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Evaluation of the petrophysical properties of sedimentary building stones in order to establish quality criteria

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HIGHLIGHTS

- ► Stones are divided in low, intermediate and high quality.
- ▶ Limestones with high porosity and low coherence show low quality.
- ► Sandstones with similar porosity but different composition show intermediate quality.
- ► Stones with low porosity show the highest quality.
- ▶ Differences in composition and pore distribution influence the quality.

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ABSTRACT

Porous sedimentary stones are frequently used in the construction of many different kinds of buildings. In order to assess the quality of each stone as a building material, it is important to analyse its particular petrographic characteristics and physical properties, as these affect its behaviour when exposed to agents of decay. We selected six stone types with different petrophysical characteristics that are commonly used as construction materials in Spain. Two limestones with high porosity and notable textural differences performed worst. The bioclastic limestone from Santa Pudia showed poor mechanical behaviour, while the micritic limestone from Huesca had the worst response to water flow. Two sandstones performed better. They had medium porosity, a similar texture and certain differences in composition. The calcare-ous sandstone from Uncastillo performed worse in terms of hydric and mechanical behaviour and consequently is less durable than the siliciclastic sandstone from Villaviciosa. The highest quality stones, in terms of their hydric behaviour and mechanical properties are the crystalline dolostone from Boñar and the travertine from Albox, both of which have relatively low porosity.

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1. Introduction

Porous sedimentary stones have been used as building materials throughout history. They are easy to work, are readily available on the earth's surface and have a high aesthetic value at a relatively low cost. However, when exposed to the environment they frequently perform worse than crystalline stones with low porosity [1,2]. This is largely due to their petrography (mineralogy and texture) and especially to their porous system. It is therefore very important to find out how these characteristics affect stone decay, so that we can reasonably predict how each stone will perform when used in construction [3–5]. For example, clay minerals, which are present as cementing material in many sedimentary stones [6,7], can cause powdering and swelling phenomena when they interact with water [8]. Textural anisotropy is another factor that can influence stone decay [9,10]. The detection of the presence of clay minerals is therefore vital when it comes to laying the stones correctly in the building so as to prevent flaking and spalling.

Water is a crucial weathering agent, both when stationary inside the stone and when in circulation [11–14]. The characteristics of the porous system affect the way the water flows through the stone. Different physical and chemical reactions take place depending on the stone composition (i.e., the presence of swelling



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clays or of preferred orientation planes). When comparing the decay in different stones, the most important factor to assess is the porous system. By analysing the stone's hydric properties we can better understand the way water circulates through the porous system, and how this affects the decay of the stone [15–20].

The decay suffered by the construction and decorative materials used in our buildings is often caused by environmental agents, which may be of natural origin or produced by humans [21]. For this reason, when choosing a particular building stone we must also consider its ability to resist attack by decay agents [22,23]. Accelerated ageing tests are a practical way of observing material decay in a short space of time, a process which under normal environmental conditions would take years [24]. These are normally cycle-based tests carried out in the laboratory with varying duration and complexity. Unfortunately, in most cases the decay is not produced by one single agent but results from a combination of two or more factors [25]. The ageing test we used does not always enable researchers to observe and characterise the decay, due to the short testing time and the variables measured, such as the variation in wave propagation parameters [26,27], or surface variations [28]. It is therefore not easy to select which decay test should be carried out to assess the quality of a particular stone. Moreover, they only give an approximate reproduction of the natural conditions to which the stones are exposed [29,30]. Despite these drawbacks, this is currently the only standard method that allows us to compare decay in different stones. Another way of predicting stone durability is through petrophysical characterisation, an indirect way of relating the stone's physical properties to its petrography [31-34]. This is possible thanks to the extensive bibliography and the experience acquired during research into the damage suffered by these kinds of stone in buildings [35–37].

The aim of this research is to determine the best petrophysical parameters to enable us to predict the durability of these porous building stones. We selected six types of sedimentary stone. They differ in terms of both mineralogy (limestones and sandstones) and texture (granular, micritic and crystalline) and therefore have different porous systems. These stones are good examples of the wide range of stones used in building in different parts of Spain [38]. We made petrographic and physical characterisations and compared the results with those obtained in salt crystallisation and freeze-thaw ageing tests. The parameters thus obtained were used to establish quality criteria for building materials, taking into account the relation between the parameters, the complexity of the data and their importance in decay processes.

2. Description of the materials

Six stone types were selected on the basis of petrographic criteria from a wide variety of ornamental stones used in buildings that belong to Spain's architectural heritage. Geographical distribution, geological setting and differences in the environment were also important criteria in the selection process. In the end we selected Villaviciosa sandstone (AV) and Boñar dolostone (DB) from the Cantabrian area, Uncastillo sandstone (AU) and Fraga limestone (CF) from the Ebro basin and Santa Pudia limestone (SP) and Albox travertine (TA) from the Betic Cordillera (Fig. 1). Samples were selected and monitored during their extraction and preparation in the quarry in order to maintain the same orientation during our studies.

2.1. Geographical and geological framework

Villaviciosa sandstone (AV), known commercially as La Marina sandstone, comes from Asturias (N Spain). This sandstone dates from the Upper Jurassic Age and has been quarried and used in building-work historically. This formation has a heterogeneous lithology with alternating grey and yellow sandstones in layers of variable width (1–4 m), together with marlstones, shales and limestones. The samples we studied belong to the grey variety [39]. This stone is mainly used locally, in restoration work in Villaviciosa and Gijón (Asturias), although it has also been used in some new constructions. A number of important historical buildings were built with this sandstone including the Revillagigedo Palace and the Laboral University in Gijón, and the churches of Santa Maria de la Oliva and Santa María de Valdedios, both in Villaviciosa.

Uncastillo sandstone (AU) dates back to the Lower Miocene Age and originates from the village of the same name near Zaragoza (NE Spain) in the northern part of the Ebro Valley region. This formation is composed of clay and sandstone alternating in sinusoidal patches. The sandstone layers vary in width (1-3 m) and facies can be distinguished by grain size [40]. The specimens we studied had mediumsized grains. This stone can be found in Roman monuments in the area around Uncastillo (Los Bañales baths and the Los Atilios mausoleum), and in mediaeval and other buildings in the region.

Fraga limestone (CF), also named Campanil limestone, is quarried close to Huesca (NE Spain). This stone formed in the Lower Miocene is located in the centre-east of the Ebro basin together with bioclastic limestones and marlstones, typical of lacustrine environments. Limestones are found in subhorizontal beds, of around 1 m in width, with organic matter and intercalated with grey marlstones [40]. This stone has been used in both religious and secular buildings and is frequently combined with other materials.

Santa Pudia limestone (SP) is quarried in Escuzar, Granada, in the Granada basin (S Spain), a depression that forms an intramountain Neogene basin. Calcareous lithoarenites and bioclastic limestones from the Miocene age outcrop on its southern and eastern edges [41]. This stone is a whitish calcarenite with coarse grains and high porosity. It is easy to work and as a result has been widely used in the historic buildings of Granada, such as the cathedral, the palace of Carlos V in the Alhambra and the Royal Hospital. Today it is mainly used in restoration work.

Boñar dolostone (DB) is quarried close to León (N Spain). This stone dates back to the Upper Cretaceous. The formation is located in the Cantabrian area and runs East–West. It has limestones, marlstones and in the upper part, crystalline dolostones. These dolostones appear in 80 cm banks, and have an earthy aspect and slight differences in colour and compactness [42]. This stone is widely used all over Spain in ancient and modern constructions. Good examples are León cathedral, the church of San Marcos and the palace of Los Guzmanes.

Albox travertine (TA) originates in Albox, Almeria, (S Spain) and is also known as Travertino Amarillo or Travertino Oro. This stone belongs to the Pleistocenic travertines located in the north of the Albox depression, in the intern Betic area related to paleo-sources associated with faults [43]. The samples we studied were brownish in colour, and had prominent bands and high porosity that was clearly visible when the rock was cut perpendicular to the bands. Travertines are frequently used as ornamental stone in Granada's historical buildings.

3. Methodology

Petrography involves the macroscopic and microscopic analysis of stones in order to assess their mineralogy and texture (including the porous system) [44,45]. Special attention is paid to the minerals and to the distribution and orientation of the pores.

3.1. Chemical and petrographic properties

Chemical composition was determined by X-ray fluorescence (Philips PW2404, XRF), while the mineralogical composition of bulk samples and clay content (i.e., fraction with grain size below 2 μ m) was obtained by X-ray diffraction (Philips



Fig. 1. Geographic location of the rocks: Villaviciosa sandstone (AV) and Boñar dolostone (DB) from the Cantabrian area, Uncastillo sandstone (AU) and Fraga limestone (CF) from the Ebro basin, and Santa Pudia limestone (SP) and Albox travertine (TA) from the Betic Cordillera.

X'PERT PRO, XRD). The powder diffraction method was used for the mineralogical analysis of the powder selected from 200 g of bulk samples. Oriented aggregates were prepared for the study of the clay fraction in which carbonates were eliminated using a 0.2 N acetic acid solution and a Kubota 2000 centrifuge was used to separate the fraction below 2 μ m. The working conditions were Cu K α radiation ($\lambda = 1.5405$ Å), a voltage of 40 kV and current intensity of 40 mA. The goniometer speed was 0.1 2θ /s and the angle ranged from 4 to 70° 2θ for the bulk samples, and 4 to 30° 2θ for the clay fraction. Diffraction data were recorded and interpreted using the XPowder program [46]. Residual Insoluble content (RI) was determined after dissolution in hydrochloric acid at 10%.

We analysed the pore system at different scales using three different methods: macroscopic observation (>1 mm), polarized optical microscopy (Zeiss Jenapol, POM) (1 mm to 10 µm) and scanning electron microscopy (Jeol-6100, SEM) with a carbon-coated polished thin section (<10 µm). From the textural model, pore type can be defined in relation to its distribution, abundance, shape and size [44]. As regards size, we measured the diameter of the pores by direct observation, which is expressed with the centil maximum $D_{\rm M}$ and mode $D_{\rm m}$. Pore access radii were obtained using a Hg intrusion porosimeter (MIP) Micromeritics Autopore III 9410, which reaches 414 MPa pressure and can measure pore radii sizes from 0.003 to 360 µm. Three samples of each stone type were analysed. The distribution curves enabled us to calculate median pore access radius ($R_{\rm m}$), the dispersion coefficient (C_d) and the percentage of pores in three different pore access radius ranges, large (>10 µm), medium (10–0.1 µm) and small (<0.1 µm) [47,48]. Dispersion coefficient (C_d) measures size range amplitude around the median including 50% of the samples and it is expressed in order of magnitude.

3.2. Physical properties

The tests were carried out on nine cubes of $5 \times 5 \times 5$ cm for each stone type. Real and apparent density and total and open porosity were obtained using different techniques. Real density (ρ_r) was determined theoretically from the mineral composition of each stone:

$$\rho_{\rm r} = \sum (c_{\rm i} \times p_{\rm i})/100 \quad (\rm kg/m^3)$$

where " c_i " is the mineral percentage and " p_i " is the mineral density for each mineral "i" of the stone.

Apparent density (ρ_b) was calculated using geometrical methods based on the volume of the specimens (ISRM 1979) [47]. Open porosity (p_o) and once more apparent density (ρ_b) were calculated using the hydrostatic method, following the UNE-EN 1936 standard [48]:

$$\rho_{\rm b} = m_{\rm o}/(m_{\rm s}-m_{\rm h})\cdot\rho_{\rm a} \quad (\rm kg/m^3)$$

 $p_{\rm o} = ((m_{\rm s} - m_{\rm o})/(m_{\rm s} - m_{\rm h})) \cdot 100$ (%)

where " m_0 " is the dry weight of the specimen, " m_s " is the saturation weight, " m_h " is the hydrostatic weight (immersed in water) and " ρ_a " the water density.

Total (p) and closed porosity (p_c) were calculated as follows:

$$p = ((\rho_{\rm r} - \rho_{\rm b})/\rho_{\rm r}) \cdot 100$$
 (%

$$p_{\rm c} = p - p_{\rm o}$$
 (%)

We also carried out of the following hydric tests: free and forced water absorption, drying, capillary absorption and water vapour permeability. Forced water absorption was obtained following the UNE-EN 1936 standard [48], which enables us to calculate the saturation degree of water content (w_s). The free water absorption test was performed according to the UNE-EN 13755 standard [49] and drying according to the NORMAL 29/88 standard [50]. These tests provide information about water content and saturation as a function of time.

The capillary rise test was carried out according to the UNE-EN 1925 standard [51]. This test allows us to determine the capillary absorption coefficient (*C*) and capillary penetration (*B*). These values were obtained from the linear behaviour observed when the square root of time was plotted against the capillary absorption of each stone over the first hour of the test. The theoretical penetration coefficient (B_T) was also obtained from a model of cylindrical capillary pores [16]:

$B_{\rm T}=C/p_{\rm o}~(mm/s^{1/2})$

where "C" is the capillary coefficient and " p_o " is the open porosity.

The water vapour permeability test was carried out according to the NORMAL 21/85 [52] standard. The coefficient (K_v) was determined. Water vapour transfer is linear and variations in weight were measured over one week.

Water absorption and drying tests were carried out on six cubic specimens $(5 \times 5 \times 5 \text{ cm})$ per stone; the capillary rise test was performed on three specimens with similar dimensions but with different orientations (*x* and *y* parallel to the stratification and selected random); the water vapour permeability test was performed on 9 tablets measuring $5 \times 5 \times 1$ cm, three in each direction.

Two mechanical parameters relating to hardness and resistance to rebound were also obtained. For the Shore hardness test, we used 4 slabs measuring $8 \times 8 \times 2$ cm of each of the six stone types and 64 indents were made at equidistant points in each slab [53]. The Schmidt hardness test was carried out using a hammer type L with low energy impact (0.735 N m) on a plate of $16 \times 16 \times 2$ cm, and 25 measurements were taken at equidistant points [54]. As the slabs were not very thick, some samples broke before the tests had finished. The hardness is measured by the height of rebound after each blow of the hammer. We then calculated the average value and the standard deviation in order to enable us to characterise the comparative hardness of the different materials.

Freeze-thaw and salt crystallization are among the most frequently used laboratory tests in our field of research because they reproduce the effects of some of the most common decay agents affecting historical buildings and because they can cause damage after just a few cycles in weak stones [55,56]. Four 5-cm side cubes per stone were used for each test. In the case of the freeze-thaw test, which assesses the effect of ice on the stones when temperature oscillates around 0° causing alternate freezing and thawing, 25 cycles were performed according to the EN 12371 standard [57]. In the case of the salt crystallization test, which studies the

Table 1

Mineral composition of the six types of stone. Legend: AV: Villaviciosa sandstone; AU: Uncastillo sandstone; CF: Fraga limestone; SP: Santa Pudia limestone; DB: Boñar dolostone; TA: Albox travertine. IR = Insoluble residue, Cal = calcite, Dol = dolomite, Q = quartz, Fpt = feldspars, FR = rock fragments, C = clays, I = illite, C/K = chlorite/kaolinite, S = smectite, P = paragonite, G = goethite.

Stone	IR (%)	Carbonat	es (%)	Silicate	Silicates (%)		Clay minerals				Other	
		Cal	Dol	Q	Fpt	FR	С	I	C/K	S	Р	G
AV	100	-	-	68	15	15	2	va	t	-	-	-
AU	54	46	-	15	10	25	4	va	a	t	-	t
CF	3	97	-	1	-	-	2	a	s/a	-	-	-
SP	3	97	-	2	-	-	1	a	a	t/s	-	t
DB	4	18	78	2	-	-	2	a	a	_	-	-
TA	1	99	-	0.7	-	-	0.3	va	S	t/s	a	-

va = Very abundant, a = Abundant, s = Scarce, t = Traces.

Table 2

Chemical composition of the six types of stone expressed in percent. Stone abbreviations are listed in Table 1.

Stone	SiO ₂	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P_2O_5	LOI	Total
AV	94.74	2.23	0.29	0.00	0.08	0.03	0.10	1.51	0.11	0.03	0.46	99.57
AU	47.80	3.43	1.80	0.05	0.59	24.73	0.38	0.62	0.21	0.05	20.40	100.06
CF	1.80	0.33	0.54	0.18	0.57	53.28	0.07	0.06	0.04	0.02	43.05	99.95
SP	2.93	0.06	0.37	0.02	0.31	52.53	0.02	0.05	0.02	0.04	43.20	99.54
DB	1.03	0.49	0.38	0.02	17.63	34.34	0.00	0.03	0.03	0.02	45.48	99.45
TA	0.00	0.00	0.05	0.01	0.31	55.33	0.01	0.00	0.02	0.00	43.46	99.19

negative effects of soluble salts dissolved in water that can crystallize inside the pore system of the stones, 15 cycles were carried out with a solution of 14% NaSO₄ - \times 10H₂O as specified in the EN 12370 standard [58]. Visual appearance and weight variations were assessed as indications of decay.

4. Results and discussions

The rocks were grouped together according to their petrographic characteristics and porosity. The first group contains the two sandstones, which have similar texture and porosity, but different composition. The second group consists of the limestones, both with high porosity but with marked variations in texture and pore system. In the third group there are two crystalline carbonates characterised by notable differences in composition and texture.

4.1. Petrographic characterisation

Table 1 shows the mineralogical composition of the stones in percentage terms. Table 2 shows the chemical composition obtained by means of XRF analysis.

AV is a sublitharenite to subarkose stone with medium-sized grains (0.25–0.4 mm). This stone has a granular aspect, with a grey to brownish colour, and is compact and coherent (Fig. 2A). It has a grain-supported texture (Fig. 2B). In mineralogical terms, it consists predominantly of quartz, and about 4% of microcline type feldspars with different degrees of weathering, rock fragments (silex, lutite) with small quantities of tourmaline, oxides and illite. The quartz grains are rounded and about 350 μ m in size, while the feldspars are smaller (300 μ m) and more angular. Grain packing is moderate and shows weak orientation. Overgrowth cement (5–10%) is mainly quarzitic with a low proportion of clay. Sometimes this stone shows weak cross-stratification.

AU is a litharenite rich in carbonate fragments (calcareous sandstone) with medium to fine grains. It has a granular aspect and a brown-yellowish colour, and is moderately compact and coherent (Fig. 2C). AU has a grain-supported texture with grains in contact and spatic and syntaxial calcite cement mainly (10–15%). Micrite and clays can be also found in the calcite cement (Fig. 2D). This stone has similar proportions of silica and carbonate. Quartz and feldspar have a mean grain size of around 250 μ m and are well sorted. Subangular quartz, chert, slate, feldspars, biotite, chlorite, muscovite and iron oxides can be found among the siliclastic components. Micrite (peloids) and bioclasts (mainly crinoids and gastropods) can be observed among the carbonate components. It has the highest clay content (illite and chlorite/kaolinite) of the stones we studied and the highest iron content due to the presence of biotite, chlorite and goethite. AU occasionally displays weak bands and weak grain orientation.

CF is a micrite to biomicrite limestone showing bioturbation (Fig. 2E) and only 3% of insoluble residue composed of quartz, clays and organic matter. This stone has a homogeneous, massive aspect, with a grey-yellowish colour. It is compact with low coherence. It has microcrystalline texture due to the transformation of carbonate mud (Fig. 2F). In mineralogical terms it is mainly composed of microcrystalline calcite (1 μ m) with bioclasts (10%) such as ostracods, bivalves and carophytes (round shapes around 150 μ m). Quartz, muscovite and iron oxides can also be found in smaller quantities.

SP is a bioclastic limestone with only 3% of insoluble residue with a higher proportion of silt-sized quartz than clays. It has a coarse-grained aspect, with visible porosity and grains, which vary from white to yellow in colour, low compactness and moderate coherence (Fig. 2G). This stone shows clastic texture with grains in contact and variable packing. Grains are composed of bioclasts (up to 5 mm), mainly bryozoans and red algae, crinoids (sometimes altered to peloids), and occasional serpulids, echinoderm and mollusc shells (Fig. 2H). Most of the grains are formed by micrite, although mirosparite can be found in the bryozoans and fibrous calcite in the molluscs. SP shows calcite sintaxial and microsparite cement in low proportions.

DB is a crystalline dolostone with fine grains and 4% of insoluble residue consisting mainly of quartz and clays. It has a massive aspect with a few, scarce spots. It has a brownish colour and is compact and coherent (Fig. 21). It sometimes has fine reddish, discontinuous veins and stylolites related to stratification. It has a crystalline, slightly heterogranular texture with subidiomorphic dolomite crystals (up to 40 μ m) (Fig. 2J). This stone keeps a granular relict texture in relation to grain size and dolomite inclusions, with bigger, cleaner crystals in the intergranular spaces. Relict grains are rounded and well-sorted, measuring around 400 μ m. Bioclasts can occasionally be identified. Intergranular spaces may be filled with calcite crystals (about 20%) or remain empty. The dolomite/calcite ratio is 80/20.



Fig. 2. (A) Villaviciosa sandstone (AV), macroscopic aspect; (B) microscopic image (POM, crossed polars, $\times 10$). AV is a siliciclastic sandstone (subarkose to sublitharenite) with medium-sized grains; (C) Uncastillo sandstone (AU), macroscopic aspect; (D) microscopic image (POM, crossed polars, $\times 10$). AU is a calcareous sandstone (litharenite) with medium to fine grains; (E) Fraga limestone (CF), macroscopic aspect; (F) microscopic image (POM, crossed polars, $\times 10$). CF is a micrite to biomicrite limestone, with ostracods and carophytes; (G) Santa Pudia limestone (SP) macroscopic aspect; (H) microscopic image (POM, crossed polars, $\times 10$). SP is a bioclastic limestone (biosparite to biorrudite), with bryozoa and red algae; (I) Boñar dolostone (DB) macroscopic aspect; (J) microscopic image (POM, crossed polars, $\times 10$). DB is a crystalline dolostone with fine crystals (40 µm); (K) Albox travertine (TA) macroscopic aspect; and (L) microscopic image (POM, crossed polars, $\times 10$). TA is a heterogranular crystalline limestone type travertine.

TA is a heterogranular crystalline limestone-type travertine with 1% of insoluble residue composed mainly of quartz. This stone has a yellow-brownish colour, low compactness and high coherence (Fig. 2K). It has an anisotropic crystalline texture with bands of different colour and composition alternating with large elongated, oriented pores. TA has grains of different shapes and sizes (micrite, sparite, fibrous) (Fig. 2L). The crystals have an average size of 300 μ m, and appear either elongated in bands or filling pores. There are also areas with dark crystals due to plant precursors and Mg and Fe oxides/hydroxides. Very fine stratification surfaces with silt-sized quartz crystals and muscovite can be observed.

4.2. Density and porous system

Table 3 shows the real density, calculated theoretically, and the apparent density and the open porosity obtained using the hydro-

static method. With density values we then calculated total and closed porosity. In TA only the geometric method values were considered as water can drop quickly by gravity in the largest pores making it impossible to measure using the hydrostatic method. Table 4 shows the different parameters of the porous system obtained by direct observation and mercury porosimetry, and the percentage of pores in three different pore access radius ranges, large (>10 μ m), medium (10–0.1 μ m) and small (<0.1 μ m).

Of the six stones, DB has the highest real density, as might be expected due to the high density of dolomite (2860 kg/m^3). The density values for the limestones were similar to that of calcite (2710 kg/m^3). Due to its high iron mineral content (see Table 2), the density value for AU was closer to that of limestone than AV, which had density values in line with its quartz content (2650 kg/m^3).

Apparent density is related to porosity. DB has the highest values due to its high real density and low porosity. SP shows

Stone	Density (kg/m ³)		Porosity (%)				
	Real density (ρ_r)	Apparent density ($\rho_{\rm b}$)	Total porosity (p)	Open porosity (p_0)	Closed porosity (p_c)		
AV	2648	2130 ± 3	19.6 ± 0.1	19.5 ± 0.2	0.1 ± 0.1		
AU	2708	2084 ± 11	23.0 ± 0.4	22.6 ± 0.3	0.4 ± 0.1		
CF	2694	1901 ± 15	29.4 ± 0.5	29.3 ± 0.5	0.1 ± 0.2		
SP	2710	1741 ± 6	35.8 ± 0.2	35.7 ± 0.3	0.1 ± 0.1		
DB	2820	2509 ± 9	11.0 ± 0.3	10.9 ± 0.3	0.1 ± 0.1		
TA	2710	2323 ± 8	14.3 ± 0.4	11.2 ± 0.1^{a}	3.1 ± 0.4^{b}		

Table 3
Density and porosity (average and standard deviation of nine specimens for each stone type).

Stone abbreviations are listed in Table 1.

^a Excluding open pores in which water flows quickly by gravity.

^b Including closed and open pores in which water flows quickly by gravity.

the lowest apparent density due to its high porosity. Open porosity (accessible to water) varies between 10 and 35% and closed porosity is very low in all these stone types. TA has large well-connected millimetric pores in which water flows freely by gravity, or closed (unconnected) pores.

The sandstones showed intermediate porosity levels (~20%). AV has intergranular pores with a mode size of about 0.2 mm, with moderate communication due to partial cementation. The distribution of the pore access radii is unimodal with the median at 8 μ m and low dispersion (C_d : 0.9). AV shows a slight trend to higher values (Fig. 3A), with a predominance of medium (9.4%) and large (8%) pore access radii over small ones (2.1%).

AU has intergranular pores with a mode size of about 0.1 mm, although smaller, well-connected pores associated with micrite are also present. The distribution of pore radii is also unimodal with a median of 6 μ m and low dispersion (*C*_d: 0.7). There is a slight predominance of small sizes (Fig. 3A), which is indicative of the gradual transition from intergranular pores to matrix pores. The percentage of pore access radii in the medium range (1.5%) is higher than in the large (4.9%) and small ranges (1.6%).

Limestones show the highest porosity (\sim 30–35%) and high pore type variability. CF shows moldic pores, sometimes expanded by dissolution to a diameter of 1 mm, together with matrix pores, which also expanded so producing good connection. Distribution is unimodal with a median at 0.2 µm and low dispersion (C_d : 0.4). This stone shows a slight trend to large pores in relation to matrix porosity overgrowth (Fig. 3B). Medium pore access sizes predominate (24.6%) over small (4%) and large ones (0.7%).

SP shows intergranular pores of around 1 mm, larger moldic pores of up to 4 mm, small intergranular pores (0.1 mm) and generally well-connected matrix porosity. Pore access radius distribution is bimodal with a mode at 70 μ m, which belongs to intergranular pores, and another mode at 0.2 μ m in relation to intragranular and matrix porosity with a median of 1 μ m (Fig. 3B). Dispersion was therefore wide (C_{d} : 1.85), with a predominance of medium-sized (19.8%) and large (>10.4%) pore access radii and relatively few small ones (3.4%). This stone is slightly more

porous than other calcarenites from the same area used as ornamental stone in Andalusia, but all are characterised by a bimodal pore size distribution [59,60].

DB has low porosity (~10%), the largest pores are intergranular in relation to the relict texture and are always smaller than 0.1 mm. DB also shows intercrystalline pores of less than 10 μ m with poor interconnection. The pore access radius distribution is unimodal with a small median (0.09 μ m), low dispersion (C_d : 0.7) and a slight trend towards smaller sizes due to the intercrystalline porosity (Fig. 3C). Small pore access radii are more common (7.6%) than medium (2.8%) and large (0.4%).

TA has low porosity (~15%) with pores of variable size, ranging from elongated pores and millimetric capillaries concentrated in bands to small equidimensional pores with good distribution. Pore communication is weak due to the calcite disposed as palisade, which closes the pore surface. The pore access radii distribution is bimodal (Fig. 3C), with one peak of large pores (80 μ m), the capillaries, and another peak of small pores (0.02 μ m), which are probably intercrystalline spaces, where water flow is limited. Most of the larger pores are out of range of mercury intrusion porosimetry, which explains why most pore access radii fall within the low range (0.07 μ m) and prevail small pores (4.6%) rather than the medium (2.5%) and large ranges (>0.8%). Travertines are heterogeneous stones, and porosity levels between 8% and 21% can be found in the same extraction area. The pore access radii determined by MIP also vary with peaks from 0.02 to 1 μ m [63].

4.3. Hydric properties

Absorption and drying tests were used to evaluate the kinetics of water flow within the stones over the course of a week (Fig. 4). Table 5 shows the water content and the degree of saturation after the first hour and at the end of the test.

CF and SP show high water absorption due to the fact that they have the highest porosity (\sim 30–35%) and the largest pore size (1–4 mm). These stones have the best connected pores. As a result, initial absorption is very fast and saturation reaches high values at the

Table 4

Porous system parameters. Stone abbreviations are listed in Table 1. Pore diameter by direct observation: centil (D_M) , mode (D_m) . Pore access radii calculated using mercury intrusion porosimetry: median (R_m) , variation coefficient (C_d) . Range amplitude around the median which includes 50% of the population.

Stone	Stone Pore diameter (mm)		Mercury intrusion porosi	Mercury intrusion porosimetry							
			Pore access radii (µm)	Dispersion coefficient	Size distribution. Absolute (relative) porosity						
	D_{M}	D _m	R _m	C _d	>10	10-0.1	<0.1	Total			
AV	0.5	0.2	8	0.94	8.0 (41%)	9.4 (48%)	2.1 (11%)	19.5 ± 0.6			
AU	0.2	0.1	6	0.73	4.9 (27%)	11.5 (64%)	1.6 (9%)	18.0 ± 1.4			
CF	1	0.5	0.2	0.41	0.7 (2.5%)	24.6 (84%)	4.0 (13.5%)	29.1 ± 0.2			
SP	4	1	1	1.85	10.4 (31%) ^a	19.8 (59%)	3.4 (10%)	33.5 ± 1.0			
DB	0.1	0.05	0.09	0.72	0.3 (3%)	5.7 (52%)	5.0 (45%)	10.6 ± 2.9			
TA	5	2	0.07	0.91	0.8 (10%) ^a	2.5 (31.5%)	4.6 (58.5%)	7.9 ± 1.5			

^a Contains some pores bigger than the maximum threshold for mercury intrusion porosimetry.



Fig. 3. Distribution of pore access radii obtained using a mercury intrusion porosimeter: (A) Villaviciosa sandstone (AV) and Uncastillo sandstone (AU), (B) Fraga limestone (CF) and Santa Pudia limestone (SP), and (C) Boñar dolostone (DB) and Albox travertine (TA).

beginning of the test (CF: 84% SP: 68% during the first hour). In addition, both limestones have small matrix pores (3.6% and 4%). Consequently the absorption continues increasing slowly for more than one week (saturation after one week is 93% and 80%). As regards drying, due to the good connection between the pores, these stones are almost completely dry and in equilibrium with their



Fig. 4. Curves of water absorption above and desorption below, showing the evolution of water content (*w*) against time ($t^{1/2}$) for the six stone types: Santa Pudia limestone (SP), Fraga limestone (CF), Uncastillo sandstone (AU) and Villaviciosa sandstone (AV), Albox travertine (TA) and Boñar dolostone (DB).

environment by the fifth day (0.05–0.02%) and show the lowest water content at the end of the test. Similar absorption and desorption values for calcarenite were found by Urosevic et al. [60] in a stone with similar porosity values.

The two sandstones had similar porosity ($\sim 20\%$) and pore size distribution. However, they behaved differently. AU water absorption is double that of AV, fast at the beginning but with a slower rate over the week (AU is 72% vs. AV 41%). This difference is attributed to the fact that AU is a calcareous sandstone with micrite in the carbonatic fraction, matrix pores and a higher proportion of medium-sized pore access radii (AU is 14.4% and AV is 9.4%), which enhance the capillary processes. During drying the two stones behave similarly: most of the water is lost during the two first days, they reach equilibrium after the fifth day and they have similar water content at the end of the test (0.15%).

TA and DB absorb less water and their initial absorption is slower and more prolonged than in the other stones. Absorption in TA is faster than in DB. TA has large pores (80 µm) with some well-connected fractions, which explains the initial absorption, and other pores that are too small for water to enter (0.05 μ m). DB has smaller pores $(50 \,\mu\text{m})$ than TA, with larger pore access (0.1 µm) and high porosity in the medium range. This justifies the slow but constant absorption. During drying the two stones behave in similar fashion. Their low porosity, small pore access radii and low number of medium-range pores produce a poorly interconnected system, which explains the slow evaporation and the high water content in these stones at the end of the test (0.25%). The variability in the pore size distribution and connectivity of travertines leads to huge differences in water absorption results, compared with stones from the same source [60] or from other countries [61].

Table 6 shows capillary water absorption and water vapour permeability coefficients. The samples were tested in the three directions, and although some anisotropy trends were observed, the standard deviation between samples did not allow us to confirm P. Vázquez et al./Construction and Building Materials 41 (2013) 868-878

Table 5
Water absorption and drying. Stone abbreviations are listed in Table 1. W_s = Saturation water content, w_t = Water content in time: S_t = saturation in time.

Stone	Saturation	Water abso	Water absorption				Drying			
w _s (%)		w _t (%)		S _t (%)		<i>w</i> _t (%)		S _t (%)		
		1 h	1 week	1 h	1 week	1 h	1 week	1 h	1 week	
AV	9.3 ± 0.2	3.3	3.8	36	41	8.9	0.15	97	1.6	
AU	10.8 ± 0.2	6.7	7.6	63	72	10.3	0.16	97	1.5	
CF	15.4 ± 0.5	13.3	14.7	84	93	15.4	0.05	98	0.3	
SP	20.4 ± 0.3	14.0	16.5	68	80	20.0	0.02	97	0.1	
DB	4.3 ± 0.2	0.96	3.0	22	68	4.2	0.22	95	5	
TA	4.8 ± 0.1	1.2	1.8	28	41	4.6	0.25	95	5	

Table 6

Capillarity and water vapour permeability. Stone abbreviations are listed in Table 1. C = capillary absorption coefficient; B = experimental capillary penetration coefficient; $K_v =$ water vapour permeability coefficient.

Stone	Capillary absorption	Capillary penetrati	Water vapour permeability		
	$C(g/m^2 s^{1/2})$	$B (mm/s^{\frac{1}{2}})$	$B_{\rm T}~({\rm mm/s}^{1/2})$	$B/B_{\rm T}$	$K_{\rm V} ({\rm g}/{\rm m}^2 {\rm day})$
AV	31 ± 3	0.46 ± 0.07	0.16 ± 0.02	2.8	149 ± 13
AU	166 ± 5	1.18 ± 0.08	0.8 ± 0.1	1.5	241 ± 6
CF	166 ± 6	0.67 ± 0.07	0.57 ± 0.03	1.2	215 ± 12
SP	353 ± 5	1.9 ± 0.5	0.96 ± 0. 02	2.0	291 ± 15
DB	3.7 ± 0.2	0.05 ± 0.02	0.036 ± 0.005	1.2	88 ± 8
TA	4.4 ± 0.4	0.20 ± 0.01	0.04 ± 0.01	4.5	53 ± 15

this characteristic. For this reason the samples were analysed without taking into account the different orientations.

Capillary absorption and capillary penetration were determined experimentally, and the latter was also calculated using an ideal cylindrical pores model. SP shows the highest capillary absorption and water vapour permeability coefficients as might be expected given that it has the highest porosity and pore radii access size. CF and AU show similar values in these properties due to the fact that the higher porosity of CF (29 > 23%, Table 3) is balanced by the higher pore access radii of AU (6 > 0.2 μ m, Table 4).

Water vapour permeability is high in both stone types, and is slightly higher in AU due to its pore size. AV shows lower values in these properties, in spite of having similar porosity values and pore radii. This may be due to its higher quartz content, with a contact angle lower than calcite [62], the different configuration of the porous system, which is far from the ideal cylindrical pores (B/B_T : 2.8), and also to the fact that it has relatively few medium range pores, the ones that enhance capillary processes.

TA and DB show similar values much lower than the other stones, in line with their lower porosity and pore size. However, capillary penetration and permeability show that water rise is higher in TA while DB shows higher permeability. This may be due to differences in the porous system. Pores in DB are homogeneous and close to the cylindrical pore model, with a high proportion of pores in the medium range $(B/B_{\rm T}$: 1.2). On the other hand, pores in TA are heterogeneous and although there are some well communicated areas where water rises quickly, in general it has a poorly connected pore system that is quite unlike the ideal cylindrical model $(B/B_T: 4.5)$. The hydric parameters were correlated to porosity and pore size. In general they show a linear relation (Table 7). In these types of stone, determination coefficients showed that open porosity is more closely correlated with capillary absorption ($R^2 = 0.90$) than with capillary penetration ($R^2 = 0.80$). There is also a close relation between open porosity and water vapour permeability ($R^2 = 0.87$). Pore radii influence the capillary penetration coefficient in carbonate stones ($R^2 = 0.96$), but not in sandstones (Fig. 5), with capillary ascent lower than expected due to the connections between the pores. As mentioned previously this may be due to the quartz content and the detritic texture, which influence the porous system model.

Table 7 Correlation equations between the parameters we obtained.

	Equations	R^2
Porosity vs Capillary Absorption	$p_{\rm o} = 4.844 \ln(C) + 3.342$	0.902
Porosity vs Capillary penetration	$p_{\rm o} = 2.314 B + 11.848$	0.797
Porosity vs Water vapour permeability	$p_{\rm o} = 0.104 \rm kV + 3.824$	0.872
Pore access radii vs Capillary rise	B = 1.854 Rp + 0.074	0.957 ^a

^a Only in carbonate stones.



Fig. 5. Correlation between pore access radii (r, in μ m) and capillary penetration coefficient (B, in mm/s^{1/2}) for the six stone types: Santa Pudia limestone (SP), Fraga limestone (CF), Uncastillo sandstone (AU) Villaviciosa sandstone (AV), Albox travertine (TA) and Boñar dolostone (DB).

4.4. Mechanical properties

There is a good correlation between the values for Shore and Schmidt hardness (Table 8). In general, in mechanical properties the differences in composition are less important than those in texture. The crystalline textures (TA and DB) show the highest values and only very small differences can be observed between the travertine, composed solely of calcite, and the dolostone, consisting mainly of dolomite. The results for AU, AV, SP and CF are very similar. All of them are within their standard deviation, and the slight differences cannot be considered significant. Nevertheless, some trends can be observed. The sandstones, with clastic texture and higher porosity, have low Shore and Schmidt hardness values. In this case, AV obtained higher values than AU, which is presumably

Table o				
Mechanical and dynamic	properties.	Stone	abbreviations	are
listed in Table 1.				

Stone	Shore value	Schmidt value
AV	85 ± 5	13±3
AU	80 ± 3	12 ± 2
CF	82 ± 6	13 ± 3 ^a
SP	60 ± 16	11 ± 3 ^a
DB	93 ± 2	19 ± 2 ^b
TA	92 ± 7	20 ± 5^{b}

^a Sample broke early.

Sample broke late.

due to the differences in composition, with a higher presence of calcite in AU and of silicates in AV. The limestones (CF and SP) had similar composition and porous volume, so the differences between them must be due to their texture and in particular their grain size. The lowest hardness values in both tests were measured in SP, a rock with a very coarse-grained clastic texture. This rock has poorly cemented grains, and is therefore susceptible to granular disintegration, which explains why it had the lowest hardness and coherence values.

4.5. Ageing test

After the tests, there were hardly any changes in the visual appearance of samples AV, AU, DB and TA. CF and SP suffered substantial loss of material in both tests, although this effect was more pronounced in the salt crystallisation test.

Fig. 6A and B shows the histograms highlighting both the increases and decreases in weight (albeit minimal) in the six stones. In these histograms, each weight gain measured in a stone during the cycles for the freeze thaw (6A) and salt crystallization tests (6B) was added along the blue bar (labelled as G), while its weight losses were added along the red bar (labelled as L). In this way, the length of each bar shows the sum of all the weight gained by samples due to the crystallization of ice or salt inside pores and fissures during the tests, and the sum of all weight losses due to pressure from ice or salt crystallization that causes fragments of stone to break off.

In the case of the freeze-thaw cycles (Fig. 6A), it is clear that SP is the stone that suffers most. The loss of material started with surface clasts and eventually reached almost 40% of its original weight. Tests carried out by other researchers showed a range of behaviour, varying from substantial decay [26,59,63] to hardly any change [64] Next comes CF, which lost up to 15% due to sample fragmentation. According to [65], the highest risk of serious decay in stones used in historical buildings is when pore throat size is between 0.1 and 10 μ m. In this study, CF is the stone with the highest proportion of this pore fraction, however SP shows more decay due to its lack of cohesion. The other materials (apart from TA) behave similarly to each other with a gain of 2–3% due to the presence of

ice crystals in new pores and/or fissures followed by a very small loss. In the case of TA the initial weight gain is followed by a loss mainly due to the water escaping from the big pores. The stone that performed best was DB, which remained practically unchanged throughout the test, with only a small weight gain followed by a negligible loss. The weight of the sandstones increased, which means new fissures were formed. Although saturation increased, the good cementation between the minerals prevented decohesion and material loss. In summary, weight gains clearly suggest that new fissures must have developed in all the stones. These are visible in CF and SP and evidenced by weight gain in TA, DB, AU and AV.

There were some differences in the salt crystallization test (Fig. 6B). SP and CF also fared worse than the other stones, but this time CF was in last position as the only stone to gain almost 10% in weight and then lose almost the same amount. Tests developed by [59.64] in similar stones but with only 20% porosity revealed a gain of 2.5% during the first cycles and a slight loss thereafter. In SP the loss of material was in the form of isolated clasts and not in big fragments as occurred in the freeze-thaw test. In CF the loss was focused on the surface in the form of consecutive layer detachments, giving the sample a rounded shape by the end of the test. This is due to the fact that SP had bigger pores, which were not as exposed to crystallisation pressure as the CF micropores. At the end of the test we submerged samples in distilled water to wash off any salt trapped in the pores and/or fissures and to measure their real weight loss (LS value, Fig. 6B). The dissolution of salts in water was controlled by a conductivity meter and washing was repeated whenever the conductivity descended to values similar to that of distilled water. CF was the only stone to lose more than 15% of its weight. AU also behaved differently. Although it apparently performed better than SP during the decay test, after the samples were washed it lost more fragments, due to the dissolution of the salt that was acting as a cement between the grains. This behaviour was also observed by a previous author in granites [28]. The reason for the different behaviour of AU (broken) and AV (almost intact) lies in their hydric properties. AU absorbs water faster than AV, so during immersion AU will have twice the water content and the salt will crystallise in more voids than in AV. AU also has smaller pore radii and higher carbonate and clay content, which can also affect its durability. DB was once again the stone that performed best.

Hence, when we compare Fig. 6A and B, it is evident that TA, DB and AV behave in a similar way in the two ageing tests because although their weight changed, they did not suffer any visible damage. The varying susceptibility to decay of the different samples, in particular SP and CF, may be due to their texture and high porosity. In SP, the main decay factor is the low cohesion between the clasts and in CF, its high percentage of pores around 0.2 μ m, especially important in the case of the pressure exerted by crystallizing mirabilite. In fact, both stones had poor mechanical behaviour, in that they broke quickly. Lastly, AU behaved differently in



Fig. 6. Behaviour of the samples after freeze-thaw (A) and salt crystallization tests (B). The histograms show the total weight gain (G, in %) and loss (L, in %) suffered by the stones and the weight loss after washing the samples at the end of salt crystallization test (LS, in %). Legend: Villaviciosa sandstone (AV), Uncastillo sandstone (AU), Santa Pudia limestone (SP), Fraga limestone (CF), Boñar dolostone (DB) and Albox travertine (TA).

each test, suffering greater decay in the salt crystallization test. Compared to AV, which has similar structure, the determining factor behind their different performance is their mineralogy. AU contains calcite cement, in which the dissolution rate in presence of a saline solution plays an important role in stone decay.

5. Conclusions

We carried out a petrophysical characterisation of six porous building stones. A detailed petrographic characterisation in which compositional (petrography and mineralogy) and textural (grain size, distribution) parameters and in particular porous system properties (volume, size, shape and distribution) were evaluated. Physical properties (density, porosity, hydric and mechanical properties) were also determined. The relationship between the different parameters was also assessed and linked with the behaviour of the stone when subjected to ageing tests.

The stones can be divided into three main groups on the basis of their durability as construction materials: low quality (Santa Pudia – SP and Fraga limestones – CF), intermediate quality (Uncastillo – AU and Villaviciosa sandstones – AV) and high quality (travertine from Albox – TA and Boñar dolostone – DB).

The limestones (SP and CF) are quite similar in composition with high calcite content (97%) although, as accessory phases there was predominance of quartz in SP and of clays in CF. Texturally, both stones are very different. SP is a bioclastic limestone with coarse grains and CF is a micritic limestone. Both stones are low quality mainly due to their high porosity (30–35%) and low coherence. As regards the porous system, SP shows large well-connected inter- and intragranular pores and low cohesion, while CF has connected moldic and regrowth matrix pores with a size more favourable to decay. As a result, SP has poor mechanical behaviour and CF responds worse to ice and salt crystallisation. CF's high degree of saturation (93%) and high pore proportion within the size range makes it the most susceptible to damage by salt crystallisation, and also more susceptible to salt-induced decay.

AV and AU sandstones have intermediate quality. The differences between them are mainly due to their mineral composition, silicates and carbonates in AU and mainly silicates (quartz) in AV. Both stones have a clastic texture with medium grain size and similar pore system distribution, with around 20% porosity volume. AU has a slightly lower pore size and pore radii access size than AV, due to the different content and nature of the cement between the grains. In consequence, AU has a poorer response to water-related decay than AV and also fares worse in the salt crystallisation and freeze-thaw tests.

TA and DB are the highest quality stones although there are huge differences between them in terms of composition, texture and porous system. TA is formed by heterogeneous calcite grains with a wide range of pore sizes and bad interconnections. In DB the main component is dolomite with a homogeneous crystalline texture and mainly intercrystalline porosity, characterised by small, homogeneous pores and pore radii access sizes. Nevertheless, both stones have quite similar pore distribution. The high quality of these stones is due to their low porosity (10%), crystalline texture and high coherence. The hydric behaviour is similar despite the differences in their petrographic characteristics. Their high quality is confirmed by the results obtained for their mechanical properties. After the ageing tests, both stones remained almost undamaged.

The durability test cannot predict the behaviour of the stone when exposed to the environment. Nevertheless it is a useful tool for comparing the durability of different stones, establishing their quality in relative terms and assessing the best way to lay them when used in building. Petrophysical characterisation is essential for predicting stone durability, and is useful even when comparing the same kinds of stone as there may be differences in the porous system and the mineralogy.

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