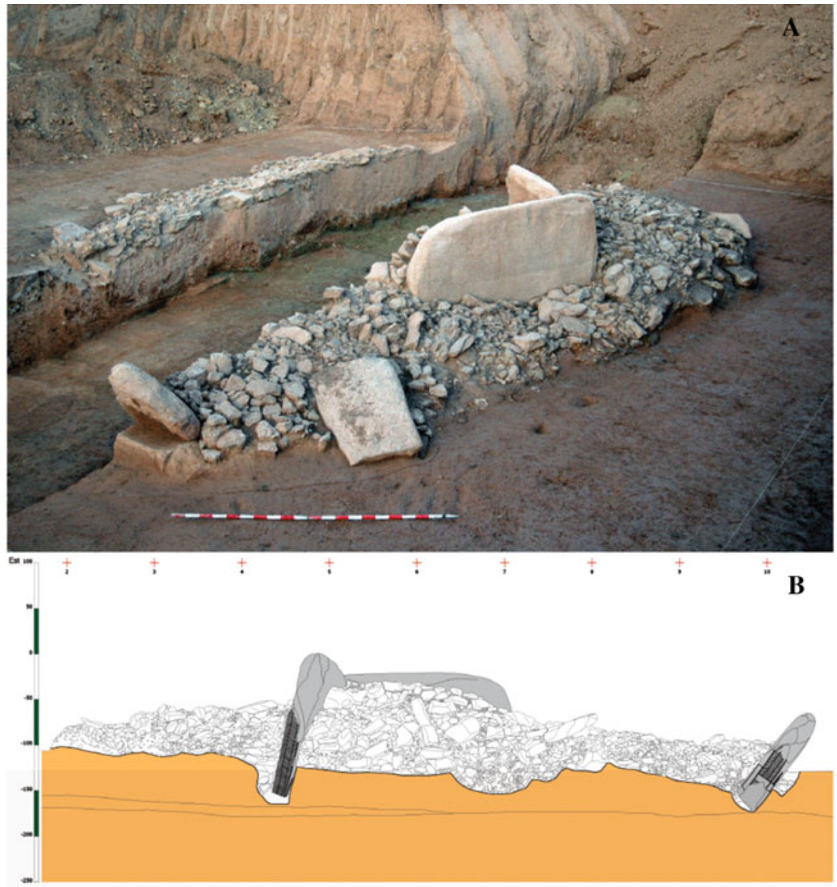

Fig. 1 Tumular cist of Reguers de Seró used as a megalithic tomb

ising light microscopy (Nikon Eclipse LV100pol). Moreover, these samples were also analysed by X-ray diffraction (XRD).

Patina characterisation consisted of collecting powdered samples from the steles by rasping the surface of the patinas with a drill and subsequently analysing them by XRD. Furthermore, small pieces of the patinas were also evaluated through polarising light microscopy (Nikon Eclipse LV100 pol) and scanning electron microscopy (SEM).

XRD analyses were performed using a SIEMENS D-500 X-ray diffractometer. Diffraction patterns in the 4–70 °2θ range were obtained with a 0.017 °2θ step scan and a 50-s counting time. Operating conditions were 40 kV and 30 mA using Cu Kα radiation (1.54061 Å) and a graphite monochromator.

Detailed studies of morphologies and qualitative chemical analysis of patinas were performed on a SEM Jeol JSM-840 and on an ESEM Quanta 200 FEI, XTE 325/D8395. Working conditions were 10 kV and 3×10^{-9} A and 20 kV and 1×10^{-9}, respectively. Samples were mounted on a stub and covered with C (graphite) prior to their study.

Patina colours were also measured. The obtained value of the colour coordinates defines the colour of the surface. The colour parameters were obtained in situ using the colorimetric method based on the CIE (*Commission Internationale de l'Eclairage*) system of colorimetry. These parameters were measured with a Minolta CM-503i spectrophotometer over the visible range (from 400- to 700-nm wavelength range). The spectrophotometer was fitted with a barium sulphate-coated integrating sphere using a standard illuminant C as a light source. The colour coordinates were calculated according to CIE (1976) recommendation using CIE $L^*a^*b^*$, C^* and h for colour space (also referred to as CIEL$^*a^*b^*$ and CIEL$^*C^*h$). A colorimeter is designed to evaluate the colour of a material according to international standards; it measures colour spaces and calculates the chromatic parameters. The employment of a "tristimulus" method is equivalent to the human eye system and always has the same illuminant. Moreover, it always takes measurements under the same instrumental conditions of light source and illumination.

3 Results

3.1 Rock characterisation

The petrographic study of the rocks forming the carved steles and outcrops allowed us to classify them as calcarenite. The steles show an acceptable degree of

Fig. 2 Neolithic carved steles of Reguers de Seró consisting of eight rectangular tombstones

conservation. These sedimentary rocks are made up of sand-sized clasts, mud and sparitic cement. The clasts represent the main petrographic component with angular to subangular monocrystalline quartz, phyllosilicates, rock fragments with different degrees of roundness (quartzites and schist), opaque minerals (iron oxides) and calcite—the latter being the main mineral phase in most of the steles (Figs. 2c and 3a). The mud phase is basically formed by micritic calcite below 5 µm in size and arranged as a microcrystalline mosaic. Finally, the sparitic cement shows crystal sizes up to 25 µm of calcium carbonate filling the porosity and binding the sand clast. The petrographic homogeneity of the carved steles suggests a common source of provenance.

The mineralogical compositions of the rock samples (steles fragments and outcrops) are summarised in Table 2. In all samples, the main mineral phase is calcite ($CaCO_3$), often accompanied by dolomite $CaMg(CO_3)_2$. Quartz (SiO_2) is also a significant mineral in such rocks, and minor proportions of k-feldspars (orthoclase, $K[AlSi_3O_8]$) and plagioclase ($(Na,Ca)[(Si,Al)_4O_8]$) are also detected. Finally, a few clay minerals (mainly illite, K_{2-x} $Al_4[Si_{6-x}$ $Al_{2-x}O_{20}]$ $(OH)_4$ and chlorite $(Mg, Al, Fe)_{12}[(Si, Al)_8O_{20}]$ $(OH)_{16}$) were determined by XRD diffraction and SEM and energy-dispersive analysis of X-rays (EDAX; SEM-EDAX).

Samples belonging to the surrounding outcrops show the same textural and mineralogical characteristics as the carved steles which strongly suggest local extraction of the raw material for their construction.

3.2 Patinas

All the carved steles include thin beige–orange patinas (Table 2). Under the stereomicroscope, they are firmly adhered to the stone showing a homogeneous and uniformed texture which modifies the aspect of the original rock (Fig. 2c). The patina layers range from 35 to 110 µm in thickness covering the surface of the steles, the iconograhic motifs, fractures and small cracks (Fig. 3b).

A summary of the main optical aspects and chromaticity coordinate values (L^*, a^*, b^*, C^* and h) of the sampled patinas and the original stone are shown in Table 3 and Fig. 4. According to CIEL*a^*b^* values, L^* indicates colour lightness or luminosity ($L^*=100$ represents perfect diffuse white and $L^*=0$ corresponding to black) and a^* and b^* the colour directions ($+a^*$ is the red direction, $-a^*$ is the green direction, $+b^*$ is the yellow direction, and $-b^*$ is the blue direction). Figure 4a shows a^*–b^* chromaticity diagram in which the analysed patinas and stone are represented. Considering that the centre is achromatic, an increase in a^* and b^* values (moving the point out from the centre) is also accompanied by an increase in colour saturation. In our case, all the analysed patinas are represented in the middle of the first quadrant of the diagram with an average a^* value of 5 (a^*, 3–7) and an average b^* value of 16 (b^*, 12–23). The detected differences are related to L^* (lightness) parameter (Fig. 4). All the sampled patinas show values up to 45 in lightness (less saturated), with the exception of

Table 1 Main characteristics of the collected patina samples

Patina samples	Stele number	Position in the tumular cist			Analysis	
		Internal face of the stele	External face of the stele	Base of the stele	SEM	XRD
1	UE-106			X		X
2				X		X
3		X			X	
4		X				X
5		X				X
11			X		X	
6	UE-107	X				X
7		X				X
8		X			X	
9		X			X	
10		X				X
12			X			X
13	UE-108	X				X
14				X		X
15				X	X	
16			X			X
17	UE-109	X				X
18			X			X
19	UE-110			X		X
20			X			X
21			X			X
Pat 1					X	X
Pat 3					X	X

samples 12 (stele 107) and 18 (stele 109) which display quite different measurements ($L^*=37$ for sample 12 and $L^*=82$ for sample 18). It is noteworthy that the higher L^* value (sample 18) also coincides with the highest b^* value. Such variations in luminosity are attributed to a darker and a paler patina, respectively. When comparing the L^*, a^* and b^* parameters of the sampled patinas to the stone measurements, some differences are detected. Whereas L^* for the stele-bearing fragments (whole rock) is in the same range as patinas ($L^*=66$), a^* (0.2) and b^* (10) parameters for whole rock are considerably lower (Fig. 4b). In this sense, the variation in total colour or ΔE^* ($\Delta E^*=(\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})^{1/2}$, where $\Delta L^*=L^*_{sample}- L^*_{standard}$; $\Delta a^*=a^*_{sample}- a^*_{standard}$ and $\Delta b^*=b^*_{sample}- b^*_{standard}$ (being the original stone used as standard), is quite variable, ranging from 8 to 30 with an average value of 20. The most disparate values are exhibited by sample 13 ($\Delta E^*=8$) and sample 12 ($\Delta E^*=30$), the last being the most shifted sample from the original rock in Table 3.

The colour has also been represented by polar coordinates C^* and h (CIE L^*C^*h). Grossi et al. (2007) considered that changes in C^* and h are more sensitive than in a^* or b^* depending on the original colour of the material. CIEL$^*C^*h$ are calculated from de CIEL$^*a^*b^*$ scale values. L^*, lightness, is the same in each scale. The colour saturation degree or C^* ($C^*=(a^{*2}+b^{*2})^{1/2}$) varies from 13 to 24 for patinas and 10 for the natural stone. In both cases, the colour saturation values are small, indicating low colour intensity. Finally, shade (chromate tone) or h ($h=\arctan(b^*/a)$) in our patinas is fairly homogeneous and ranges between 67° and 79° with an average value of 70°. The h value for the original stone is slightly higher (89°).

Comparison between L^* and C^* parameters is shown in the Cartesian diagram of Fig. 4b. It is observed that a main group of samples is represented by $C^*_{a^*,b^*}$ between 15 and 20 and L^* between 40 and 50, evidencing homogeneous colour and lightness. A second group of samples plot at higher L^* (up to 56), and only sample 12 shows lower L^* (37). Moreover, the stele-bearing fragment (whole rock) shows lower $C^*_{a^*,b^*}$ (10) when compared to the sampled patinas. Similar results are detected in the polar diagram h–C^* (Fig. 4c).

Microscopic observations evidence that despite the homogeneity and good development of the patina, its contact with the underlying stone is irregular. This is

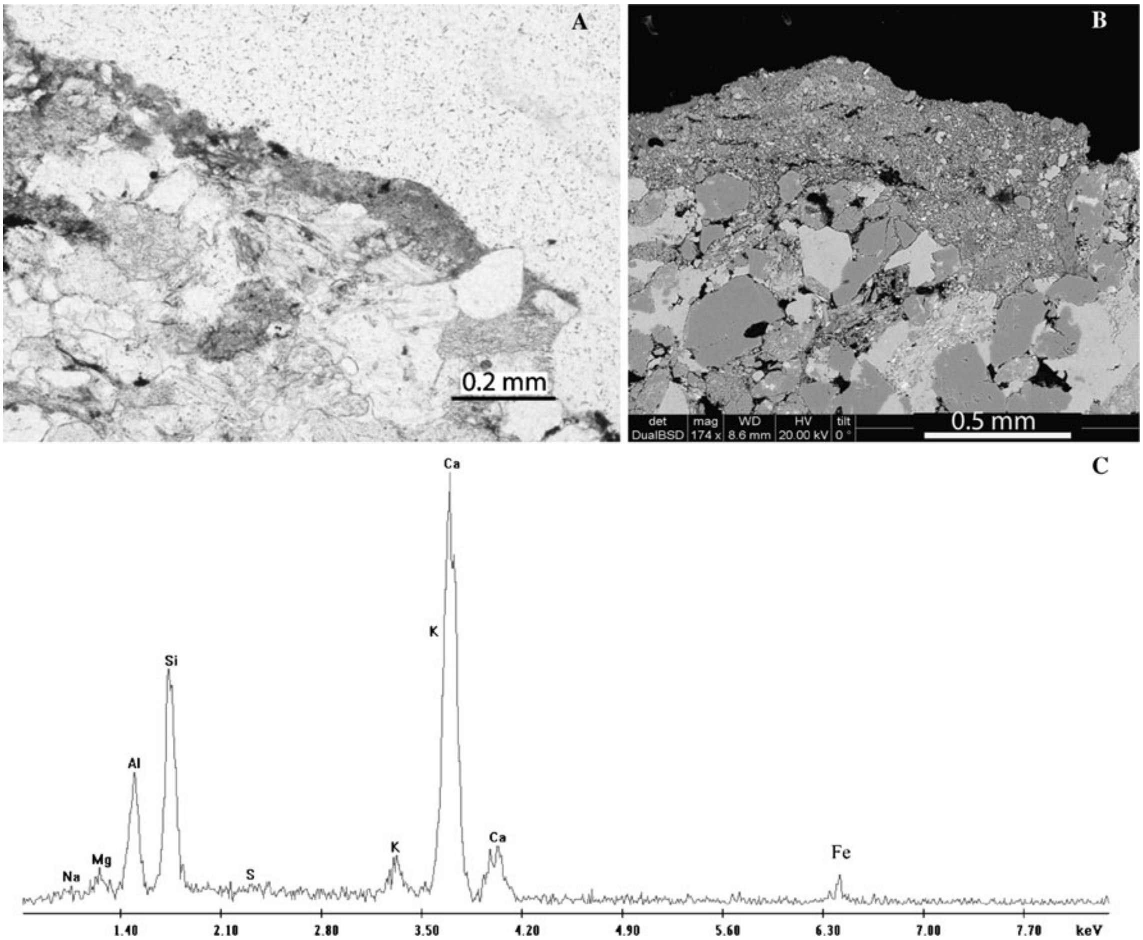

Fig. 3 Patina layers ranging from 35 to 110 μm in thickness covering the surface of the steles, the iconograhic motifs, fractures and small cracks

mainly related to the mineral and textural characteristics of the stele. Reguers patinas are mainly formed by a micritic level characterised by a granular texture (Fig. 3b). Some idiomorphic crystals, of a different composition and belonging to the rock substrate, are embedded in the microcrystalline calcite crust. Occasionally, perpendicular microfissures are built up in the patina surface, and in most of those cases, they are refilled with micrite.

The main mineral phase forming the patinas is calcite (~60–90%, determined by XRD). Other minor or trace minerals coexisting with the calcite are dolomite, quartz, clay minerals (chlorite and illite), feldspars and gypsum ($CaSO_4{\cdot}2H_2O$; Table 2). Comparing the obtained mineral phases of the patinas to the minerals of the original stone, it is evident that the high calcite contents cannot be explained exclusively by entrained whole rock calcite fragments but must be considered a neoformed phase. The same occurs with gypsum. Due to the absence of this mineral phase in the calcarenite, its presence in the patinas indicates an authigenic origin. Clay minerals included in the patinas are attributed to the sediments which covered the megalith before its excavation or to feldspar decay. The contents of dolomite and quartz (avg. 5.1% and 7.5%, respectively, determined by XRD) are coherent with the entrainment of stele-bearing dolomite and quartz fragments (avg. 11.2% and 15.5%, respectively).

SEM-EDAX analyses confirmed the chemical composition of the patinas previously detected by XRD. In both cases, the main component is Ca (Fig. 3c), corresponding to the calcite mineral phase.

A thin (approx. 25–50 μm) external and discontinuous gypsum level was detected by SEM in some of the analysed patinas (Fig. 5), evidencing the presence of an embryonic sequence formed by micrite and gypsum. These observations correlate to the XRD analyses of a few patinas containing this mineral phase. The morphological aspect of gypsum is shown in Fig. 5b. It mainly presents a botryoidally and homogeneous texture with microcrystal aggregates, the latter ranging from 7 to 11 μm in size and showing spherical shapes composed of radial crystals. Locally, radial crystals of gypsum (approx. 25–30 μm in size) refill the small pits (Fig. 6)

Table 2 Percentage of the mineral phases in stele-bearing fragments, outcrops and patinas

Sample	Chlorite Clay minerals	Illite (%)	Quartz (%)	K-feldspar (%)	Plagioclase (%)	Calcite (%)	Gypsum (%)	Dolomite (%)
Whole rock								
RS-1	0.0	3.4	17.9	0.0	8.9	57.6	0.0	12.2
RS-3	0.3	2.1	9.0	1.2	3.9	55.4	0.0	28.1
RS-4	0.0	2.7	14.2	0.0	22.8	59.6	0.0	0.7
RS-5	0.0	3.0	20.8	0.0	3.3	69.1	0.0	3.8
Outcrops								
RS-7	0.3	2.8	16.8	0.0	3.7	57.3	0.0	19.2
RS-8	0.0	5.5	32.9	0.0	5.1	53.3	0.0	3.1
RS-9	0.0	6.1	35.7	0.0	8.3	46.3	0.0	3.7
Patinas								
1	0.4	2.0	4.8	0.3	1.2	76.1	9.6	5.8
2	0.6	2.8	10.5	0.5	2.5	67.5	0.0	15.7
4	0.1	0.7	6.8	0.0	0.8	87.7	2.3	1.6
5	0.7	2.4	6.3	0.0	0.6	82.3	4.2	3.4
6	0.3	2.5	5.2	0.0	1.7	80.2	0.4	9.7
7	0.5	2.2	3.7	0.0	1.5	74.3	14.2	3.6
10	0.4	3.3	13.8	0.5	3.1	72.6	0.0	6.4
12	0.2	3.0	11.8	0.3	2.9	70.8	0.0	5.2
13	0.3	1.6	4.7	0.0	2.0	85.2	0.4	5.8
14	0.2	2.8	6.8	0.0	0.8	80.2	0.0	9.2
15	0.3	2.7	6.6	0.0	0.5	81.8	0.0	8.1
16	0.4	2.0	7.3	2.3	1.4	82.9	0.3	3.4
17	0.4	2.2	6.9	0.9	1.3	84.7	1.6	2.0
18	0.3	2.1	11.7	0.7	1.6	78.5	0.0	5.1
19	0.4	2.1	4.0	0.0	1.4	90.1	0.0	2.2
20	0.6	2.7	7.3	0.7	2.7	79.8	2.5	3.8
21	0.4	2.5	6.3	0.4	1.1	85.2	1.0	3.2
pat 1	0.0	4.8	9.0	0.0	0.8	85.3	0.0	0.0
pat 3	0.0	2.6	9.1	0.0	4.0	57.0	25.0	2.3

% is a semiquantitative calculation by a calibration line. Analyses were carried on by XRD

4 Discussion

Patinas developed on natural or monumental stones of the Mediterranean area (e.g. rock buildings, outcrops, old quarries and caves) have been systematically studied (e.g. Garcia-Valles et al. 1997, 2002, 2003; Gorbushina and Krumbein 2000; Hoffland et al. 2004). In these cases, patinas are formed in atmospheric conditions, and most of them show a common textural/mineralogical sequence associated to changes in the environment. The sequence mainly consists of several layers, which, from the outer to the inner zone, are: (1) present bioactivity and/or biological remains; (2) a gypsum-rich layer; and (3) a calcitic (micritic) layer. The main mineral components are calcite and gypsum, but Ca oxalates and Ca phosphates are also found associated to inorganic or biological activity. Finally, quartz and clay minerals are also present.

Comparing the textural and mineralogical characteristics of the Reguers patinas to the typical Mediterranean sequence, it becomes clear that significant differences exist. The absence of a well-defined mineralogical succession together with the lack of authigenic minerals such as Ca oxalates and Ca phosphates and the low contents on gypsum (only present in a few samples) suggest that the Reguers patinas were developed in quite different environmental conditions.

The development of calcite (neoformed mineral phase) in the studied patinas is strongly related to the interaction between the stone and the patina, as evidenced by the smooth irregular borderlines. Several types of mineral transformation of rock surfaces—including recrystallisation of whole rock calcite and dedolomitisation—can lead to the development and evolution of patinas. In both recrystallisation and dedolomitisation processes, the calcite and dolomite crystals of the rock are replaced by small crystals of calcite (micrite), which leads to the formation of a micritic layer. Although an inorganic origin of such micritic layers is assumed, SEM-EDAX analyses also show that

Table 3 Chromaticity coordinate values measured on the Reguers patinas

Sample	L^*	a^*	b^*	C^*	h	ΔE
Stele 106						
Sample 1	51	5	15	16	72	17
Sample 11	44	7	16	17	67	24
Sample 2	56	7	20.0	21	72	16
Average	50.4	6.1	17.1	18.2	70.3	19.0
Stele 107						
Sample 9	48	5	15	16	72	19
Sample 12	37	4	12	13	73	30
Average	42.4	4.3	13.6	14.3	72.4	24.5
Stele 108						
Sample 13	67	3	17	17	79	8
Sample 14	41	5	14	15	71	26
Sample 15	43	6	15	16	68	24
Sample 16	45	5	15	15	72	22
Average	49.2	4.7	15.1	15.8	72.7	20.0
Stele 109						
Sample 17	49	5	16	17	72	19
Sample 18	82	7	23	24	73	22
Average	65.6	6.2	19.8	20.7	72.5	20.5
Stele 110						
Sample 19	48	5	17	18	72	10
Sample 20	70	5	18	18	75	23
Sample 21	46	7	18	19	69	20
Average	58.0	5.7	17.7	18.6	72.3	34.5
Rock sample	66	0.2	10	10	89	

some of the Ca is presumably related to the presence of microorganisms, as evidenced in Fig. 7 in which globular and elongated bodies of calcite are observed. Such remains of calcified aggregates are commonly associated to bacteria (e.g. Urzì and Realini 1998, Urzì et al. 1999, Garcia-Valles et al. 2000). The local presence of regular small circular pits (approx. 33 μm) can be related to organic activity (Fig. 8, e.g. lichens), also named biopitting (e.g. Sterflinger and Krumblein 1997; Sterflinger et al. 1997). The well-developed and homogeneously distributed micritic layer in the patinas favours a major protection of the original stone texture as well as their anthropogenic motifs. The textural and compositional characteristics of such layer (e.g. calcite crystal size) play a protective effect on the stone surface. Water or organisms may penetrate into the rock only through those points where the layer is broken (mechanically or biologically). In those cases, it produces expansion when adsorbed by the clay minerals of the matrix and contributes to the stone deterioration (Garcia-Valles et al. 1996).

The development of a homogeneous micritic patina clearly masks the original colour of the stone. This is

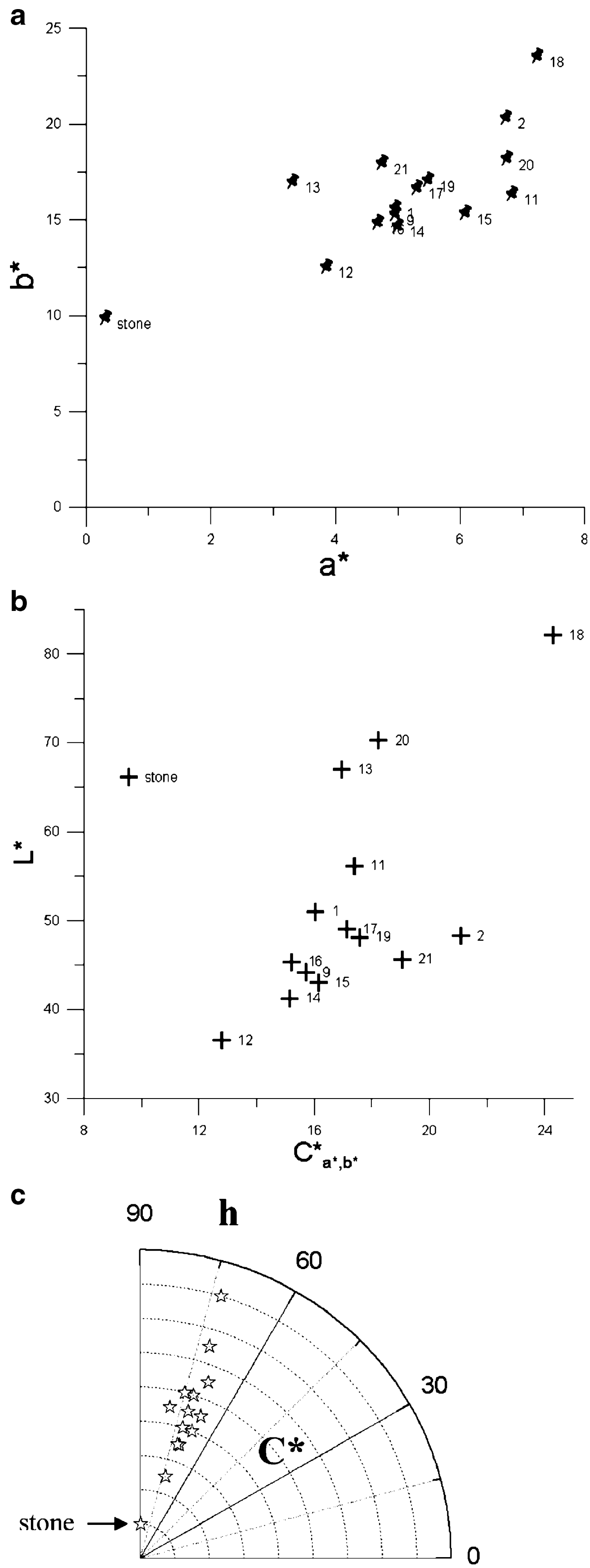

Fig. 4 Chromatic parameters used to define colour and lightness

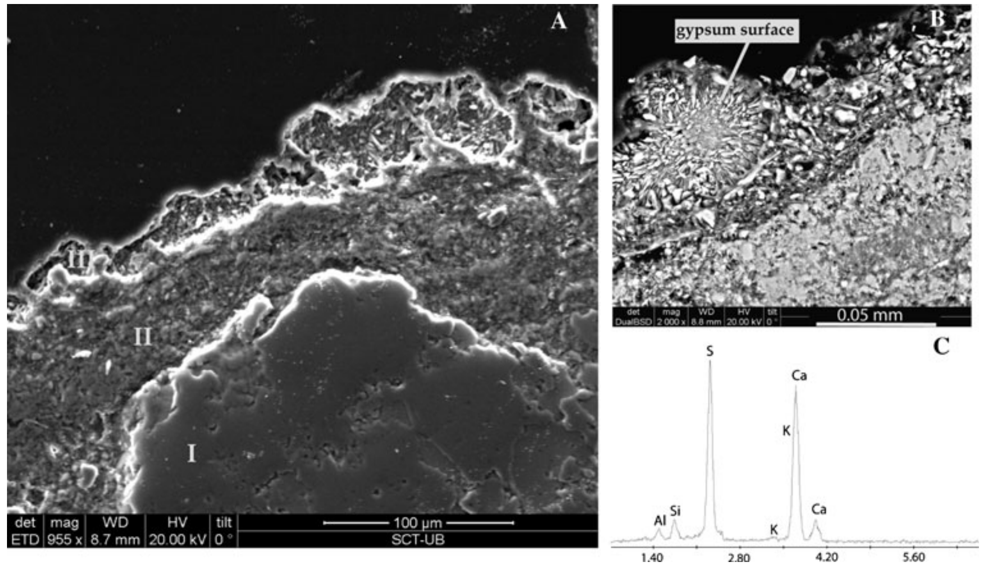

Fig. 5 Thin external and discontinuous gypsum level detected by SEM

evidenced in Fig. 4 where the different chromatic parameters used to define colour and lightness show significant differences between the original stone and the formed patinas.

In general, the formation of gypsum in patinas is linked to several inorganic processes (Maravelaki-Kalaitzaki 2005) which include sulphation—only in polluted environments—(e.g. Amoroso and Fassina 1983; Charola and Ware 2002; Toniolo et al. 2009), transformation of calcite, dry deposition of particles from the atmosphere (e.g. Garcia-Valles et al. 1997) and biological processes (e.g. Rozanov 1961; Garcia-Valles et al. 1997; Garcia-Valles et al. 2000). In the case at hand, the transformation of calcite from the patina to gypsum is the most convincing process considering the location of the megalith in a rural environment, the absence of atmospheric particulate (e.g. spherules) in the gypsum layer and the non-appearance of microorganism evidence related to gypsum. However, radial crystals of gypsum refilling small pits might be attributed to bioactivity.

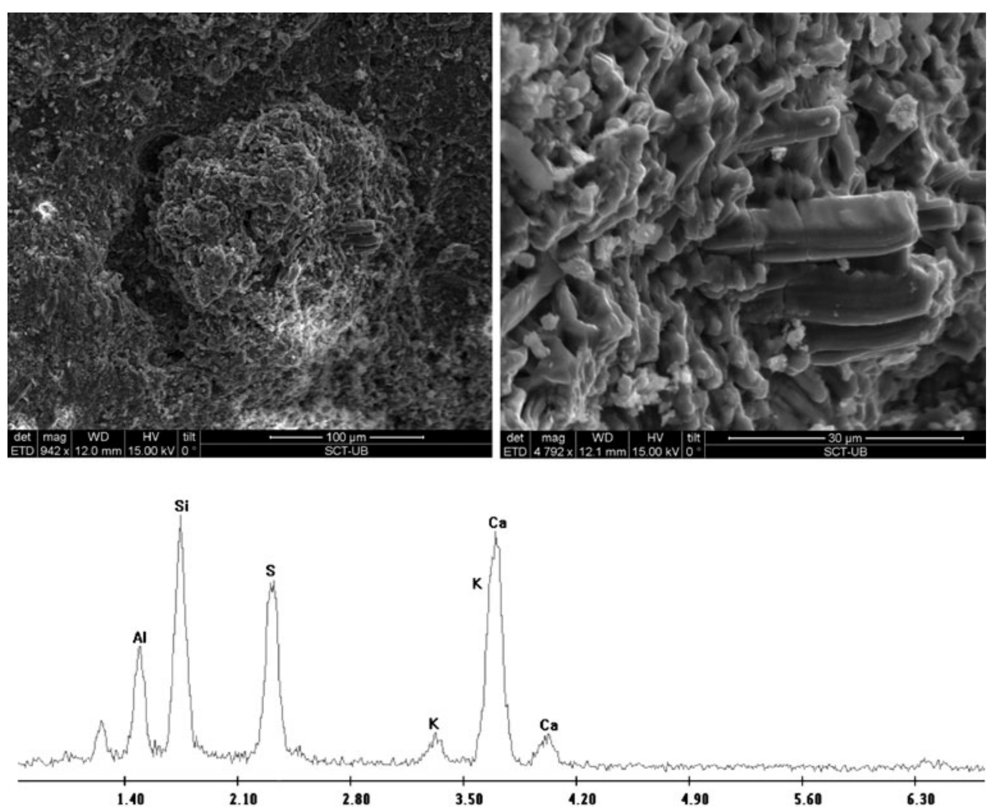

Fig. 6 Radial crystals of gypsum (approx. 25–30 µm in size) refilling the small pits

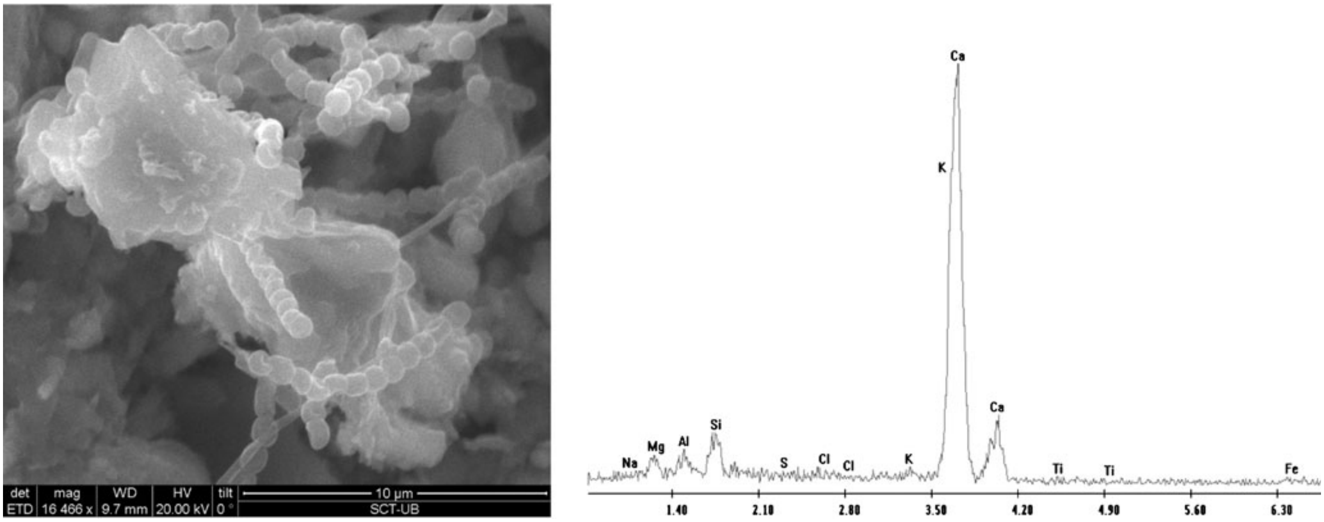

Fig. 7 Observed globular and elongated bodies of calcite

4.1 Environmental conditions for the development of the Reguers patinas

The textural and mineralogical results obtained from the Reguers patinas clearly differ from the typical patinas of the Mediterranean basin, suggesting diverse environmental conditions for their formation. In order to better reconstruct the environment in which the Reguers patinas were developed, an important fact to consider is that the Neolithic steles were not always exposed to atmospheric agents but were buried from an age younger than 4150± 50 years to the recent excavation. Therefore, another fact to consider is that the Reguers patinas could also have developed during these burial conditions. Several arguments supporting the formation of such patinas in a burial environment are:

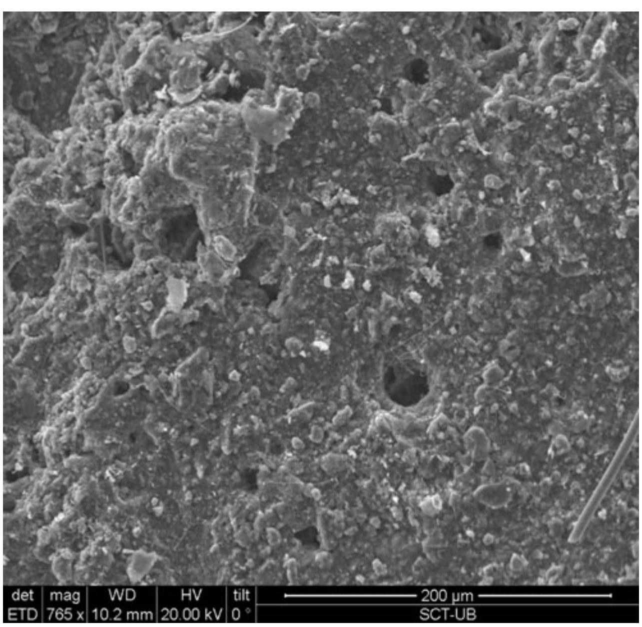

Fig. 8 Local presence of regular small circular pits (approx. 33 μm) which can be related to organic activity

1. The Reguers patinas form a continuous cover on the surface of the steles as well as within the partially eroded iconograhic motifs. The actual state of the Neolithic steles evidences the action of weathering processes through time (e.g. erosion, mainly evidenced in the inscription groves), as well as the anthropogenic activity which modified the original megalith by “sawing” and repositioning some pieces in order to construct the tumular cist (López et al. 2010). In this context, the constant and homogeneous distribution of the patinas along the surface of the steles, totally covering their surface, suggests that they probably developed after the man-made modifications, in a period in which the archaeological site was buried and sealed by the products of the Senill ravine, and thus submitted to burial environmental conditions.
2. In general, the colour of patinas developed in atmospheric conditions is variable depending on their situation in the monument (Maravelaki-Kalaitzaki 2005). In fact, the textural and mineralogical sequence systematically detected in those cases normally consists of three distinct coloured layers. From the inner to the outer zone of the sequence, the layers become darker, with the most external level (formed by gypsum) becoming a “black crust” (Toniolo et al. 2009). Such progressive darkness is classically related to bioactivity and/or to atmospheric pollutants (e.g. hydrocarbon combustion; Cnudde et al. 2009). Contrary to the

typical Mediterranean patinas, the Reguers patinas are characterised by a homogeneous and constant beige–orange colour throughout. The absence of heavy metals mainly contained in flying ashes and other depositions from atmospheric dust favours the development of the kind of analysed patinas in burial conditions.

3. The classical textural and mineralogical sequences of patinas developed in atmospheric conditions are often accompanied by laminated and stromatolitic layers, usually overlying the micritic level. Analyses of such layers indicate the presence of other mineral phases such as Ca oxalates and/or Ca phosphates, mainly related to biological activity (Blázquez et al. 1997; Valls del Barrio et al. 2002). In the case of the Reguers patinas, the absence of laminated and stromatolitic fabrics within the calcite layer, as well as the non-appearance of oxalates and phosphates, may indicate a low contribution of microorganisms in the generation of the Reguers patinas.
4. As noted above, gypsum represents an important neoformed mineral in patinas developed in atmospheric conditions and constitutes the most external layer of the Mediterranean sequence. In the case of the Reguers patinas, gypsum content is low and discontinuous (only observed in some samples). This fact, and especially the absence of atmospheric particulate such as spherules of gypsum in the patinas, favours a burial environment inductive to the intermittent development of gypsum in the Reguers patinas. Sporadic draining of sulphur-rich waters (probably used in agriculture) could attack the calcite from the already formed patina or from the stone and transform it to gypsum.

5 Conclusions and recommendations

The textural and mineralogical homogeneity of the gravestone steles, as well as of the rocks outcrops around, allows us to infer that the source in which the rocks were extracted is very proximal if referred to the archaeological site.

One of the main features of the Reguers steles is the presence of beige–orange weathering patinas developed on their surface. The formation of these patinas is related to a burial environment attending their textural (i.e. absence of a well defined sequence as well as particular morphologies displayed by different minerals in atmospheric conditions) and mineralogical characteristics (i.e. low and intermittent contents on gypsum, non-appearance of oxalates or phosphates). Nevertheless, further study of patinas on stone developed in burial conditions is necessary in order to fully understand their texture and mineralogy as well as their mechanisms of formation.

Finally, the homogeneous distribution of weathering patinas on Neolithic steles surfaces completely covering the stones evidences the importance of such patinas in the conservation of the megalith. The protective role played by these patinas indicates that no previous treatment of such steles would be necessary on an eventual exhibition in atmospheric conditions.

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