Micro-porosity and minero-petrographic features influences on decay: Experimental data from four dimension stones

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H I G H L I G H T S
_ Associated MIP and hygroscopic sorption are effective in the characterisation of micro-porosity.
_ Joint MIP and hygroscopic sorption allowed detecting the presence of hygroscopic clay minerals.
_ Mineralogical and petrographic features allowed interpreting the results of the two techniques, when contrasting.
_ On the whole the suggested methodology allowed deciphering the simulated weathering processes.

A B S T R A C T

Sedimentary stones have been used since long as dimension stones, constituting the primary building material of several monumental structures all over the world. The understanding of their behaviour when exposed to weathering factors is crucial for preservation, replacement and restoration intervention.

Although not directly involved with decay mechanisms, micro-pores (i.e. open pores with radius <0.1 mm) and their interconnection to the wider ones are important for air and water flow inside rocks. In fact, micro-pores are not directly the site of ice or salt crystallization, nor of oil and gas entrapment, but are the main pathway for fluids during both adsorption and evaporation processes. The study of narrow pores is therefore crucial to predict e.g. stone durability and physical properties. This study presents the study on four different sedimentary lithotypes vastly employed as dimension or ornamental stones in Italy, both sound and artificially weathered. In particular, coupled MIP and hygroscopic sorption based micro-porosimetry were used to uncover liability to relative humidity variation, in association with a thorough mineralogical characterization. The MIP intrusion pattern attained pore shapes and typology description for the different rock types; but only the hygroscopic sorption helped deciphering the ongoing processes. Moreover, the coupling of petrography and petro-physical analyses (i.e. MIP and hygroscopic sorption based micro-porosimetry) pointed out that phyllosilicates have a role in decay processes of rocks due to swelling and/or suturing of the adjacent voids.

Keywords:
Dimension stone
Sedimentary rocks
Durability
Micro porosity
Hygroscopic sorption based porosimetry
Salt weathering

1. Introduction

Availability, workability, mechanical performances and appearance are some of the factors that, for centuries, induced selection and usage of natural lithic materials to build or ornate structures [1,2]. Even if, generally, sedimentary stones present lower durability and mechanical performances if compared to volcanic or metamorphic lithotypes their availability as raw materials, aptitude for workability, and visual appearance allowed sedimentary stones wide employment throughout men's history as dimension and ornamental stones.

In order to be able to perform adequate replacement and restoration intervention, or to plan preventive care and monitoring it is necessary to characterize the main internal factors leading to decay when exposed to weathering factors [3]. The mineralogy of the diverse rock typology comprised under this genetic category has high variability as well as diverse textures and structures. One of the most variable factor is porosity, ranging from low values in compact sandstones and limestones to high values in less compacted sediments (e.g. biocalcarenites, bioclastic limestones) [4]. The bearing of pore size distribution to different kind of weathering has been since long addressed [5–9]. Several analytical techniques providing a precise evaluation of the pore space and other related values as tortuosity, formation factor, etc. were implemented for their high-resolution performances in describing pore networks (in particular: X-ray Computed Tomography, NMR, ultrasounds, and resistivity) [10,11].

Several authors recognize the importance of predicting rock durability when dealing with Cultural Heritage, stating that the analysis of porosity is crucial to foresee rock performances [8,12].

In particular micro-pores (i.e. open pores with radius < 0.1 mm) even if not connected with the main fluid flow processes, as capillary rise, are the main pathway for air, water and their solutes (i.e. water vapour, pollutants etc.). Accordingly micro-pores are the site of the processes related to fluid-rock interaction (i.e. evaporation, hydration, deposition, etc.), having a major role in weathering mechanisms [13,14]. Micro-pores, being the site of condensation, are also important to describe the thermo-hygrometric properties of buildings [15,16]. Several techniques are currently applied to get information about micro-pores (e.g. size, shape, distribution).

Between 0.001 and 0.1 lm the relative pore volume and the opening size distribution can be determined by means of Mercury Intrusion Porosimetry (MIP), Brunauer-Emmet Teller (BET), small-angle neutron scattering (SANS), image analysis and techniques based on the hygroscopic behaviour of micro-pores [11,17,18]. These techniques could also be efficiently combined between them [8] or with opportune image analysis [9] or physical techniques (e.g. ultrasounds [19,20], and permeametry [21]), in their resolution ranges, to define the micro-pore space. MIP is a popular technique to characterise porous materials, allowing the reconstruction of open pore radius distribution generally from c. 0.01 to c. 70 mm.

It is to take into account that the required calculation introduces approximations by simplifying the real geometry of the pore network (i.e. the calculations are based on input parameters (c, h) with questionable values, refer to cylindrical voids and do not take into account the so-called ink-bottle effect). Moreover structural features of the samples are usually not considered (e.g. the risk of damaging the material by exerting high pressure) [22–24]. However, mathematical models are used to correct these approximations, and to recast several parameters, as pore typology and shape, tortuosity and grain-size [18]. A process similar to the BET technique of adsorption controls the hygroscopic behaviour of micro-porous materials (Fig. 1): the surfaces of the porous system accumulate water molecules until the equilibrium moisture content content is reached. At increasing relative humidity (RH), the adsorption continues with the formation of subsequent molecular layers with lower binding forces, until equilibrium state is reached.

Assuming isothermal conditions, the sorption isotherm describes the accumulated water volume vs. the relative humidity value.

The Kelvin equation correlates RH and capillary radius allowing the construction of a micro-porosimetric curve reflecting the hygroscopic behaviour of the analysed material.

The hygroscopic behaviour of materials as a key to interpret decay processes is critical for the following reasons: i) it is linked with the presence of micro-pores, and ii) it is connected with the presence of hygroscopic materials both as primary rock-forming minerals, or secondary minerals e.g. salts precipitated form circulating solutions. In fact the so-called hygroscopic minerals (e.g.

phyllosilicates and salts) attract water into their structure, increasing their volume and causing a mechanical shock (i.e. micro-cracks) to the rock structure (e.g. turning from anhydrite to gypsum the crystal volume increases of about 60%) [25–27]. Usually, for a better understanding of the amount of stress induced by RH variation and the consequent moisture condensation or evaporation processes inside the rock core, swelling tests are performed, but this quantification is not the aim of this research.

This study addresses the micro-porous range by means of MIP and hygroscopic sorption based porosimetry in order to explore the advantages of coupling the techniques. Four different sedimentary lithotypes vastly used as dimension or ornamental stones, both sound and salt weathered, were analysed. The obtained porosimetric curves were associated with a detailed minero petrographic analysis to investigate the micro-porosimetric characteristics of materials and their modification after salt crystallization.

Following the preliminary characterization of the microporous network, the onset and development of a secondary porosity were detected, along with a revision of the application of MIP to investigate micro-porosity, and the disclosure of the potentiality of hygroscopic sorption in deciphering weathering mechanisms.

Moreover, the coupling of petrography and petrophysical analysis (i.e. MIP and hygroscopic sorption based micro-porosimetry) allowed investigating the connection between phyllosilicate occurrence in the stone and decay processes.

2. Experimental

2.1. Materials

The addressed lithotypes, differing by relative abundance of components (e.g. minerals, fossils, oxides and hydroxides) or grain-size (Table 1), have widespread use as dimension and ornamental stones in the Italian Cultural Heritage. The selection criteria were i) difference in mineral-chemical composition, and ii) differentiation in the open porosity values, in order to establish correlations

between these parameters and durability. Macigno Sandstone (MS), Breccia Aurora (BA), Rosso Verona (RV) and Vicenza Stone (VS) were the selected stones (Fig. 2).

MS is a turbiditic sandstone, with very fine to medium grained sandy clasts mainly of quartz (SiO_2) and feldspars (albite ($Na(AlSi_3O_8)$), orthoclase ($Al_2O_3|K_2O|6SiO_2$))), secondary calcite ($Ca(CO_3)$) and phyllosilicates of the montmorillonite-chlorite series (Na-Ca-Al-Si_4O_{10} - O) [28]. The lithotype presents bluish-grey fresh cut surfaces, and yellowish surfaces when weathered. The clayey cement is scarce and, with a few calcite, wraps the clasts. A net of narrow pores can be evidenced along grain boundaries and inside clay minerals, which wrap the main quartz grains. This rock, quarried in Tuscany, has been used since long time as dimension stone. It has been widely employed for architectural ornamental elements (e.g., capitals, columns, corbels, etc.), and during the Florentine Renaissance was preferred by Brunelleschi and Michelangelo to emphasize structural elements and give movement to the facades [29]. Nowadays this lithotype is widely employed as paving stone in outdoor.

BA is a polygenic breccia consisting mostly of calcareous variegated fragments, cemented by calcite. The mineral composition mainly encompasses calcite ($CaCO_3$), accessory quartz (SiO_2), illite ($K_{0,5}(Al,Fe,Mg)_3(Si,Al)_4O_{10}(OH)_2$) and montmorillonite-chlorite (Na-Ca-Al-Si_4O_{10} – O). The brecciated texture helps classifying the rock as an intrasparite, where the sparry matrix shows stepped recrystallization and rhombohedral cleavage. Micro-porosity results diffuse, especially along the suture veins. This lithotype was used in the past in the area near Brescia as ornamental stone for inlays; while now is widely used for internal cladding and paving.

RV is an organogenic nodular limestone with marly matrix, corresponding to a bio-intra-micrite. The mineral composition comprises calcite ($CaCO_3$), accessory quartz (SiO_2), and illite ($K_{0,5}(Al,Fe,Mg)_3(Si,Al)_4O_{10}(OH)_2$). The cementing veins are filled by micrite, phyllosilicates and Fe-oxides, and the compact micritic nodules include dispersed bivalve and ammonoid molluscan casts replaced by sparry calcite. Pores occur at nodule boundaries and along clayey veins. For its easy workability this lithotype was used since the roman era as building stone (e.g. in the Arena of Verona), during modern age has been widely employed as ornamental stone for

little sculptures, architectural ornament, inlays, mosaics, claddings, and paving.

Vicenza Stone is a bioclastic limestone, often recrystallized and cemented by micrite matrix, with rare oxides and hydroxides that account for the bulk yellowish colour. The texture is heterogeneous,

with coarse to fine grain size, and high porosity. Fossils are replaced by sparry calcite and cemented by abundant micrite matrix. Porosity has a heterogeneous distribution, and is mainly classifiable as intra-clastic, even if also inter-clastic and microporosity are diffuse. As the provided samples showed two different grain size, two sets Coarse-grained (CGV) and Fine-grained (FGV)

were analysed. The use of Vicenza Stone is widespread over the centuries both as dimension stone and as raw materials for sculpting or architectural ornaments, particularly Palladio and his school promoted the widespread use of this lithotype in monumental complexes.

2.2. Methods

2.2.1. Polarized light optical microscopy - MOLP

MOLP has been carried out at the laboratories of the Department of Earth, Environment and Life Sciences (DiSTAV) of the University of Genoa (Italy) with a petrographic microscope coupled

with an Optikam B5 microscopy digital USB camera with a 2592⁄1944 pixels (5Mpixels) resolution, equipped with Optika Vision Lite and Optika View acquisition software. The thin sections were prepared polishing the samples to 30 μm thick.

2.2.2. Scanning electron microscopy - SEM

The SEM analysis was carried out using a Tescan Vega 3 LM scanning electron microscope equipped with an Apollo X detector and a Microanalysis TEAM energy dispersive system (EDS), installed at the DISTAV, University of Genoa, Italy. Microphotographs were acquired with an optimized ratio between back scattered and secondary electrons, using graphite-sputter-coated 3D samples under high-vacuum conditions.

2.2.3. X-Ray powder diffractometry - XRPD

XRPD was carried out at the DiSTAV laboratories (University of Genoa, Italy) by an automated Philips PW 1140 Xchange diffractometer, equipped with the X'pert plus, X'pert data collector, X'pert data high score and X'pert organiser softwares for powder analysis of ICDD phases. The instrument operates with a cobalt (Co) anode and powdered rock specimen (0.2 g of powder up to 100 lm). The first run (from 0_ to 70_ 2θ) allowed characterising the mineralogy of the bulk specimen. The separated clay fraction underwent ethylene glycol and thermal treatment to discriminate clay phases affected by swelling.

2.2.4. Mercury intrusion porosimetry – MIP

The analyses were performed at the Department of Civil, Chemical and Environmental Engineering (DICCA) of the University of Genoa with the Pascal 140 and 240 combined system. The first prepares the sample and carries out low-pressure porosimetry from vacuum up to 400 kPa, measuring very large pores and particles. The second is a high-pressure module (up to 200 MPa pressure), allowing the determination of porosity down to the micro-pores. The Solid_ software, that allows recasting several values (e.g., density, total and incremental pore volume, porosity, pore size distribution, etc.), runs the porosimeters. A dried fragment (c. 1 g) was tested for each lithotype and conservation condition.

2.2.5. Hygroscopic sorption based porosimetry

The water adsorption properties were addressed following the ISO 12571:2013 normative, using a climatic chamber at the University of Zaragoza. The chamber was set at 21 _C and the humidity range steps were fixed at 25%, 50%, 75%, 90%, and 95%. The volume of adsorbed water was determined at equilibrium reached. Cubic specimens had 2.5 cm side, and the time to reach the equilibrium was established to 24 h. The dataset encompasses the average values calculated over six specimens per rock type with their standard deviation.

2.2.6. Ageing process

Decay was induced following the procedure described by Benavente et al. [30], in the laboratories of the University of Zaragoza. The samples were immersed for 1/10 of their height in a saturated saline solution, for 15 cycles alternating 12 h at 40 _C with an RH of the 80% and 12 h at 30 _C with the 60% of RH. In order to maintain the solution Na2SO4 saturated, the latter was renewed each 5 cycles. The test was carried out on six cubic samples (2.5 cm side) of each rock. Before the porosimetric characterization, the precipitated salts were removed with several cycles of deionised water washing.

2.3. Results

For the purposes of this study, only the results related with the open porosity fraction with radius opening lower than 0.1 μm will be discussed.

2.3.1. MS

The analysis of the distribution of open pore access radius obtained with MIP for the sound sample highlights a monomodal distribution with a peak centred at 0.1 lm (Fig. 3a). After salt weathering the same lithotype shows an equidisperse distribution of open pore access radius, registering a solid increment of pore volume with the opening of micro-pores (open pore access radius <0.1 lm) and the widening of the pre-existing porosity up to 1.2 lm of access radius (Fig. 3a). The pressure/intruded volume plot (Fig. 4a) highlights the evolution from intra-granular porosity to inter-granular porosity associated with decay processes. Meanwhile the hysteresis pattern between intrusion and extrusion curves suggests the evolution from cylindrical to platy pores. On the whole, the MIP showed a great difference between percentage values in volume of the sound and weathered open porosity (Table 2). Moreover, the interconnection level increases due to decay, with the decrease of the inversely proportional parameter of tortuosity (Table 2). The analysis of the hygroscopic properties of this lithotype evidenced a high capability of the structure (i.e. pore network and mineralogical composition) to attract water (Fig. 5). The comparison with the weathered sample set enlightened that the MS is severely affected by salt crystallization with a relevant increase in hygroscopic properties, but fairly in microporosity (Fig. 5) (Table 3), probably due to local dissolution and micro-cracks. The comparison between MIP and the hygroscopic sorption based porosimetry curves for sound and salt-weathered samples (Fig. 6a) highlights the difference between the two datasets. The discrepancies compared with sound rock samples derive from the occurrence of expandable phyllosilicates. Conversely, the curves for the weathered specimens suggest that the μ–cracks open inside the phyllosilicates, decreasing their hygroscopic activity.

2.3.2. BA

The MIP curve of the sound sample shows a peak at about 2 μm (Fig. 3b) for inter-particle cylindrical (Fig. 4b) pores. The profile of the porosimetric curve of the weathered sample has a different trend, with a peak at 20 μm of access radius (Fig. 3b). The analysis of the pressure/intruded volume plot (Fig. 4b) highlights that the pore remains cylindrical and inter-granular. The stability of the open porosity and tortuosity values suggests that the different trends of the porosimetric curves are connected with the natural variability of stone texture. The hygroscopic properties of sound and weathered BA are scarce, with no significant changes due to weathering (Fig. 5) (Table 3). Changes in the total open porosity volume % value, or variations in the tortuosity index were not recorded by MIP (Table 2). Only the absolute value of tortuosity (σ), for sound and weathered samples, highlights low interconnection of the pore structure (Table 2). The comparison between the two porosimetric techniques (Fig. 6b) for both sound and salt weathered samples does not highlight relevant discrepancies, considering the standard deviation.

2.3.3. RV

The MIP curve of the sound specimen shows a uniform distribution of pore access radius, with the exception of two peaks, at r _ 0. 01 µm and in a range between 10 and 60 **l**m (Fig. 3c). Pores showed mainly intra-granular distribution and needle or platy shape (Fig. 4c). Conversely, the profile of the porosimetric curve of the weathered sample (Fig. 3c) presents a different trend, with increment of pores with access radius between 9 and 60 µm. The pressure/intruded volume plot (Fig. 4c) highlights the evolution from intra-granular porosity to inter-granular porosity with decay processes. On the whole, the MIP analysis showed an increase of the open porosity volume value after weathering (Table 2). The interconnection level (tortuosity σ = 2.209) remains constant, suggesting a pore widening mechanism rather than the formation of new cracks for mechanical or chemical action (Table 2). The hygroscopic behaviour points out a slight increase in micro-porosity possibly connected with dissolution processes (Fig. 5) (Table 3). The comparison between curves of MIP and hygroscopic based porosimetry curves (Fig. 6c) for sound and salt-weathered samples highlights that the MIP overestimates the µ-porous range, probably for compression exerted on the micrite-phyllosilicates veins; in fact the weathered sample, which probably suffers from **l**cracks formation with veins and phyllosilicate swelling, presents almost parallel curves.

2.3.4. FGV

The MIP porosimetric pattern (Fig. 3d) of the sound sample shows a bimodal distribution, with a peak between at 0.1 and 0.2 µm and a second peak with ra >10 µm. The pore network is mainly composed of intra-particle spherical porosity (Fig. 4d). The profile of the porosimetric curve of the weathered sample has different trends (Fig. 3d), presenting micro-porosity widening and the shrinkage of the wider radius of access with a peak shift to 9 µm. The analysis of the pressure/intruded volume plot (Fig. 4d) highlights a slight increment of intra-particle porosity with spherical shape. The analysis of the porosimetric curves and the intruded volume/pressure plot suggests both a mechanical action with the enlargements of the small pores (throats) and a chemical weathering by dissolution (widening of pores), followed by precipitation of secondary calcite inside the larger pores, with a diminution of the pore access radius of the widest voids. MIP data showed a solid increase of open porosity volume percentage after weathering (Table 2). The interconnection level of the sound sample increased due to decay (Table 2). FGV shows a slight increase in hygroscopic sorption behaviour pointing out a growth in microporosity (mainly centred on 0.1 µm open pores radius access) possibly connected to dissolution processes (Fig. 5) (Table 3). The comparison between the two porosimetric techniques (Fig. 6d) for sound and salt-weathered samples showed that MIP overestimates the micro-porous range in the sound samples, probably for the massive micrite matrix affected by compression. The salt weathered sample shows µ-cracks development in the matrix, resulting in two parallel comparable curves.

2.3.5. CGV

The MIP curve for the sound sample has a bimodal distribution (Fig. 3e), with the first peak between 0.1 and 0.2 μm and the second at open pore access radius >10 μm. The pore network is mainly composed by intra-particle spherical porosity (Fig. 4e). The profiles of the sound and weathered porosimetric distribution curve are very similar (Fig. 3e), except for the % amount of pore size and the slight enlargement of the peak at 0.18 μm, indicating the formation of μ-cracks. In fact, the weathered sample has a higher open porosity, resulting in a volume increase of the main peaks. The analysis of the pressure/intruded volume plot (Fig. 4e) highlights a slight increment of intra-particle porosity with spherical shape. The analysis of the porosimetric curves and the intruded volume/pressure plot suggests i) a mechanical action with formation of μ-cracks, and ii) a chemical weathering by dissolution inside the narrowest pores, iii) in turn followed by precipitation inside the larger pores, iv) associated with an overall increment of open porosity. On the whole, the MIP highlighted a clear increment of void volume after weathering (Table 2). Also the interconnection level of the pore network increased, due to decay (Table 2). As in the fine-grained type, the CGV shows a slight increase in hygroscopic sorption behaviour pointing out a growth in microporosity (mainly centred on 0.1 μm open pores radius access) possibly connected with dissolution processes (Fig. 5) (Table 3). The comparison between MIP and hygroscopic-based porosimetry (Fig. 6e) highlighted that in sound samples MIP overestimates the μ-porous range, probably for the compressibility of the massive micrite matrix; conversely, the patterns for the weathered samples are comparable, suggesting the development of micro-cracks within the matrix.

3. Discussion

Pores with access radius smaller than 0.1 μm represent a first rank factor in moisture transport and diffusion processes. Micropores are crucial both for the evaporation kinetics and the particulate, pollution and substances with a defined molecule size penetration [6]. Therefore, their study is crucial in conservation of porous material such as stones and artificial lithics. The coupling of MIP and hygroscopic sorption based porosimetry allowed a good description of the micro-porous network and of its variation (by means of typology and source). The acquired dataset shows a higher susceptibility to salt decay for the most porous rocks (i.e. Vicenza Stone), with the modification of the micro-pores both for chemical and mechanical processes. Also, RV and MS proved a relevant susceptibility to decay, with the mechanical opening of micro-pores. The induced weathering suggests a careful use of this lithotypes in outdoor locations for their precarious durability. BA, having the most compact structure, proved the most durable. The analysis of the results on the whole helped finding out defects of the MIP techniques when applied to investigate microporosity in rocks with a great abundance of micrite. Moreover, the association of petrography and petro-physical analysis (i.e., MIP and hygroscopic micro-porosimetry) highlighted the presence of phyllosilicates and their role in decay processes, e.g. contributing to the interpretation of the structural evolution of Macigno Sandstone. The presence of expandable phyllosilicates (e.g. minerale from the montmorillonite-chlorite series of mixed layers minerals found in MS) induces both a high susceptibility to RH variation and to salts or other alien substances [31]. The swelling due to increment of humidity in the environment generates an increase in volume depending on the mineral, the relative amount of water and the surroundings. Repeated cycles of adsorption and evaporation, generating a swelling/shrinking pair, as a hydraulic ram generating cracks [32]. The precipitation of salts between the swelled layers of the phyllosilicates induces a higher stress to the fabric resulting in μ-cracks opening inside the minerals, thus decreasing their hygroscopic activity, and the whole rock fabric petrophysical properties [33].

4. Conclusions

The combination of the different techniques proved to be a valid tool for understanding the influence of the mineralogical composition in hygroscopicity, and to evaluate the consequent weathering processes. Hygroscopic porosimetry, if coupled with MIP, in presence of phyllosilicates and other hygroscopic minerals (or compounds), highlighted the possibility of RH variation to trigger the weathering due to swelling.

Conflict of interest
None.

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References
[1] D. Pereira, B. Marker, The Value of Original Natural Stone in the Context of Architectural Heritage, (n.d.). doi:10.3390/geosciences6010013.
[2] D. Pereira, B.J. Cooper, Building stone as a part of a World Heritage Site: ‘‘Piedra Pajarilla” Granite and the city of Salamanca, Spain, Geol. Soc. London, Spec. Publ. 391 (2014) 7–16, https://doi.org/10.1144/SP391.3.
[3] P. Vázquez, F.J. Alonso, L. Carrizo, E. Molina, G. Cultrone, M. Blanco, I. Zamora, Evaluation of the petrophysical properties of sedimentary building stones in order to establish quality criteria, Constr. Build. Mater. 41 (2013) 868–878, https://doi.org/10.1016/j.conbuildmat.2012.12.026.
[4] D. Benavente, P. Lock, M. Ángeles García Del Cura, S. Ordóñez, Predicting the capillary imbibition of porous rocks from microstructure, Transp. Porous Media. 49 (2002) 59–76, https://doi.org/10.1023/A:1016047122877.
[5] M. Angeli, D. Benavente, J.P. Bigas, B. Menéndez, R. Hébert, C. David, Modification of the porous network by salt crystallization in experimentally weathered sedimentary stones, Mater. Struct. Constr. 41 (2008) 1091–1108, https://doi.org/10.1617/s11527-007-9308-z.
[6] S. Yu, C.T. Oguchi, Role of pore size distribution in salt uptake, damage, and predicting salt susceptibility of eight types of Japanese building stones, Eng. Geol. 115 (2010) 226–236, https://doi.org/10.1016/j.enggeo.2009.05.007.
[7] D. Benavente, S. Sanchez-Moral, A. Fernandez-Cortes, J.C. Cañaveras, J. Elez, C. Saiz-Jimenez, Salt damage and microclimate in the Postumius Tomb, Roman Necropolis of Carmona, Spain, Environ. Earth Sci. 63 (2011) 1529–1543, https://doi.org/10.1007/s12665-010-0815-9.
[8] E. Molina, G. Cultrone, E. Sebastián, F.J. Alonso, L. Carrizo, J. Gisbert, O. Buj, The pore system of sedimentary rocks as a key factor in the durability of building materials, Eng. Geol. 118 (2011) 110–121, https://doi.org/10.1016/j. enggeo.2011.01.008.
[9] V.C. Van den Eynde, F.J. Mateos, R. Paradelo, Degradability of building stone: Influence of the porous network on the rate of dissolution of carbonate and evaporitic rocks, J. Cult. Herit. 14 (2013) 89–96, https://doi.org/10.1016/j. culher.2012.05.003.
[10] V. Cnudde, M.N. Boone, High-resolution X-ray computed tomography in geosciences: A review of the current technology and applications, Earth- Science Rev. 123 (2013) 1–17, https://doi.org/10.1016/j.earscirev.2013.04.003.
[11] E. Mueller-Huber, J. Schoen, F. Boerner, Pore space characterization in carbonate rocks – Approach to combine nuclear magnetic resonance and elastic wave velocity measurements, J. Appl. Geophys. 127 (2016) 68–81, https://doi.org/10.1016/j.jappgeo.2016.02.011.

[12] D. Benavente, Why pore size is important in the deterioration of porous stones used in the built heritage, Macla. 15 (2011) 41–42, https://doi.org/10.1007/ s12665-010-0815-9.transported.
[13] W. Wedekind, R. López-Doncel, R. Dohrmann, M. Kocher, S. Siegesmund, Weathering of volcanic tuff rocks caused by moisture expansion, Environ. Earth Sci. 69 (2013) 1203–1224, https://doi.org/10.1007/s12665-012-2158-1.
[14] M. Ondrášik, M. Kopecky´ , Rock pore structure as main reason of rock deterioration, Stud. Geotech. Mech. 36 (2014), https://doi.org/10.2478/sgem- 2014-0010.
[15] Z. Karaca, Water absorption and dehydration of natural stones versus time, Constr. Build. Mater. 24 (2010) 786–790, https://doi.org/10.1016/ j.conbuildmat.2009.10.029.
[16] L. Zhang, L. Yang, B.P. Jelle, Y. Wang, A. Gustavsen, Hygrothermal properties of compressed earthen bricks, Constr. Build. Mater. 162 (2018) 576–583, https:// doi.org/10.1016/j.conbuildmat.2017.11.163.
[17] A.P. Radlinski, Small-angle neutron scattering and the microstructure of rocks, Rev. Mineral. Geochemistry. 63 (2006) 363–397, https://doi.org/10.2138/ rmg.2006.63.14.
[18] H. Giesche, Mercury porosimetry: a general (practical) overview, Part. Part. Syst. Charact. 23 (2006) 9–19, https://doi.org/10.1002/ppsc.200601009.
[19] O. Buj, P.L. López, J. Gisbert, P.L. Lòpez, J. Gisbert, Characterization of pore system and their influence on decay rates caused by salt weathering on limestones and dolostones quarried in Abanto (Zaragoza, Spain), Mater. Construcción. 60 (2010) 99–114, https://doi.org/10.3989/mc.2010.50108.
[20] G. Cultrone, L.G. Russo, C. Calabrò, M. Uroševicˇ, A. Pezzino, Influence of pore system characteristics on limestone vulnerability: A laboratory study, Environ. Geol. 54 (2008) 1271–1281, https://doi.org/10.1007/s00254-007-0909-1.
[21] A.S. Ziarani, R. Aguilera, Pore-throat radius and tortuosity estimation from formation resistivity data for tight-gas sandstone reservoirs, J. Appl. Geophys. 83 (2012) 65–73, https://doi.org/10.1016/j.jappgeo.2012.05.008.
[22] C. Dubois, P. Couchot, A. Calleja, E. Boeglin, A. Chambaudet, Specific mercury porosimetry for low-porosity materials, Meas. Sci. Technol. 9 (1998) 2016– 2022, https://doi.org/10.1088/0957-0233/9/12/014.
[23] S. Roels, Characterisation of pore structure by combining mercury porosimetry and micrography, Mater. Struct. 34 (2005) 76–82, https://doi.org/10.1617/ 13555.
[24] V. Cnudde, A. Cwirzen, B. Masschaele, P.J.S. Jacobs, Porosity and microstructure characterization of building stones and concretes, Eng. Geol. 103 (2009) 76– 83, https://doi.org/10.1016/J.ENGGEO.2008.06.014.
[25] R.A.J. Wüst, J. McLane, Rock derioration in the royal tomb of seti I, valley of the kings, Luxor, Egypt, Eng. Geol. 58 (2000) 163–190, https://doi.org/10.1016/ S0013-7952(00)00057-0.
[26] I. Jiménez-González, C. Rodríguez-Navarro, G.W. Scherer, Role of clay minerals in the physicomechanical deterioration of sandstone, J. Geophys. Res. Earth Surf. 113 (2008) 1–17, https://doi.org/10.1029/2007JF000845.
[27] J. Ruedrich, T. Bartelsen, R. Dohrmann, S. Siegesmund, Moisture expansion as a deterioration factor for sandstone used in buildings, Environ. Earth Sci. 63 (2011) 1545–1564, https://doi.org/10.1007/s12665-010-0767-0.
[28] S. Scrivano, L. Gaggero, J. Gisbert Aguilar, T. de Kock, H. Derluyn, V. Cnudde, Texture and mineralogy influence on durability: the Macigno Sandstone, Q. J. Eng. Geol. Hydrogeol. 50 (2017) 393–401, https://doi.org/10.1144/qjegh2016- 107 |.
[29] M. Coli, C. Tanini, M. Haines, E. Pandeli, G. Pini, F. Bencini, The ‘‘Pietra Serena” stones of Brunelleschi’s Cupola, J. Cult. Herit. 9 (2008) 214–221, https://doi. org/10.1016/J.CULHER.2008.01.002.
[30] D. Benavente, M.A. García Del Cura, A. Bernabéu, S. Ordóñez, Quantification of salt

weathering in porous stones using an experimental continous partial immersion method, Eng. Geol. 59 (2001) 313–325, https://doi.org/10.1016/ S0013-7952(01)00020-5.

[31] J. Delgado Rodrigues, Evaluación del comportamiento expansivo de las rocas y su interés en conservación, Mater. Construcción 51 (2001) 183–195, https://doi.org/10.3989/mc.2001.v51.i263-264.363.

[32] K. Hall, A. Hall, Weathering by wetting and drying: some experimental results, Earth Surf. Process. Landforms 21 (1996) 365–376, https://doi.org/10.1002/ (SICI)1096-9837(199604)21:4<365::AID-ESP571>3.0.CO;2-L.

[33] E. Sebastián, G. Cultrone, D. Benavente, L. Linares Fernandez, K. Elert, C. Rodriguez-Navarro, Swelling damage in clay-rich sandstones used in the church of San Mateo in Tarifa (Spain), J. Cult. Herit. 9 (2008) 66–76, https://doi. org/10.1016/j.culher.2007.09.002.