An experimental investigation into the salt-weathering susceptibility of building limestones

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Abstract

Dimension and ornamental stones used for built heritage are frequently affected, under all climates, by intense weathering induced by the transport of saline solutions. Accordingly, researchers addressed the weathering mechanisms induced by salts (primarily Na_2SO_4), the stresses generated in the host material, and the durability of ornamental and dimension stones. This study investigates the behaviour of four sedimentary lithotypes, differing in texture and structure (Breccia Aurora, Rosso Verona, and fine- and coarse-grained Vicenza Stone) exposed to a selection of saline solutions, aiming at evaluating their susceptibility to weathering and the influence of petrographic features on durability. The chosen Na_2SO_4 , MgSO_4 , Na_2CO_3 , NaCl , and KNO_3 solutions include the anions characterizing the major saline sources affecting built heritage: capillary rise, acid rain, atmospheric particulate deposition, bird or other animal scat, and de-icing salt contamination.

The petrophysical properties of unweathered and salt-weathered samples were characterized by relative mass variation estimation, capillary rise, and hygroscopic absorption-based porosimetry. Scanning Electron Microscopy coupled with microprobe allowed studying the morphological changes triggered by weathering and analysing the chemical composition of the efflorescence crust.

The whole of data, consistently with literature, allowed inferring pore type and distribution as the main intrinsic parameters controlling salt weathering susceptibility. Moreover, Na_2SO_4 and Na_2CO_3 proved to be the most harmful, probably due to their ability to crystallize in different hydration stages at room temperature. The comparative analysis of the induced weathering can help to choose suitable dimension stones for new buildings or restoration replacements.

Keywords Salt weathering · Limestones · Pore network · Salt susceptibility · Dimension stones

1 Introduction

Within natural materials, dimension stones in monumental structures and artefacts are studied correlating mineralogic-petrographic and petrophysical characteristics to durability. The added cultural value encourage to study these materials to understand weathering phenomena and the response of each material to diverse environmental parameters, to preserve them (Török and Přikryl 2010).

Salt crystallization has a significant effect on the weathering of exposed ornamental and building stones (Amoroso and Fassina 1983; Siegesmund and Snethlage 2014). The significance of soluble salts as weathering agents derives

from their ubiquitous occurrence in a wide range of environments (e.g., urban, desert, coastal, and rural; Goudie and Viles 1997; Smith et al. 2005), and their activity under wide ranges of relative humidity and temperature (Puehringer 1983; Sun and Zhang 2019). Therefore, proper conservation of stone artefacts relies on understanding the parameters involved in salt weathering, in particular the role of salt crystallization (Çelik and Aygün 2019).

Crystallization is the process common to all salt species inducing weathering in the host stone. The most common model considers a saline solution circulating inside the pore network, where salt precipitation begins when water starts to evaporate or temperature raises (Cardell et al. 2008; Castellazzi et al. 2013; Grementieri et al. 2017). This process occurs where the dynamic balance between evaporation rate and solution supply rate slows down or ceases. The evaporation rate depends on rock properties (permeability and pore size) and on environmental conditions (relative

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humidity, RH; temperature, T; Cardell et al. 2003; Gremietteri et al. 2017). The supply rate depends on the properties of the solution (flux, surface tension, contact angle, viscosity) and of the rock core (permeability, pore size, and path length; Scherer 2004). If the evaporation rate is lower than the solution supply rate, then crystallization occurs at the material surface, causing the formation of efflorescence. If the evaporation rate is higher than the solution supply rate, then salts precipitate within the pore network, causing subefflorescence and mechanical damage.

Previous studies have focused primarily on crystallization pressure (Flatt 2002; Scherer 2004; Steiger 2005), thermal expansion (Ruedrich and Siegesmund 2007), hydraulic pressure (McMahon et al. 1992), wetting–drying pairs (Sun and Zhang 2019) and chemical weathering caused by the dissolution of minerals with weaker ionic strength than that of the saline solution (Cardell et al. 2003). These processes may all be valid and possibly co-occur, however, the most significant is the crystallization pressure. Crystal formation is favoured in larger pores, and once space is filled with a crystal, the residual solution in the smaller neighbouring capillary is affected by a curvature change due to a change decrease in saturation, and maximum pressure is exerted on pore walls (Steiger 2005). All the available models underline the importance of pore size and shape as a sink for salt contamination (Everett 1961; Fitzner and Snethlage 1982; Nicholson 2001; Flatt 2002; Benavente et al. 2004a, b; Angeli et al. 2008; Yu and Oguchi 2010).

To monitor the weathering induced by saline solutions, several petrophysical characteristics could be taken into account, including (i) pore size distribution (Ordóñez et al. 1997; Prikryl et al. 2003; Yu and Oguchi 2010; Akin and Özsan 2011; Di Benedetto et al. 2015), (ii) effective porosity (Yavuz and Topal 2007), (iii) water absorption by capillary uptake and total immersion (Dessandier 2000; Benavente et al. 2006), (iv) ultrasound velocity (Nicholson 2001, 2002; Sousa et al. 2005; Alonso et al. 2008; Ceryan et al. 2008), and (v) weight loss (Zedef et al. 2007).

Sulphates, chlorides, carbonates, and nitrates, combined with different cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and NH_4^+), are the most common trigger for deterioration in dimension stones (Siegesmund and Snethlage 2014). Also deterioration caused by alums, nitrites, and oxalates have been reported (Arnold and Kueng 1985; Arnold and Zehnder 1990). Identification of the dissolved anions is crucial to interpret the origin of contamination: carbonates and sulphates can originate from rock-forming minerals, circulating water, dissolution of mortars, or pollution. Chlorides are present in coastal environments and organic matter and, rarely, as a result of the salt-storage-function of a building. Nitrates are typical of organic-matter-rich water and phosphates of water containing fertilizers or bone matter. The presence of oxalates indicates the reaction of minerals with organic

matter, usually with artificial products for stone conservation treatment. Unlike anions, the identification of cations is not fundamentally important to the interpretation of the origin of weathering phenomena.

The susceptibility of diverse lithotypes to salt weathering has been studied through different, more or less standardized, ageing procedures (Lubelli et al. 2018). Usually, to reduce the number of variables (e.g., concentration of solutes, chemical interactions, environmental variables; Angeli et al. 2010), contamination by a single saline solution is considered. However, water in the pore network contains more than one species of solute, that consequently interact (Cardell et al. 2008). Some studies have considered several solute-species mixtures, but no reliable model was derived because of the numerous concurring variables (Arnold 1981; Robinson and Williams 2000).

Based on the literature review carried out by the RILEM technical committee 271 ASC (Lubelli et al. 2018), the continuous partial immersion test method (Benavente et al. 2001) was used to assess the behaviour of a selection of saline solutions. Saline solutions (Na_2SO_4 , MgSO_4 , Na_2CO_3 , NaCl , and KNO_3) were applied to several well-characterized lithotypes; then, diffusion and physical behaviour (hygroscopicity and potential hydrate formation) were analysed and compared.

The study was carried out on a selection of rocks with homogeneous mineralogical composition but differing in texture and structure. The analysed lithotypes are all limestones employed as building or ornamental stones, and are characterized by different structural features due to their petrogenesis (Scrivano et al. 2018). Limestones are widespread as ornamental stones, but their mineralogical composition (mainly CaCO_3) makes them liable to weathering processes, being calcite highly soluble in acidic waters (Schiro et al. 2012).

Five different saline solutions were designed to identify whether salt precipitation induces chemical interactions within the analysed stones and to evaluate its importance with respect to mechanical stress induced by crystallization. Na_2SO_4 , MgSO_4 , Na_2CO_3 , NaCl , and KNO_3 saline solutions were selected based on the mineral phases observed in efflorescence in real case studies (Arnold and Zehnder 1991; Siegesmund and Snethlage 2014; Siedel 2018). Moreover, Na_2SO_4 is normally used in determining stone durability to salt decay for its presence in acid rains and its highly destructive impact on stone structure (UNI EN 12, 370: 2001; UNI EN 13, 919: 2002; McMahon et al. 1992; Tsui et al. 2003; Ruiz-Agudo et al. 2007; Angeli et al. 2008, 2010; Diaz Gonçalves and Brito 2014). Ruiz-Agudo et al. 2007; Akin and Özsan 2011 report also the use of MgSO_4 in testing stone resistance. In this study, this saline solution was used because it forms minerals with different hydration state (epsomite: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; hexahydrate: $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$;

pentahydrate: $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$; and starkeyite: $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$). The same behaviour characterizes also Na_2SO_4 (mirabilite: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; thenardite: Na_2SO_4) and Na_2CO_3 (natron: $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; thermonatrite: $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) solutions, evidencing the influence of environmental conditions in the salt weathering process. Low solubility characterizes nitrates, that easily occur as efflorescence (Siegesmund and Snethlage 2014), and KNO_3 was selected to represent the chemical activity of nitrate compounds. Finally, also a NaCl solution was used, as in material testing procedures (UNI EN 14, 147:2003), to recreate sea spray effect on stone artefacts.

The objective of the study was to investigate the weathering mechanisms from different saline solutions, and to evaluate the influence of mineralogical and textural features on the degree of salt weathering, i.e. the control of petrophysical features on the durability of the analysed ornamental and dimension stone. Moreover, as each of the tested saline solutions represents specific environmental agents, the response of the lithotypes helps the selection of the dimension stones for diverse uses. For example, a pronounced susceptibility of a lithotype to NaCl advises against its use in a coastal environment.

Moreover, the study aims at deciphering the interaction between the solutes and the intrinsic textural and structural weaknesses of the chosen lithotypes. The identification of this behavioural pattern could help establishing protocols useful to define conservation strategies. For example, recognizing the features influencing susceptibility to a certain type of solution can be crucial in choosing the appropriate repair stone (% of open pores) or type of mortar to avoid the establishment of new fluid circulation equilibrium or chemical interaction (Lopez-Arce et al. 2009).

2 Materials

Four sedimentary carbonatic lithotypes differing in fabric, commonly used as ornamental stones (Scrivano et al. 2018), were selected as test materials (Table 1). To evaluate accurately correlations between pore network characteristics, and rock weathering susceptibility to each type of saline solution, the selection was based on homogeneous mineralogy and chemical composition, and on different pore network characteristics. The selected stones are the following:

1. Breccia Aurora (BA), a polygenic breccia consisting mainly of variegated micrite fragments cemented by sparry calcite. Micro-porosity is diffuse, especially along suture veins
2. Rosso Verona (RV), a bioclastic nodular limestone (bio-intramicroite) whose matrix is composed predominantly of micrite and Fe-oxides. Pores occur primarily along

micrite–phyllosilicate veins at the boundaries with the nodules

3. Vicenza Stone (VS), a bioclastic limestone cemented by abundant micrite matrix and in which the fossil fraction is commonly recrystallized. The pale-yellow colour of VS is due to rare oxides and hydroxides that are dispersed in the matrix. This lithotype has heterogeneous texture, with coarse- (CGV lithotype) to fine- grain size (FGV lithotype), high porosity, and diffuse micro-porosity (Scrivano et al. 2019)

BA and RV are mainly made up of compact micrite nodules or clasts cemented by veins of sparry calcite (BA), and micrite + phyllosilicate (RV). The grain size and textures control porosities and properties of the two lithotypes (Scrivano et al. 2018). Also, FGV and CGV have different grain size, resulting in different pore size distributions (Scrivano et al. 2019).

Starting from the mercury-intrusion-porosimetry (MIP) pore range distribution data already discussed in Scrivano et al. 2018 and summarized in Table 1, the Salt Susceptibility Index (SSI; Yu and Oguchi 2010) was calculated. This parameter links the pore size distribution of the lithotype with its liability to salt weathering. For SSI values lower than 4, the lithotype is supposed to have salt weathering resistance, while for values higher than 4 the material should be subject to salt decay.

All the studied lithotypes were employed as building materials in a different part of Italy and with different functions. In particular, FGV and CGV were adopted for stairs, walls and other architectonic uses, as well as for sculpture. Under the different condition of use, weathering patterns are developed; those linked to saline solutions are mainly registered for outdoor staircases and wall basements that can suffer even severe material loss. RV and BA are primarily employed as cladding or paving in sheltered locations, however, salt induced weathering can easily become the first origin of differential erosion.

3 Methods

3.1 Salt induced weathering

The salt-induced weathering tests were carried out at the University of Zaragoza (Spain) following the continuous partial immersion procedure described by Benavente et al. (2001), using five different saturated saline solutions: Na_2SO_4 , MgSO_4 , Na_2CO_3 , NaCl , and KNO_3 . This test alternates temperature and relative humidity cycles in a climatic chamber, to generate precipitation and dissolution from the saline solution by the wick effect. The specimens were

Table 1 Petrography and main physical characteristics of the analysed materials (modified after Scrivano et al. 2018)

Litho- type	Abbrevia- tion	Petro- graphic definition	Texture	Minerals [volume %]	Allochems	Porosity type	Open poros- ity [volume %]	Volume weight [g/ cm ³]	Open porosity recast by mercury intrusion porosimetry [Volume %]						SSI
									Ø < 0.1 µm	0.1 < Ø < 0.25 µm	0.25 < Ø < 1 µm	1 < Ø < 7.5 µm	7.5 < Ø < 25 µm	25 < Ø < 75 µm	
Breccia aurora	BA	Brecciated lime- stone— intras- parite	Breccia	Cal (99%) Qtz (0.5%) Mnt-Chl (0.5%)		Inter- granu- lar	0.6 ± 0.1	2.69 ± 0.1	0.2	0.0	0.1	0.3	0.0	0.0	1.2
Rosso verona	RV	Biomicrite	Nodular	Cal (98.5%) Qtz (0.5%) Ill (1%) oxides (trace)	Bivalves ammo- nites	Inter- granu- lar and intra- granu- lar (in phyl- losili- cates and altered miner- als)	1.7 ± 0.1	2.82 ± 0.1	0.7	0.0	0.0	0.0	0.5	0.5	0.9
Vicenza stone	Fine grained: FGV coarse grained: CGV	Biomic- sparite	Clast sup- ported	Cal (99.9%) oxides and hydrox- ides (trace)	Nummulites foraminif- era red algae sponges corals bryozo- ans	Intra- and inter- granu- lar, vugs, fenes- tral inter- granu- lar	22.9 ± 0.1 23 ± 0.1	2.66 ± 0.1 2.49 ± 0.1	5.1 3.3	5.2 7.3	4.6 3.9	5.7 2.8	7.2 5.0	0.0 4.6	7.5 6.6

Open porosity and density values were recast from mercury intrusion porosimetry (MIP), SSI salt susceptibility index (SSI) was calculated after Yu and Oguchi 2010. Cal = calcite; Qtz = quartz; Mnt-Chl = montmorillonite-chlorite; Ill = illite

immersed to a depth of one-tenth of their height in a saturated saline solution for the complete duration of the experiment, in fact the solution level was monitored every 12 h to ensure that the experimental conditions were preserved. The test consisted of 15 cycles of 24 h, in which 12 h were at 40 °C with 80% RH, then followed by 12 h at 30 °C with 60% RH. To make sure that the solutions remained saturated, they were replaced every five cycles. Six 3 × 3 × 3 cm cubic specimens of each lithotype were tested with each salt solution (total 120 specimens). Three specimens of 6 underwent 10 treatment cycles, while the other 3 specimens underwent all 15 cycles to estimate the further evolution of the decay process. After visual inspection, and before petrophysical characterization, the specimens were rinsed with deionized water until they stopped forming efflorescence at the surfaces while drying. The process removed the salts from the porous network allowing a direct study of the pore structure.

3.2 Weathering evaluation methodologies

3.2.1 Visual inspection

The visual inspection procedure is recommended (UNI EN 12,370:2001; Lubelli et al. 2018) for evaluating saline solution-induced damage. In the present study, before rinsing off the efflorescence, macro-photographs of the specimens were acquired using a Canon EOS Rebel T3 device. The images were compared with images of the unweathered specimens, to evaluate the modifications induced by the saline solutions and the morphology of the efflorescence crusts.

Visual inspections were made after each cycle. Empirical values from 0 to 3 were assigned to the specimens based on their physical appearance: 0 = intact specimen, 1 = very minor change (minor rounding of corners and edges) with no decay of the integrity of the specimen, 2 = evidence of disaggregation or cracks, 3 = specimen without cohesion.

3.2.2 Relative mass variation

The calculation of the percentage of relative mass loss (ΔM) is recommended to represent physical deterioration according to UNI EN 12,370:2001. In the present study, relative mass loss (ΔM) was calculated by recording the mass of the dried specimen before (m_0) and after salt weathering and rinsing (m_d) by the following equation:

$$\Delta M = [(m_d - m_0)/m_0] \times 100 \quad (1)$$

The samples before and after weathering were oven-dried at 50 °C to record the exact dry mass. According to literature (Alves et al. 2017) also the Mass Increase (MI), representing salt crystallization as sub-efflorescence and efflorescence,

was recorded following Eq. 1 and considering the mass of the specimens dried before rinsing as m_d .

3.2.3 Scanning electron microscopy

Scanning Electron Microscope (SEM) images of the surface of 20 salt-contaminated specimens (specifically cut 1 cm × 1 cm × 2 cm parallelepipeds, see Table 2) were obtained with a Tescan Vega 3 LMU SEM coupled with a microanalysis TEAM energy dispersive system (EDS) at the Department of Earth, Environment, and Life Sciences (DISTAV), University of Genoa, Italy. The specimens were mounted on aluminium stubs by carbon tape and then coated with gold sputter. SEM photomicrographs were taken under high-vacuum conditions at 200×, 500×, and 1000× magnifications by a backscattered electron signal.

3.2.4 Hygroscopic properties

The hygroscopic properties of the samples, before weathering and after the salt removal from the pore network by repeated rinsing, were tested using the method specified in ISO 12,571:2013. The testing was carried out at the University of Zaragoza on 120 specimens using a climatic chamber set to maintain a temperature of 21 °C at varying relative humidity (see Table 2). The relative humidity was stepwise varied at 25%, 50%, 75%, 90%, and 95%. Once the specimens reached the equilibrium for each humidity step (c. 24 h), the mass of absorbed water was determined. The porosimetric curve of pores smaller than 0.1 µm was calculated by correlating the relative humidity and the capillary radius, expressed by Kelvin Eq. (2)

$$\varphi = \exp \left[-\frac{2\sigma \cos \theta}{r \rho_w R_D T} \right] \quad (2)$$

where φ is the relative humidity value; σ is the surface tension of water; θ is the wetting angle; r is the capillary radius; R_D is the water vapour constant; T is the absolute temperature; and ρ_w is the water density at T .

3.2.5 Capillary uptake

The UNI EN 15,801:2010 test procedure was followed to measure the capillary uptake. The oven-dried cubic specimens were placed onto a water saturated bedding layer and were weighed at determined time intervals, whose frequency depends on the pore network characteristics of the addressed lithotype. The test was stopped when the weight difference between two consecutive measurements was below 1% of the whole specimen mass. The mass data were acquired using a precision balance (accuracy = 0.01 g), and the absorbed

water per unit area (Q_i) at each time lapse was calculated using:

$$Q_i = [(m_i - m_d)/A] \quad (3)$$

where m_i is the mass of the sample at each time interval, m_d is the mass of the dried sample, and A is the area of the face in direct contact with the bedding layer. A relationship was established between Q_i and time.

The specimen set is made of six 3 cm × 3 cm × 3 cm cubic samples, for each lithotype and saline solution, i.e., 240 capillary measurements were carried out before and after salt weathering on 120 total specimens (see Table 2).

4 Results

4.1 Visual inspection

The visual analysis of the weathered specimens before rinsing (Fig. 1; Table 3) shows that Na_2SO_4 and Na_2CO_3 are the most weathering-effective saline solutions among those analysed. Sample deformation observed after Na_2SO_4 and Na_2CO_3 contamination (i.e., powdering and breakage of the specimens) suggest respectively dissolution processes for FGV and CGV and swelling of the micrite–phyllosilicate veins in RV. The MgSO_4 solution caused minor rounding in FGV and CGV, and moderate swelling of the veins in RV. The NaCl and KNO_3 solutions affected mostly the surfaces of the specimens, producing efflorescence as fluffy and crust-like forms.

4.2 Relative mass variations

The relative mass loss data recorded for the different salts and lithotypes (Table 4) highlights that Na_2SO_4 and Na_2CO_3 saline solutions are exceptionally damaging to carbonates (Fig. 2). In particular, FGV and CGV underwent severe weathering, with weight loss of *c.* 30% after 15 cycles in the Na_2SO_4 solution, and disintegration after 15 cycles in the Na_2CO_3 solution. The weathering rate for CGV was higher than for FGV, resulting in higher mass variation after 10 cycles. The Na_2CO_3 saline solution caused the breakage of a part of the RV samples along the micrite + phyllosilicate joints, introducing high variability in the recorded results. The crystallization after MgSO_4 solution caused a minor material loss in the more porous lithotypes (i.e., FGV and CGV), whereas the compact lithotypes (i.e., RV and BA) were unaffected. The NaCl and KNO_3 saline solutions did not cause a substantial material loss in any of the analysed materials.

Plotting the final Mass Loss (ML) against open Pore volume (P) for each specimen (Fig. 3; Alves et al. 2017)

Table 2 Summary of the number and sizes of the specimens studied with each method

Lithotype	SEM	Visual inspection		Relative mass variation		Capillary absorption		Hygroscopic properties	
		n° of samples	Size [cm]	n° of samples	Size [cm]	n° of samples	Size [cm]	n° of samples	Size [cm]
BA	Unweathered	1	1 × 2	1	3 × 3	6	3 × 3	6	3 × 3
	Salt weathered	10		30		30		30	
RV	Unweathered	1		1		6		6	
	Salt weathered	10		30		30		30	
FGV	Unweathered	1		1		6		6	
	Salt weathered	10		30		30		30	
CGV	Unweathered	1		1		6		6	
	Salt weathered	10		30		30		30

Fig. 1 Visual inspection. Photographs of the most significant specimens for each lithotype, saline solution, and time of exposure. FGV and CGV treated with Na_2SO_4 and Na_2CO_3 solutions show signs of deformation by deliquescence. RV micrite + phyllosilicate veins are

more prone to decay compared with the host rock. KNO_3 was crystallized on every lithotype as a thick crust on the surface of the specimens

evidences that VS specimens usually have a higher mass loss, while despite having comparable open Pore volume BA and RV have different behaviours.

The ratio between MI and open Pore volume (P) (Fig. 3) shows that low porosity lithotypes (*i.e.*, BA and RV) usually host comparable amounts of salt inside the pore network. A greater variability occurs for FGV and CGV; precipitation of MgSO_4 , NaCl and KNO_3 from the respective solutions corresponds to comparable mass increase, while Na_2SO_4 mass in percentage increases by a half, and Na_2CO_3 solution generates a double mass increase.

4.3 Scanning electron microscopy

The Na_2SO_4 -weathered specimens have several efflorescence morphologies, ranging from a compact crust (Fig. 4a, c), to fine aggregates of anhedral microcrystals (Fig. 4b–d) and whiskers (Fig. 4b). In FGV and CGV, different efflorescence morphologies coexist (Fig. 4c). Moreover, the SEM images show that calcite is widely affected by dissolution along crystallization planes (Fig. 4d) and that stepwise precipitation of secondary calcite has occurred on the surface (Fig. 4a, c, d).

The specimens treated with the MgSO_4 solution developed variably fractured salt crusts, with dissolution or dehydration pits (Fig. 4f, g). The precipitation of fine-grained saline aggregates, rarely in whiskers, is associated with major cracks across the crusts, (Fig. 4f, g). The MgSO_4 saline solution proved aggressive, causing the dissolution of primary calcite (Fig. 4e), the formation of secondary calcite (Fig. 4f) and tabular lamellae of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; Fig. 4g, h).

Only BA and RV, of the four Na_2CO_3 -weathered specimens, could be inspected using SEM analysis at the end of the weathering cycles because FGV and CGV were completely pulverized during the weathering experiments. At the surfaces of the specimens, the salt forms a crust with waxy texture due to thermal dissolution (Fig. 4i) and fine aggregates (Fig. 4l) with rare spherulites of radiating crystals. A secondary precipitation of calcite overprints the pristine primary texture (Fig. 4i, l). The surface of RV shows patterns of stepwise crystallization under changing environmental conditions (Fig. 4l).

The NaCl -weathered specimens have several efflorescence morphologies, ranging from a compact (Fig. 4m, n) to a composite crust composed of hollow-faced cubes (Fig. 4m), whiskers (Fig. 4n), euhedral crystals (Fig. 4o), and skeletal crystals (Fig. 4o, p). No evidence of secondary precipitation of calcite was found at the surface of the specimens.

The KNO_3 solution formed a compact salt crust with rare filaments; moreover dissolution features of the carbonatic substrate were observed (Fig. 4s, t). Notably, the onset of

Table 3 Visual inspection after 15 cycles. Empirical ranking from 0 to 3, assigned to the different appearances of the materials after weathering: 0=intact, 1=minor change with no decay of the integrity of the specimen, 2=disaggregation or cracks, 3=no resistance

	Na_2SO_4	MgSO_4	Na_2CO_3	NaCl	KNO_3
BA	0	0	0	0	0
RV	1	1	2	0	0
FGV	3	1	3	0	0
CGV	3	1	3	0	0

Table 4 Summary of relative mass variation data, microporosity increase–decrease and SSI adequacy

Lithotype	Salt	MI after 10 cycles [% i.w.]	MI after 15 cycles [% i.w.]	ML after 10 cycles [% i.w.]	ML after 15 cycles [% i.w.]	Increase in micropores [% total volume]	Adequacy of SSI
BA	Na ₂ SO ₄	− 0.1 ± 0.2	0.1 ± 0.1	0.04 ± 0.01	0.07 ± 0.05	0.06 ± 0.01	++
	MgSO ₄	0.15 ± 0.04	0.52 ± 0.06	0.03 ± 0.02	0.02 ± 0.07	− 0.001 ± 0.001	++
	Na ₂ CO ₃	0.16 ± 0.02	0.5 ± 2.05	0.03 ± 0.03	0.08 ± 0.01	0.07 ± 0.01	++
	NaCl	0.2 ± 0.03	0.28 ± 0.03	0.01 ± 0.02	0.03 ± 0.02	0.22 ± 0.1	++
	KNO ₃	0.87 ± 0.67	1.64 ± 0.5	0.001 ± 0.001	0.01 ± 0.01	0.1 ± 0.01	++
RV	Na ₂ SO ₄	0.1 ± 0.0	0.6 ± 0.4	0.15 ± 0.05	2.11 ± 0.6	0.76 ± 0.2	+
	MgSO ₄	0.44 ± 0.4	0.88 ± 0.28	0.14 ± 0.6	0.33 ± 0.5	0.34 ± 0.1	++
	Na ₂ CO ₃	0.37 ± 1.22	2.58 ± 4.45	33.95 ± 57.21	33.5 ± 57.6	− 0.16 ± 0.1	−
	NaCl	0.54 ± 0.08	0.61 ± 0.01	0.17 ± 0.09	0.09 ± 0.03	0.3 ± 0.1	++
	KNO ₃	0.78 ± 0.7	1.37 ± 0.12	0.13 ± 0.04	0.17 ± 0.09	0.27 ± 0.1	++
FGV	Na ₂ SO ₄	6.0 ± 7.1	2.3 ± 6.7	15.65 ± 4.63	34.01 ± 12.2	1.9 ± 0.1	++
	MgSO ₄	9.45 ± 0.53	15.61 ± 0.39	2.08 ± 1.29	1.43 ± 0.92	5.26 ± 0.2	+
	Na ₂ CO ₃	17.3 ± 4.28	32.91 ± 3.68	46.72 ± 46.3	100 ± n.d	5.71 ± 0.1	++
	NaCl	10.15 ± 0.8	13.38 ± 0.56	0.17 ± 0.02	0.12 ± 0.07	3.33 ± 0.2	−
	KNO ₃	12.22 ± 0.7	14.33 ± 7.21	0.25 ± 0.07	0.19 ± 0.04	3.24 ± 0.2	−
CGV	Na ₂ SO ₄	3.8 ± 3.6	7.8 ± 1.1	25.46 ± 13.24	27.97 ± 8.51	1.9 ± 0.1	++
	MgSO ₄	9.37 ± 0.83	14.83 ± 0.35	2.33 ± 1.29	2.18 ± 0.6	5.56 ± 0.1	+
	Na ₂ CO ₃	18.84 ± 4.39	30.15 ± 6.61	72.98 ± 46.8	100 ± n.d	7.78 ± 0.2	++
	NaCl	9.77 ± 0.78	13.25 ± 0.99	0.2 ± 0.09	0.18 ± 0.01	3.53 ± 0.1	−
	KNO ₃	11.41 ± 1.67	15.16 ± 0.93	0.17 ± 0.15	0.16 ± 0.07	3.46 ± 0.2	−

Mass Increase (MI) and Mass Loss (ML) for 10 and 15 cycles are reported with their standard deviation. For SSI adequacy: ++ = very adequate; + = adequate; − = inadequate

crystal nucleation occurred along the cleavages of calcite crystal (Fig. 4q), and secondary calcite developed on the earlier crust (Fig. 4r).

4.4 Hygroscopic properties

Hygroscopic-based porosimetry of the unweathered and of 15 cycles-weathered specimens (for all the samples except for FGV and CGV in Na₂CO₃ solution, whose data are referred to the samples at 10 cycles), allowed identifying changes in micro-pore distribution (Fig. 5). In RV, FGV, and CGV in Na₂SO₄-treated specimens, a class of pores smaller than 0.002 µm developed, along with an increase in the frequency of pores measuring 0.003–0.1 µm. In FGV and CGV, a significant increase in the number of pores with *c.* 0.1 mm diameter occurred. A similar modification of the pore network was also observed in MgSO₄-treated specimens. In FGV and CGV, NaCl and KNO₃ induced modifications in the distribution of micro-pores. Finally, BA specimens were not affected by any of the tested solutions.

4.5 Capillary uptake

The capillary uptake was measured before and after the weathering test with different saline solutions for all

specimens (Fig. 6). In particular, after *c.* 45 h (Fig. 6, left side) the weathered specimens absorbed less water than the unweathered ones, except for BA and RV after NaCl and KNO₃ contamination. Conversely, in the first two minutes of the test (Fig. 6 right side), the water content for the weathered samples shows a faster increase. The BA specimens show a slight decrease in the velocity of capillary rise when exposed to the Na₂CO₃ and MgSO₄ solutions, whereas an increase in velocity occurred in the Na₂SO₄-, NaCl- and KNO₃-weathered specimens. The capillary dataset for RV showed a slight decrease in the velocity of water absorption for all weathered specimens. The FGV and CGV lithotypes are affected by an increase in capillary absorption rates for all specimens.

5 Discussion

The precipitation of salt crystals occurred inside and outside the pore network, depending on the physical features of the pore network or on the solutions. Precipitation is associated inside the stone with modification of petrophysical parameters, and outside with evidence of salt crusts at the macroscale. Following salt precipitation, also deterioration by cracks, efflorescence and sub-efflorescence,

Fig. 2 Relative mass variation. The diagrams show the mass variation relative to the initial mass (in percent) for each saline solution. The different colours correspond to different lithotypes: gray=BA; orange=RV; green=FGV; purple=CGV. The data are averaged

for the set with 10 cycles of weathering (triangles+dashed lines) and for the set with 15 cycles of weathering (squares+solid lines). Salts=dry mass of the samples with salts, water=mass of the wet samples after rinsing, dry=dry mass of the samples after rinsing

Fig. 3 Relative mass variations. Top: Plot of final mass loss (ML) against maximum mass increase (MI) expressed as % of the total volume. Bottom: Plot of mass increase (MI) in [g], against pore volume (P) in [cm³]. Circle=BA; square=RV; triangle=FGV and rhombus=CGV

chemical reactions, grain loss, and rounding developed. Cracks develop in the RV samples mainly along the micrite + phyllosilicate veins. This texture, characterized by higher porosity than the nodules and by highly reactive surface, due to the fine calcite diameter, is the weakest element of the lithotype.

Grain loss and rounding characterize mainly the two bioclastic VS limestones. Efflorescence, sub-efflorescence and chemical reactions affect at different extent all the lithotypes. The chosen solution are generally weakly acidic, fact that explains the patterns of secondary precipitation in every sample. Conversely, Na₂CO₃ having pH around 10, have a basic behaviour, more effective in dissolving mineral phases.

Under SEM, several distinct efflorescence morphologies for the different saline species were revealed. Herein, some of the saline solutions, under alternating hydration–dehydration, and variable temperature–humidity rate during the testing procedure, allowed crystals to precipitate and subsequently modify. Furthermore, the diverse patterns of crystallization depend on the environmental conditions: euhehedral crystals or compact crusts represent precipitation from solution in a damp environment, whereas skeletal forms and cracks appear to be the most diffuse crystallization habits developed during evaporation (Rodríguez-Navarro et al. 2000; Charola et al. 2007, 2017; Lopez-Arce et al. 2009; Lubelli et al. 2018). The development of overlapping series of different morphologies can be interpreted as signs of a stepwise crystallization influenced by the environmental conditions.

The most porous lithotypes, FGV and CGV, presented the highest SSI values and, in fact, were the most liable to material loss and modification of their hydric properties. In particular, the stones showed high weathering rates when exposed to Na₂SO₄, Na₂CO₃, and MgSO₄ solutions. The modification of the micro-pore network, i.e. increase in capillary rise during the first minutes of soaking, and hygroscopic sorption variations, took place during exposure to all saline solution, and was confirmed by relative mass variation (Table 4). Moreover, as the complete capillary absorption dataset includes a decrease of the total content of water absorbed by the specimens, the widening of the larger pores, can be inferred as related with mechanical stresses and calcite dissolution. The latter is assumed after the observation of secondary calcite re-precipitation for all the saline solutions. Moreover, the formation of tabular crystals of calcium sulphate, probably gypsum, on the specimens treated with

Fig. 4 SEM photomicrographs (various magnifications) at the surfaces of the control specimens for each lithotype and saline solution tested. Different crystallization shapes and phases are focussed

sulphate solutions confirms that chemical reactions occurred at the rock surface.

Despite its low SSI parameter, RV was affected by Na_2SO_4 and Na_2CO_3 solutions. Visual inspection and SEM images showed that the most conspicuous crystallization occurred at the micrite–phyllosilicates veins, sparing the compact nodules, with consequent differential behaviour between the two zones with diverse porosity (Benavente et al. 2007). The differential durability of nodules and veins place this lithotype in the category of dual-porosity materials. Therefore, the SSI value rather reflects the hardness of the nodules, whereas the veins are more weatherable. In RV the pore network within the micrite–phyllosilicates veins was modified by pore enlargement (Scrivano et al. 2018) especially after Na_2SO_4 , MgSO_4 and Na_2CO_3 salt contamination. The joints interested by the mechanical and chemical stresses induced by the saline solutions explains the small rate of decay, compared to CGV and FGV.

The compactness of BA resulted in high resistance to salt decay, as demonstrated by the slight modification of hydric properties and the virtual lack of mass loss, consistent with the values of SSI.

The main difference in the behaviour of RV and BA resides in the veins. In fact, while the recrystallized veins of BA are as compact as the breccia clasts, the micrite + phyllosilicates joints cementing the micritic nodules of RV are characterized by diffuse inter-granular + intra-granular pores resulting in a widespread reactive surface. Moreover, the different behaviour of nodules and veins in the lithotype

led to differential weathering and breaking, especially in RV + Na_2CO_3 .

Overall, the SSI proved efficient in predicting the behaviour of homogenous lithotypes (i.e. BA, FGV and CGV), however, this index does not consider the chemical activity of the different saline solutions, thus overrating the susceptibility of FGV and CGV to MgSO_4 , NaCl and KNO_3 .

Generally, the most compact fabric (BA and RV nodules) account for a greater durability to salt action, while high open porosity values (FGV and CGV) and abundance of micrite (RV) caused higher susceptibility to decay; in particular, FGV, CGV and RV micrite + phyllosilicate veins showed low durability for sulphate and carbonate contamination. Therefore, caution must be adopted when using these stones in outdoor for the presence of acid rains, and in the presence of lime-based bedding mortars and high capillary-rise rate.

6 Conclusions

The experiments on the four carbonatic sedimentary stones allow the following conclusions:

1. The rocks with the more compact textures (BA) are less susceptible to decay compared with the more porous (FGV, CGV) or more heterogeneous structures (RV), suggesting a link between a higher specific reactive surface and higher weathering susceptibility

Fig. 5 Hygroscopic-sorption-based porosimetry. Bar diagrams showing the calculated micro-pore distribution for each lithotype and saline solution before (u, blue bars) and after (s, red bars) weathering. FGV and CGV show wide variations in the micro-porosimetric distribution profile

2. The use of different saline solutions enabled determining the impact of each salt on the stone. Na₂SO₄ and Na₂CO₃ were found to induce the highest weathering rates in the tested materials due to their chemical interaction with the rocks and the liability to crystallize under different hydration states
3. The SEM-EDS microanalysis revealed that sulphates interact chemically with the carbonate substrate, forming secondary minerals (mainly gypsum)
4. The hydric test methods were effective for recording porosimetric variation; in particular, capillary absorption assessed the enlargement of capillary pores during the weathering process

Fig. 6 Capillary absorption. A comparison of mean values representing unweathered (black lines) and salt-weathered (Na_2SO_4 = red; MgSO_4 = orange; Na_2CO_3 = green; NaCl = blue; KNO_3 = purple) specimens. The variations in the pore networks are highlighted by the different profiles of the Q_i vs. $\sqrt{t}$ curves

5. The SSI proved not completely reliable because it does not take into account the properties of the different saline solutions, and their chemical interaction with the host rock. Moreover, SSI depends on porosimetric distribution calculations that are possibly affected by textural or compositional inhomogeneities of the addressed lithotypes
6. The susceptibility to salt decay of RV, FGV, and CGV advises against their use in outdoor for new constructions and suggests cautions when dealing with dimension stone blocks used in historical structures

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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