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SPECIAL ISSUE

Surface changes on crystalline stones due to salt crystallisation

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Abstract This study assesses the changes on the surface of crystalline stones due to salt crystallisation. Efflorescence was forced to grow on the surface of granite and marbles through 60 cycles of salt crystallisation with sodium sulphate. Changes on surface roughness, gloss and colour were measured every 15 cycles and the specimens were examined with naked eye and SEM. Sodium sulphate produces damage which depends on mineral composition. Results show that granites experience a mechanical decay with an increase in roughness. Peaks of mica can be observed on the surface and cracks widen and grow deeper. Colour and gloss do not show any significant change, although gloss decreases with an increase in surface roughness. In marbles, the decay is mainly chemical. Surface roughness increases due to dissolution of the calcite. White marbles exhibit yellowing. Gloss decreases during the first cycles—as grain boundaries become more visible—but tends to regain almost its initial value as the number of cycles increases. In this case, gloss does not show any relation with surface roughness.

Keywords Surface roughness · Colour · Gloss · Granites · Marbles · Sodium sulphate

Introduction and objectives

Surface aesthetics is one of the main criteria to select a stone for ornamental or decorative purposes. In urban environments, stone slabs are used as cladding and façade ashlar in buildings and monuments. Crystalline stones such as granite and marble are commonly selected due to their glossy surface when polished. These polished surfaces are entirely exposed to urban weathering agents.

Roughness, gloss and colour are key properties to assess surface decay. A detailed visual study is also important in any damage evaluation. The increase in surface roughness of stones is one of the most important consequences of weathering (Benavente et al. 2003; Fischer et al. 2011; Warke et al. 2011).

Surface roughness and irregularities such as porosity, distinct crystal boundaries, cleavages and fillings in cracks inhibit the proper reflection of the light and decrease the brightness (Erdogan 2000). The combined use of contact surface analysis devices and glossmeters in different stone slabs is common, since the simple measurement of gloss does not give enough information (Görgülü and Ceylanoglu 2008). Weathering can also induce chemical changes as oxidation or precipitation, producing a change in the colour of the stones (Grossi et al. 2007).

Many authors have studied the relation between roughness and gloss in different surfaces and finishes, and most

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of them have concluded that gloss is higher at lower surface roughness (Fletcher 2002; Klanjsek Gunde et al. 2007). On the other hand there are authors who cannot find any relation between roughness and gloss in a determinate range of values or orientation of the specimens (Pinheiro Sousa et al. 2007; Juuti et al. 2007). This is the case of natural stones, due to the fact that the gloss of a polished stone depends mainly on its mineral composition and surface finishes (Huang et al. 2002; Pinto Ribeiro and Braga Paraguassú 2008). Therefore, for the same roughness finish, mineral composition and textural aspects are the only responsible parameters for gloss.

The commercial value of ornamental stones depends, among others, on their colour (Gökay and Gundogdu 2008). There are many external factors that influence on the apparent colour of the stone. Solar radiation angle during a day produces differences in the stone colour, more evident in the chromatic parameters than in lightness. Changes on the surface finish, mainly related to roughness, may also cause colour variations (Benavente et al. 2003). At similar surface finish, colour will depend on mineralogical composition and texture. Many authors have focused their research on colour distribution in natural stones. In cities and industrial areas, the deposition of pollutants leads to the formation of soot patinas and black crusts. The consequence is a total change on the visual appearance of buildings stones, such as blackening (Grossi et al. 2003; Grossi and Brimblecombe 2004; Török et al. 2011).

One of the weathering processes which can affect the stone surface is salt crystallisation. In particular, sodium sulphate is one of the most damaging salts to porous stones. The Na_2SO_4 system includes several phases (Grossi et al. 1997; Steiger and Asmussen 2008). However, only thenardite in phase V (anhydrous) and mirabilite (decahydrated) are stable at room temperature and relative humidity conditions. An additional metastable heptahydrate phase ($Na_2SO_4 \cdot 7H_2O$) has been also found in laboratory experiments (Saidov et al. 2012). There is a threshold for the direct crystallisation of mirabilite or thenardite from the salt solution. If the temperature is higher than 32.4 °C thenardite crystallises; if temperature is lower, the crystallisation of mirabilite or thenardite depends on relative humidity. At room temperature experiments, mirabilite crystallised from a supersaturated solution. Further evaporation leads to the dehydration to thenardite.

Salt crystallisation pressures inside the stone generate stress that may cause the stone to crumble (Winkler and Singer 1972; Grossi and Esbert 1994; Rodriguez-Navarro and Doehne 1999; Flatt 2002; Tsui et al. 2003; Coussy 2006). However, in natural conditions, salt crystallisation as sodium sulphate efflorescence is very common. It is well known that mirabilite crystallisation as efflorescence causes less damage than as subflorescence (Selwitz and Doehne 2002; Rodriguez-Navarro et al. 2000). Nevertheless, even small quantities of soluble salts can be concentrated into small areas (e.g. limit of capillary rise) where considerable deteriorations can be produced (Arnold 1976; Charola and Lewin 1979).

The main aim of this study is to evaluate the change in the surface of crystalline stones, such as granites and marbles, caused by salt efflorescence. Sodium sulphate was forced to precipitate as efflorescence through accelerated ageing test. Decay was assessed throughout the test by surface roughness, colour and gloss measurements, as well as by visual observations and scanning electron microscopy. The relation between surface decay and the measured properties was assessed by statistical analysis.

Materials and methods

Materials

Four granites and three marbles, with different colour, grain size and mineral composition, have been selected. The granites are currently quarried in Galicia, North-West of Spain. Their commercial names are Gris Alba, Grissal, Rosa Porriño and Rosavel. Gris Alba is a two-mica, grey, medium and homogeneous grain sized monzogranite. Grissal is a coarse, heterogeneous monzogranite with grey alkali feldspar. Rosa Porriño is a coarse, heterogeneous sienogranite with red alkali feldspar. Rosavel is a porphyritic quarztsienite, with pink alkali feldspar megacrystals up to 60 mm (Streckeisen 1976). The three marbles are different varieties from Macael, in the South-East of Spain. Their commercial names are Blanco Macael, Tranco and Amarillo Triana. Blanco Macael is a white, coarse-grained calcitic marble with 1 % of magnesium. Tranco is also a calcitic marble, with smaller grain size and orientated bands of different grey shades. Amarillo Triana is a yellow dolomitic marble with the smallest grain size. It shows orientated mica as accessory minerals, and filled fissures with a length of centimetres. The porosity is very low in all stones, specially the marbles. The main characteristics of the selected stones are summarised in Table 1.

Crystallisation test

The resistance of a material to salt crystallisation is usually assessed by standardised ageing tests. In this case we followed the standard *UNE-EN 12370* 1999. This standard specifies 15 cycles of immersion in a sodium sulphate solution followed by drying at 105 °C. At this temperature, evaporation is fast and the salt might crystallise within the stone pores as subflorescence, in the case of the granites. Moreover, this temperature may cause additional thermal

Table 1 Characteristics of the stones selected

Trade name	Colour	Composition (%)				Grain size (mm)		Open porosity (%)		Classification (Streckeisen 1976)
		A	P	Q	M	α	σ	α	σ	
Granites										
Gris Alba	Light grey	37	23	25	15	4	2	1.1	0.1	Monzogranite
Grissal	Grey	35	32	25	8	11	4	0.8	0.1	Monzogranite
Rosa Porriño	Pink	50	14	30	6	14	6	0.9	0.1	Syenogranite
Rosavel	Light pink	60	20	12	8	24	7	1.1	0.1	Quartz syenite

Trade name	Colour	Composition (%)		Grain size (mm)		Open porosity (%)	
		C	D	α	σ	α	σ
Marbles							
Blanco Macael	White	100	–	1.3	0.9	0.4	0.1
Blanco Tranco	White–grey	100	–	0.7	0.4	0.4	0.1
Amarillo Triana	Yellow	5	95	0.2	0.1	0.9	0.3

A Alkali feldspar, *P* plagioclase, *Q* quartz, *M* mica, α average, σ standard deviation, *C* calcite, *D* dolomite

damage to both marbles and granites (Battaglia et al. 1993). To achieve a low evaporation rate that allows the salt to migrate to the surface and produce efflorescence, and to avoid the thermal effect, the drying stage was carried out at laboratory conditions (20 h at 20 °C and 50 % RH). This triggers an initial crystallisation of mirabilite as efflorescence, which later dehydrates to thenardite.

Four slabs of each type of stone of dimensions 10 × 10 × 2 cm and polished surface were tested. Sixty cycles were carried out. The number of cycles was increased in relation to the standard as efflorescence is less damaging than subflorescence. The damage was assessed by visual examination and by measuring roughness, gloss and colour, before and during the experiment. For every 15 cycles, one slab was removed, cleaned and measured again. The samples were cleaned until the increase in the conductivity of the solution was less than 5 % of clean water values, and salts were not observed on the surface. The slabs were dried in a vertical position to avoid the stagnation of the solution on the surface. The same methodology was applied to smaller samples (3 × 2 × 0.5 cm) for SEM examination.

Evaluation

Roughness, colour and gloss parameters were measured to analyse surface changes during the cycles. Statistical analysis was carried out with the results in order to know the significance of the variations before and after the cycles. Changes were also assessed by means of visual and SEM observation.

Roughness

Surface roughness was measured using a contact profilometer Mitutoyo Surftest SV-2000N2, with a diamond tip that moves on the surface of measure with constant speed. Table 2 shows the profilometer characteristics.

Table 2 Profilometer characteristics

Detecting method	Differential inductance method
Stroke	800 μm
Measuring force	0.75 mN
Tip material	Diamond
Tip shape	60° Conical
Tip radius	2 μm
Measuring speed	0.05–5 mm/s
Measuring length	50.8 mm
Stroke/accuracy	8 μm/0.0001 μm–800 μm/0.01 μm
Lateral resolution	1 μm

Table 3 Evaluation conditions

Profilometer	Mitutoyo SV-2000N2
Profile length	50 mm
Measuring speed	2 mm/s
Stroke	800 μm
Slab orientation	Yes
Number of profiles	50
Spacing	0.5 mm
Parameters	R_a, R_p, R_v, R_y
Filter/cut-off length	Gaussian Lc: 25 mm and Ls: 0.08 mm

The conditions to evaluate roughness were selected taking into account the initial roughness, mineral distribution, mode of alteration of the stones and statistical analysis (Alonso et al. 2007; Vázquez et al. 2007; Alonso et al. 2008) and showed in Table 3. We have selected the following four parameters to define roughness:

- R_a: *Arithmetical mean deviation of the profile*. Arithmetical mean of the absolute values of the profile deviations (Z_i) from the mean line. It represents the average of the roughness for each stone
- R_p: *Maximum profile peak height*. Maximum value of the profile deviations (Z_i) from the mean line
- R_v: *Maximum profile valley depth*. Absolute value of the minimum value of the profile deviations (Z_i) from the mean line
- R_y: *Maximum height of the profile*. Sum of the highest and the lowest point from the mean line

Table 4 shows that the values of the initial roughness parameters are higher in granites than in marbles. In all the stones, valleys values are greater than peaks, so they condition maximum roughness.

Gloss

Gloss was measured with a MINOLTA 60 glossmeter. The principle of glossmeter is based on a light beam that strikes the surface at an angle of 60°; the glossmeter measures the intensity of the reflected light and compares it with a reference value, which in our device is 95.6. The number of measurements required was estimated by means of the accumulated average until the stabilisation of the values. In this case, both granites and marbles needed 30 measurements to obtain a representative value of reflectivity. The greatest error by repetition of three series of measures on the same specimen was lower than 0.5 (%). Table 5 shows the values of reflectivity for the studied stones.

Table 4 Roughness parameters of sound stones

Trade name	R_a (μm)		R_p (μm)		R_v (μm)		R_y (μm)	
	α	σ	α	σ	α	σ	α	σ
G. Alba	1.0	0.1	6.1	2.6	22.0	3.6	28.2	3.4
Grissal	1.0	0.4	5.5	1.7	25.0	10.7	30.5	11.9
R. Porriño	1.2	0.2	4.0	0.3	30.4	7.5	34.4	7.7
Rosavel	1.2	0.5	5.3	1.5	30.5	14.6	35.8	15.0
B. Macael	0.4	0.1	1.9	0.4	14.8	1.7	16.7	2.0
Tranco	0.4	0.1	2.2	0.1	13.2	2.9	15.4	3.0
A. Triana	0.4	0.1	1.7	0.8	12.6	3.1	14.3	3.6

Values obtained from the average of 50 profiles

α Average, σ standard deviation

Colour

Colour was measured and quantified with a MINOLTA CR-200 colorimeter using the illuminant C, beam of diffuse light of 8-mm diameter, 0° viewing angle geometry, specular component included and spectral response closely matching the CIE (1932) standard observer curves. Measurements are expressed following the CIE L^* a^* b^* and CIE L^* C^* h^* systems (UNE-EN ISO 105-J03 1997). ΔE^* is introduced as the total colour change, to compare the variations before and after the tests as follows:

$$\Delta E^* = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2}$$

The colour determination in a heterogeneous material requires a previous study about the number of measures needed, which is related to the colour and grain size or heterogeneities. The number of data points was determined by calculation of the cumulative average until the stabilisation of the values. Due to the large grain size of Rosavel alkali feldspars, and Grissal heterogeneity, a minimum of 100 data points is required in each slab. Table 5 shows the average colorimetric parameters of the sound stones.

Visual and SEM examination

The observations are carried out after the test. In the case of SEM examination, a Jeol-6100 has been used in order to observe the progress of the decay, paying special attention to the evolution of each mineral individually as well as the development of cracks. The specimens were coated with gold and observed under secondary electrons.

Table 5 Colour and gloss parameters of sound stones

Trade name	Gloss (%)		L^*		a^*		b^*		C^*	h^*
	α	σ	α	σ	α	σ	α	σ		
Gris Alba	60.9	5.8	65.8	0.8	−1.8	0.1	3.9	0.2	4.2	65.2
Grissal	59.1	3.9	62.1	0.6	−2.8	0.1	2.3	0.1	3.4	37.8
Rosa Porriño	79.6	2.9	61.3	1.1	2.8	0.7	10.7	0.8	10.6	−76.4
Rosavel	79.1	3.5	68.3	0.8	−1.3	0.1	6.1	0.2	6.3	79.5
Blanco Macael	95.3	1.8	77.5	2.7	−2.4	0.1	−0.9	0.2	2.6	−19.7
Blanco Tranco	81.0	4.6	76.0	0.5	−2.5	0.1	−0.6	0.1	2.5	−13.8
Amarillo Triana	70.9	3.7	76.4	1.9	0.8	0.4	20.7	0.7	20.7	87.8

α Average, σ standard deviation

Statistical analysis

The values of the roughness, gloss and colour parameters of the different slabs of each sound stone were contrasted using the Kruskal–Wallis one-way analysis of variance by ranks. Most results showed that the values of the parameters are significantly different for the diverse slabs. Hence, to evaluate the final damage, each slab was individually compared every 15 cycles with the sound sample using the Mann–Whitney U statistic test for two independent samples. We choose this test as the points of measurements were different before and after experimentation. The variation in the parameters was considered significant if $p < 0.05$.

The relationships between the different techniques and parameters were analysed by a principal component analysis. These analyses are used to identify the most useful techniques to be recommended in future studies.

Results

Roughness

Roughness increases with the cycles. All the roughness parameters show a significant change before and after the test in all the stones tested. Variations are more evident in granites than in marbles. Figure 1 shows average roughness (R_a) variation with cycles in all the studied stones. Figure 2 shows R_p versus R_v, which give information about the type of weathering: higher R_p means mica changes over the surface (values over 0) and R_v crack growing and mica detachment (increase in deep values below 0). Since these two parameters are extreme variations, roughness maximal ($R_y = R_p + R_v$) was also plotted in this Fig. 2. All the results were expressed in percentage to give an idea about the magnitude of the variation.

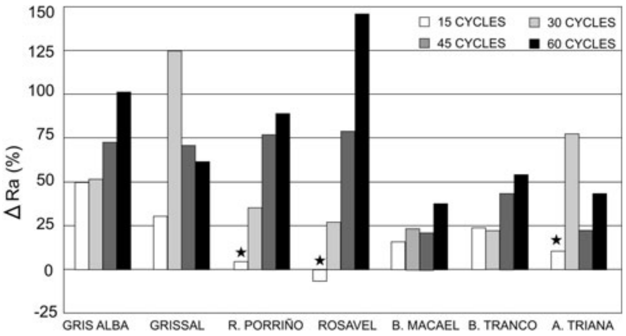

Fig. 1 Variation in R_a in all the studied stones. Results are expressed in percentage in relation to the cycles. *Stars* mean no significant change at $p < 0.05$. Values increase with the cycles. Grissal and Amarillo Triana's behaviour is due to material heterogeneity and mineral distribution

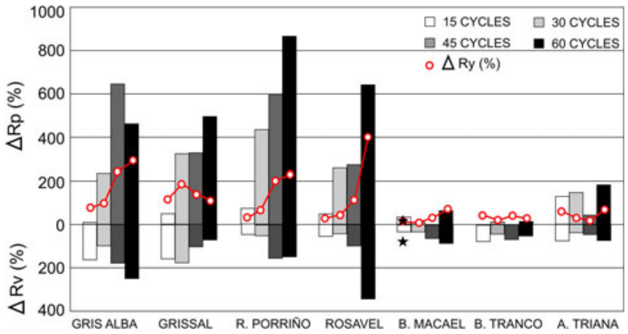

Fig. 2 Variation in extreme roughness R_p versus R_v in columns and R_y in line with the cycles. Results are expressed in percentage. *Stars* mean no change at $p < 0.05$. Initial peak values are much lower than valleys. However, their variation is much more important after salt crystallisation. Increase in peaks is higher in granites and Triana marble due to the presence of mica

Within the granites, Rosavel shows the highest variations in most of the parameters followed by Alba (two micas granite) (Figs. 1, 2). Rosa Porriño, with the biggest and more cracked quartz crystals, shows the deepest valleys after the test. Peaks have increased more than valleys (Fig. 2). In general, minerals exhibit different behaviours: there is an increase in mica peaks while feldspars remain intact (Fig. 3).

In marbles, variations in average values (R_a) are more noticeable than in maximum values (R_y), particularly in Amarillo Triana (the dolomitic one with mica) (Fig. 1). This means a change in the whole surface due to the composition and small grain size. After 60 cycles, the profiles have higher and more dispersed values of both R_a and R_y. Tranco does not show a noticeable change in peaks, while Blanco Macael exhibits higher values (Fig. 2). Amarillo Triana exhibits the highest variations, due to some evident increase in both peaks and valleys (Fig. 4).

Gloss

Results show different behaviours between granites and marbles. In general, granites show a small gloss diminution at the beginning of the test (15 and 30 cycles), which intensifies with the number of cycles (45 and 60) (Fig. 5). Gris Alba exhibits an increase during the first 30 cycles. Marbles show a considerable gloss decrease during the first 30 cycles, followed by a recovery until almost initial values. This behaviour is more evident in white marbles (Blanco Macael and Tranco) (Fig. 5), where changes of gloss can be observed with the naked eye.

Colour

Granites hardly show any change in colour, while white marbles exhibit significant variations during the first

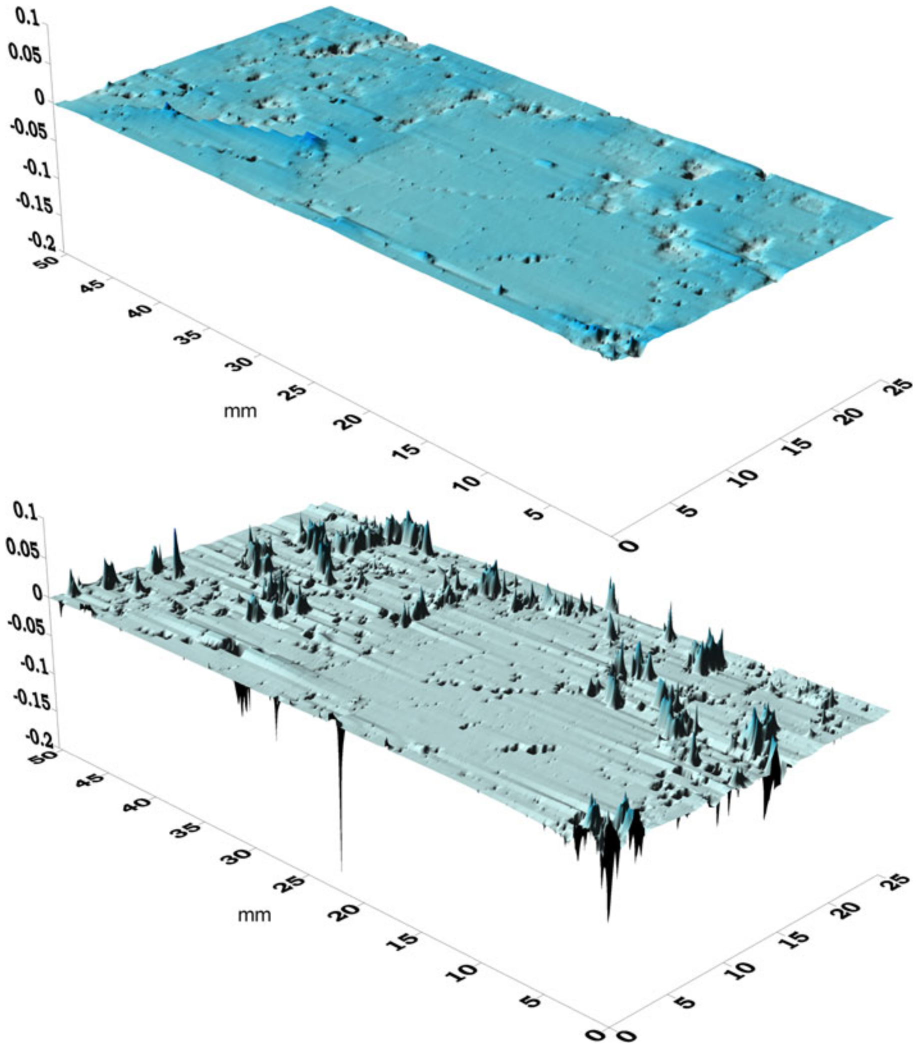

Fig. 3 Tridimensional image of Rosavel before and after 60 cycles. *Peaks* belong to mica and the *flattest areas* to alkali feldspar

cycles. Changes in stones can be grouped in relation to their original colour.

Lightness shows a decrease in pink granites, significant from 30 cycles. White marbles show a noticeable increase in L^* during the first 15 cycles, and then a decrease towards the original values with the number of cycles. Regarding the chromatic parameters, grey granites (Gris Alba and Grissal) do not show any systematic change. Within pink granites, Rosavel exhibits a yellowing (increase in b^*) that is more evident with the number of cycles. Marbles exhibit remarkable differences between calcitic (white) and dolomitic (yellow) ones. Yellowing (increase in b^*) is evident from the first 15 cycles in calcitic marbles even with naked eye. The parameter b^* also tends to decrease to the original values at the end of the cycles. Amarillo Triana hardly shows any colour variation, just a slight yellowing (increase in b^*) at the end of cycles.

ΔE^* is higher than 3 units in Tranco, which shows a clear yellowing (Fig. 6). Rosa Porriño and Blanco Macael have values closer to 3, but yellowing is only slightly evident in the marble.

Surface examination

Mirabilite efflioresce during the evaporation stages as transparent, acicular crystals, which revert after a few hours to thenardite, as white, powdery and acicular shape efflorescence. In marbles, efflorescence can be observed as big crystals in almost the whole surface. In granites, the big crystals concentrate on quartz and feldspar, whereas small crystals accumulate within the exfoliation planes of the biotite. This agrees with previous observations of different crystallisation habits in relation to the humidity of the surface (Arnold and Zehnder 1985; Zehnder and Arnold 1988; Rodriguez-Navarro et al. 2000; Vázquez et al. 2008).

After 15 cycles and subsequent cleaning, a change on the surface in both granites and marbles was observed with the naked eye. In granites, damage is related to biotite crystals which rise over the surface and then detach when the

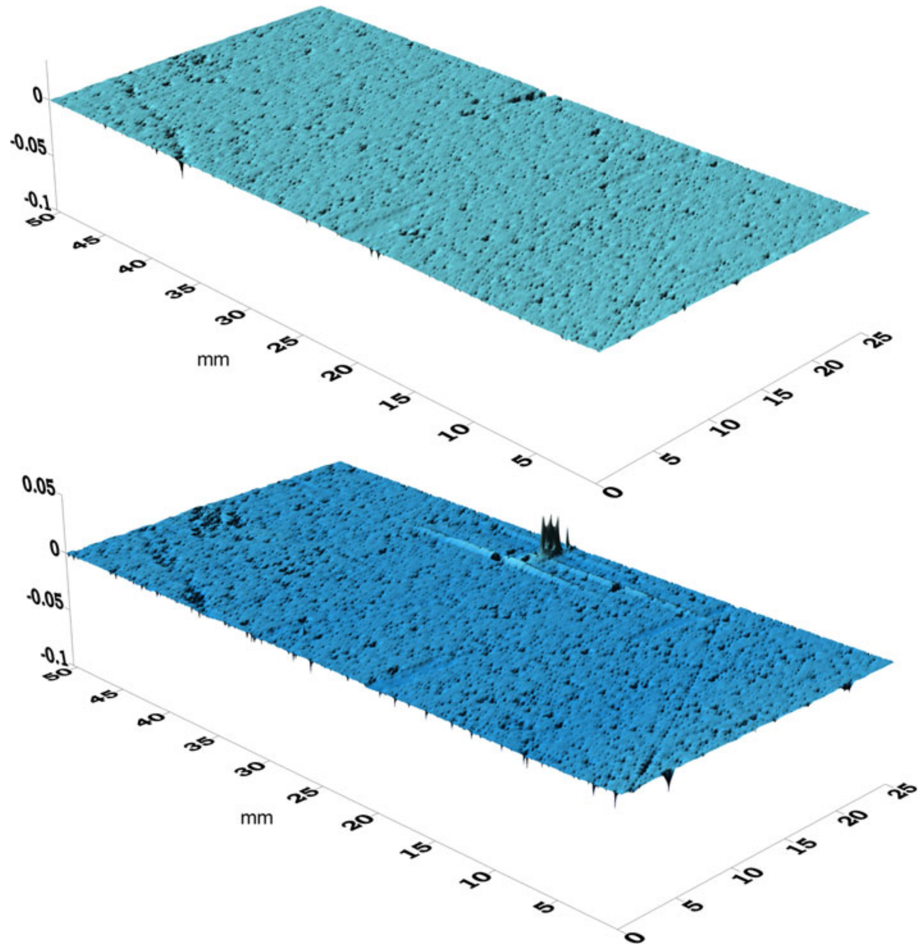

Fig. 4 Tridimensional image of Amarillo Triana before and after 60 cycles. *Peaks* belong to isolated mica

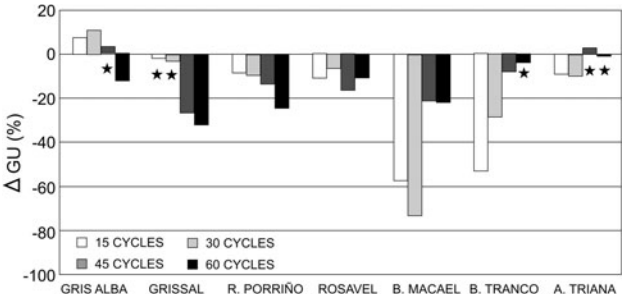

Fig. 5 Bar graph with changes of gloss with the cycles. Stars means no significant change at $p < 0.05$

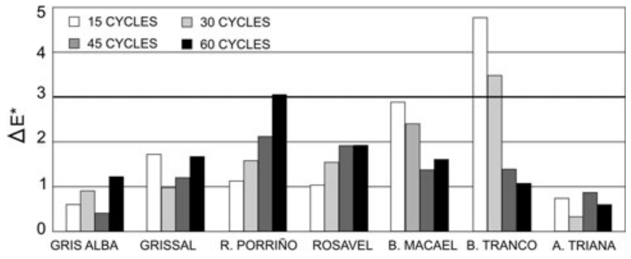

Fig. 6 Bar graph with total colour change (E^*) at 15, 30, 45 and 60 cycles. Values over 3 are considered significant

specimen is re-immersed into the solution because the salt that cemented the mica to the stone dissolves. White marbles show a slight yellowing and a visible loss of gloss in the first 15 cycles, associated with open grain boundaries. After 45 and 60 cycles, the slabs seem to recover this initial gloss, with the disappearance of grain boundaries marks.

SEM examination

In granites, each mineral exhibits different decay patterns. The total decay is then related to the mineral proportion and grain size. SEM examination confirms the visual biotite damage (Fig. 7a). During the last cycles, biotite laminae fold. This occasionally causes the growth of cracks perpendicularly to the cleavage (Fig. 7b). Muscovite (in Gris Alba granite) shows a similar but less intense decay process. Sodium-rich plagioclases hardly show any decay, while the calcium-rich ones exhibited etching (Fig. 7c). Alkali feldspars show a loss of material, mainly in grain boundaries, pre-existent cracks and in exfoliation planes (Fig. 7d). Quartz exhibits a similar pattern to alkali feldspars, although the decay is very low and mainly associated with crack edges (Fig. 7e, f).

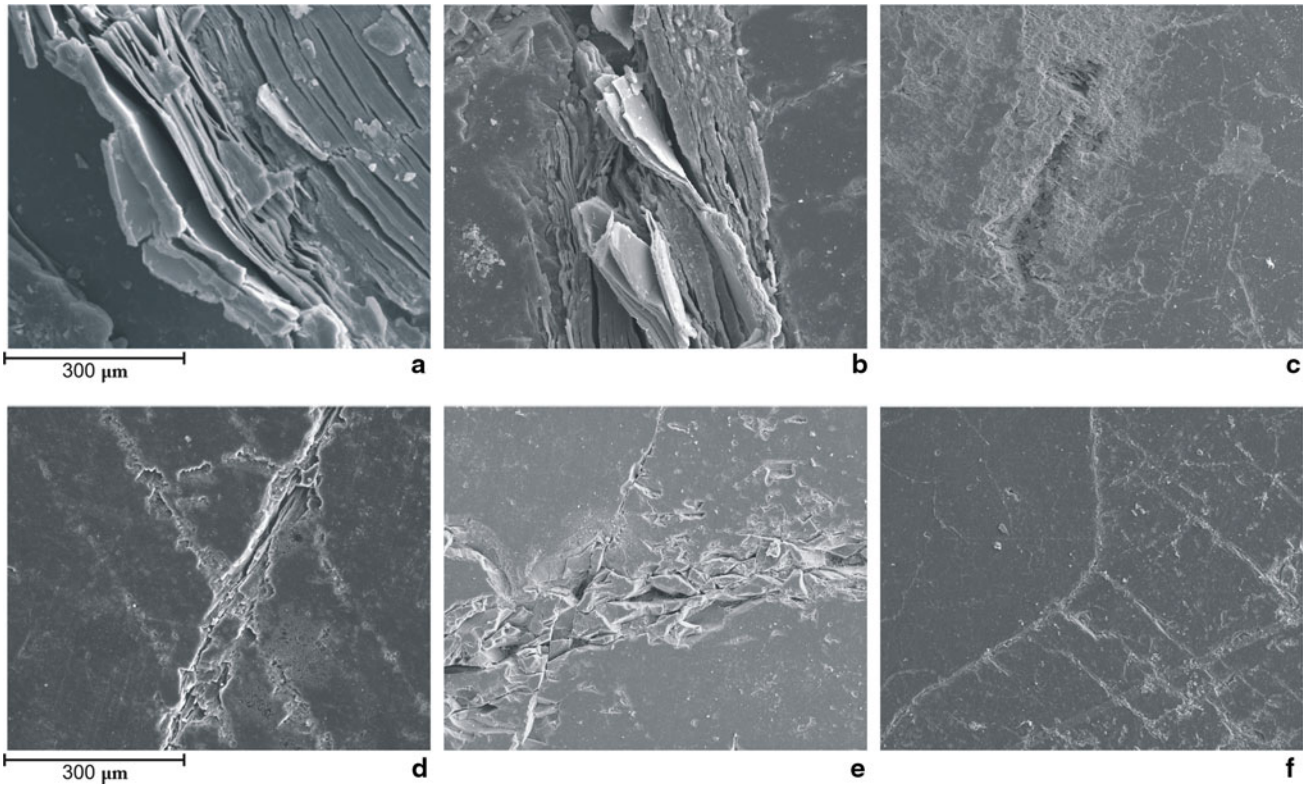

Fig. 7 Decay mineral of granites. **a** Biotite with cracks perpendicular to exfoliation planes. **b** Biotite showing lamina rise. **c** Weathered calcitic plagioclase with a loss of material. **d** The decay in alkali feldspar are concentrated in grain boundaries and exfoliation lamellae. **e** Salt crystallization affects quartz mainly in crack areas. **f** Differences between quartz (*left*) and alkali feldspar (*right*) decay

In marbles, damage depends on the crystal orientation. After 15 cycles, grain boundaries are more noticeable, and also growth-ridges associated with manufacturing polishing scratches. At the end of the test, the surface seems to recover the initial smoothness (Fig. 8). Amarillo Triana (the dolomitic marble) also exhibits different decay patterns depending on the composition of the crystals. Calcite crystals are attacked while dolomite remains almost intact (Fig. 8b).

EDX analysis on the surface of Blanco Macael evidences a change in composition. The sound stone, after 15 cycles, has a small percentage of Mg (around 1 %). However, Mg disappears from the surface probably due to dissolution from the 30 cycles on.

Discussion (physical and chemical damages)

Sodium sulphate efflorescence produces decay when it crystallises on granites and marbles. In both stones, the salt crystallises on the whole surface and within pre-existent

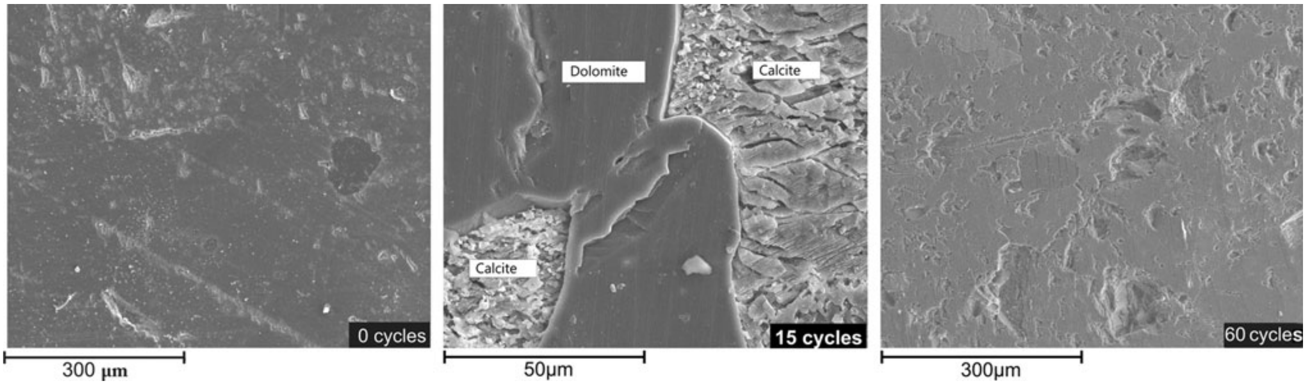

Fig. 8 Marbles decay along salt crystallisation test. Tranco at 0 and 60 cycles and Triana at 15 cycles. At 15 cycles, dissolution is observed at the end of the test, and the marble exhibits a smoother surface due to calcite recrystallisation

cracks or defects. The type of damage differs depending mainly on the mineral composition.

In granites, the main changes are in surface roughness and are the consequence of physical damage related to mica (López-Arce et al. 2010) and quartz, and probably some physico-chemical decay of mainly Ca-rich feldspars (Vázquez 2010). The rise of mica over the surface produces an increase in the average roughness (R_a) and in the peak values (R_p). When mica detaches of the stone, the roughness profile shows deeper valleys (R_v). Quartz showed a loss of material close to cracks' borders and an increase in the length and width of cracks (especially in Rosa Porriño). Alkali feldspar exhibits damage in exfoliation planes, mainly in the porphyritic granite (Rosavel). Plagioclase shows similar alterations in morphology as alkali feldspars. Nevertheless, salt attacks Ca-rich rather than Na-rich zones, pointing to chemical weathering as well. The decay in these minerals also produces a higher value of R_v. The loss of gloss is very slight in all granites.

Marbles exhibit mainly chemical damage with noticeable variations between calcite and dolomite, and principally results changes in gloss and colour, more pronounced on calcitic marbles. They also show an increase in roughness with the cycles, according to Martínez-Martínez et al. (2007). In white marbles, this chemical damage is probably through dissolution of calcite (Cardell-Fernández et al. 2008), which has a dissolution coefficient 20 times higher in sodium sulphate solution than in pure water, and might react with sulphate ions to produce calcium sulphate salts. Moreover, the differences in the rate of dissolution seem to be related to the calcite crystals orientation. In the dolomitic marble, only isolated calcite crystals show dissolution due to the fact that calcite dissolves more rapidly than dolomite (Appelo and Postma 1993) (Fig. 8b).

An ion chromatography analysis of marbles efflorescences evidenced the presence of Ca^{2+} together with Na^+ and SO_4^{2-}. RUNSALT software (Bionda 2006) based on the thermodynamic model of ECOS (Price 2000), hints at 20 °C and 50 % RH to a potential 5 % of glauberite $Na_2Ca(SO_4)_2$ and 95 % thenardite in the efflorescence, confirming a chemical weathering. However, this needs future research.

There is also a physical damage with the accessory mica rising over the surface as in granites, increasing greatly the roughness of the stone compared with the rest of the marbles. The difference between granites and marbles is also evidenced as the surface properties vary. In granites, the evolution with the cycles in surface roughness and gloss shows a significant and negative correlation ($R = -0.6$) whereas no significant relationship was found in marbles ($R = -0.12$).

Additionally, we have carried a principal component analysis including all the parameters of the different techniques used in this study: gloss, roughness parameters (R_a, R_p, R_v, R_y) and colour parameters (L^*, a^*, b^*, C^*, h^*) in the case of granites and colour change (ΔE^*) in the case of marbles. In each case, we have chosen parameters which drove to the highest factor differences.

In granites, we found three factors which explain 93 % of the variance. The first and second factors explained about 40 % of the variance each. Factor 1 correlates with all the chromatic parameters of the colour. Factor 2 is positively loaded in all the roughness parameters, and negatively loaded with gloss. Factor 3 is correlated with the lightness (Table 6). The evolution of the factor scores of the granite samples shows that the factor 1 (colour) gives information about the type of granite whereas factor 2 (roughness and gloss) gives information about the degree of deterioration on the surface. This last factor shows a clear variation with the number of cycles (Fig. 9). This means that firstly roughness and secondly gloss, are the most useful techniques (rather than colour) to study the surface evolution in granites.

In marbles, we also found three factors which explain around 91 % of the variance. Factor 1 explains around 46 % of the variance and it is positively related to R_v and R_y. Factor 2 explains 29 % of the variance and is positively correlated to gloss and negatively to the colour change. Factor 3 explains about 17 % and is loaded in R_a and R_p. Although the general behaviour of the white marbles is different to the yellow one, it seems that those parameters related to intergranular fissure growth (factor 1) tend to increase with the number of cycles (Fig. 9). From the evolution of factor 2, it is also clear that white marbles undergo a strong colour change between the sound stones and the first 15 cycles. After that, the evolution is more scattered in the yellowing. This change corresponds to a

Table 6 Factor load for each parameter in granites

	F1	F2	F3
Gloss	−0.46	**−0.65**	−0.52
R_a	−0.21	**0.86**	−0.30
R_p	−0.15	**0.92**	0.06
R_v	−0.27	**0.86**	−0.27
R_y	−0.23	**0.96**	−0.12
L^*	0.29	−0.24	**−0.89**
a^*	**−0.96**	−0.16	0.17
b^*	**−0.98**	−0.12	0.00
C^*	**−0.98**	−0.09	0.10
h^*	**0.95**	0.20	0.14
Explained variance (%)	40	40	13

Factor 1 shows a strong correlation with chromatic parameters. Factor 2 is positively loaded with roughness parameters and negatively with gloss

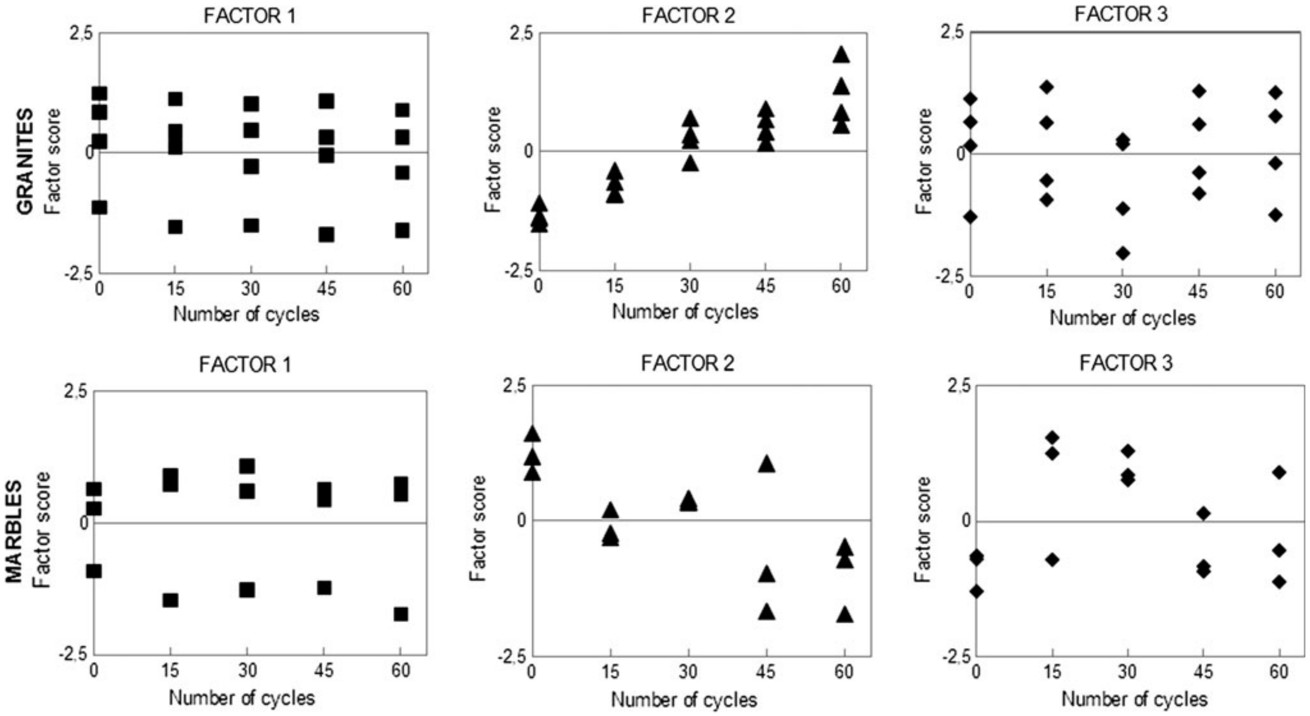

Fig. 9 Principal component analysis results in relation to cycles. *Upper* principal component analysis in granites. *Bottom* principal component analysis in marbles

Table 7 Factor load for each parameter in marble

	F1	F2	F3
Gloss	0.02	**−0.94**	−0.00
R_a	−0.21	0.21	**0.87**
R_p	0.20	−0.11	**0.90**
R_v	**0.96**	0.04	0.28
R_y	**0.98**	0.06	0.17
ΔE	0.12	**0.94**	0.08
Explained variance (%)	46	**29**	17

Factor 1 shows a strong correlation with R_v and R_y due to grains and boundary dissolution. Factor 2 is negatively loaded in gloss and positively in colour change

yellowing, and this means that marbles react very quick to the salt. In the yellow marble this change is less evident. Factor 2 is negatively loaded in gloss (Table 7), and also the strongest variation is exhibited in the first 15 cycles. This is due to the fact that, during the first 15 cycles, an erosion (dissolution) is produced in the grain boundaries, increasing roughness and reducing gloss. After the 15 first cycles, a recrystallisation is observed (Fig. 8c) so the gloss returns gradually to almost the initial values. Factor 3 corresponds to R_p and R_a. They did not vary very much in cycles in comparison to R_v or R_y. In the last 60 cycles, we found a strong variation in R_p in Amarillo Triana, which responds to the mica standing out the surface. This is a punctual variation related only with this type of mica containing marble so these parameters are not recommendable to study marble decay. It seems that, in the case of marbles, the surface roughness technique is useful but only in the parameters related with fissure growth, not in general surface roughness, due also to the polished finish. However, changes in colour seem to be more important to evaluate weathering in the marbles than in the granites, especially the white ones.

Gloss is a property related to the surface finish. In cases of mechanical variation, gloss gives information about the decay. In cases where chemical changes are produced, the mineral gloss is also lost. This technique has to be used complementary to other techniques in order to know if the decay is mechanical or chemical. If the surface suffers both mechanical and chemical decay the information given by gloss measurement is not reliable.

Conclusions

- Sodium sulphate produces damage on the surface of the stones and this can be verified by the measurement of different surface properties. These variations are strong enough to be observed with the naked eye, such as an increase of roughness in granites or the loss of gloss in marbles.
- The damage produced differs depending on the mineral composition. The growth of efflorescence produces

mechanical damage in the granites, with crack opening and mica detachment. However, in marbles, the damage is produced by dissolution, and not by the pressure produced within the pore system due to the salt crystal formation.

- Silicate minerals suffer mainly mechanical decay, resulting in an increase in surface roughness. Carbonates suffer chemical decay due to calcite dissolution. This results in changes mainly in gloss, and colour and to a lesser extent to surface roughness.
- Surface roughness measurements proved to be a suitable method to assess the damage on the surface of stones, mainly when they are polished. Peaks and valleys variations provide information about the decay such as dissolution, crack opening or mica detachment. Colour measurement seems to be reliable in light and uniformly coloured stones. Gloss can be used to determine mainly mechanical damage. When damage is both chemical and mechanical, gloss measurements are less reliable.

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