



---

*Research article*

## **Historical Quarries, Decay and Petrophysical Properties of Carbonate Stones Used in the Historical Center of Madrid (Spain)**

**David M. Freire-Lista <sup>\*</sup> and Rafael Fort**

Instituto de Geociencias IGEO (CSIC, UCM) Spanish Research Council CSIC–Complutense University of Madrid UCM. 28040 Madrid, Spain

**\* Correspondence:** Email: [dafreire@geo.ucm.es](mailto:dafreire@geo.ucm.es).

**Abstract:** The carbonate stones that make up the four fountains of the 18<sup>th</sup> century located in the *Paseo del Prado* of Madrid (Spain) are studied. The documentary search in historical archives, together with the petrographic, cartographic and paleontological studies permitted to determine that the fountains have been built with dolostone of the *Castrojimeno* Formation, with gastropods of the *Trochactaeon Lamarcki* specie of the Santonian (Upper Cretaceous). The historical quarries from which the ashlar have been extracted is located in *Redueña* Village. The petrophysical properties of this dolostone (effective porosity, bulk density, mercury intrusion porosity, ultrasound wave propagation velocity, micro-roughness and color) have been calculated and compared with *Colmenar de Oreja* limestone. Each of the four fountains has a circular pylon at the base, a central column that holds a smaller pylon and is topped by a sculpture that serves as a spout. A bomb destroyed three ashlar of the basal pylon, column, small pylon and the sculpture of the SE fountain, during the Spanish Civil War, in 1936. These damaged elements were replaced by other carved limestones from *Colmenar de Oreja* in 1944. The four sculptures had been replaced in 1996 with resin replicas and the originals are preserved in the *San Isidro. Los orígenes de Madrid* museum. The study of the petrophysical properties of the sculptures located in the museum allowed us to determine the decay of different stone types. The analysis of micro-roughness was employed to define that the dissolution

effect on the sculptures is different between dolostone and limestone. *Redueña* dolostone is more resistant to dissolution effect than *Colmenar de Oreja* limestone.

**Keywords:** dissolution; micro-roughness; limestone; dolostone; heritage; decay

## 1. Introduction

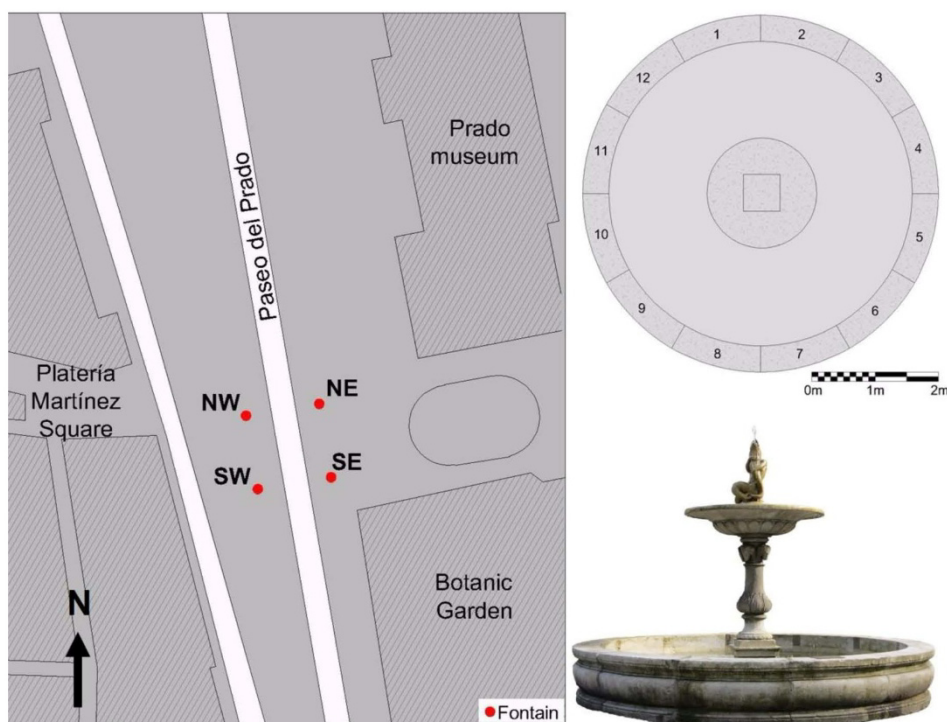
Carbonaceous stones have been used in the carving of sculptures throughout history [1], however the passage of time makes it sometimes unable to know the type of stone used in monuments. The location of historic quarries is one of the disciplines of geology applied to heritage conservation necessary for the conservation of heritage assets [2]. In order to locate the original quarries of the stones used in the monuments an exhaustive documentary search must be done, accompanied by a cartography and fieldwork.

The four fountains, also known as “*Las Fuentecillas*” because of their small dimensions, form the vertices of an imaginary square in the *Paseo del Prado* in Madrid (Spain). Two of the fountains are on the sidewalk of the *Prado* museum and the other two are situated in the opposite, in the pedestrian median of the *Paseo del Prado* (Figure 1). Located in one of the most touristic areas of Madrid, it has been one of the most beautiful landmarks of the urban project of the *Paseo del Prado* for more than two centuries, promoted by King Carlos III in the 18<sup>th</sup> century that consists of a landscaped zone and sculptural sets like the four fountains besides the fountain of Cibeles, Neptune and Apollo and buildings dedicated to the culture and the scientific popularization as the *Prado* museum.

The architect Ventura Rodríguez projected the fountains consisting of a circular basal pylon with an internal diameter of approximately 4.7 m and an external diameter of approximately 5.53 m. This pylon is made of 12 ashlar and in the center containing a column carved by Narciso Albedo, in which sculpted vegetal motifs appear and animals: eight leaves superimposed in the lower part and four bear heads, sculpted by José Rodríguez. Each column is topped by a small circular pylon with 20 leaves on which is placed a sculpture of a triton child holding upright a dolphin whose mouth flows the water (spout). These four sculptures were finally elaborated by Alfonso Bergaz and Roberto Michel. All were carved out of carbonate stone (Figure 1) and they were installed in 1782.

The carbonatic building stones traditionally used in Madrid have been mainly *Redueña* dolomite and *Colmenar de Oreja* limestone. *Redueña* stone includes limestone and dolomicrites, normally of cream colour tones. Its historical quarries were very dispersed, notably the villages of *Redueña*, *Guadalix de la Sierra*, *El Molar*, *Venturada* and *Torrelaguna*, as well as other towns in *Guadalajara* [2].

The *Castrojimeno* Formation outcrops in *Redueña* and has several members of dolomites with different concentrations of cretaceous fossils. Members without fossils are those that have been studied so far.



**Figure 1. A. Location map of the four fountains in the *Paseo del Prado* of Madrid. B. Fountain plant. D. General view of the fountain.**

*Colmenar de Oreja* limestone come from Southeast of Madrid and contain miocene fossils. This stone has been widely used in Madrid's monuments due to its whitish color.

The fountains have suffered aggressions throughout its long history. However, the petrographic studies, aimed at the characterization and conservation of the stones, have not been carried out so far.

Therefore, the aim of this study is to figure out the characteristics of the stones used in the sculptural complex known as the four fountains of the Plaza Murillo in Madrid (Spain) and determine their origin and compare the type of decay of each stone. Moreover, this study focused on future restoration works. In addition, the petrophysical properties are compared between two levels of *Redueña* dolostone and *Colmenar de Oreja* limestone.

Geographic, orographic and especially geology show great importance when it comes to the selection of construction materials. The stones used for sculptures must have characteristics of proper durability, styling, polishing and cost determined for each need. Mass media, transportation and tools of the 18<sup>th</sup> century were precarious and the work with stones were hard, thus some works had prolonged for years to complete. The architects usually chose the stone according to the distance of it quarries, the price, the use, the finish required for the stone. The geology of the area near Madrid contains different types of igneous, metamorphic and sedimentary rocks.

The petrographic characterization is a classic stone characterization technique [3,4], which together with cartographic study and paleontological study allows us to localize the historical quarries

of stones used in the construction of historical buildings or monuments. Ultrasonic auscultation is used to obtain the stones characterization by identifying the ultrasonic wave propagation velocity, which has a strong dependence on porosity, fractures and alteration. Ultrasound is useful to determine the anisotropy of rocks, which in turn is also closely related to their durability and decay [5,6]. In general, ultrasonic velocity is directly proportional to the durability of the stone and inversely proportional to its anisotropy [7,8].

Effective porosity and apparent density also provide information on the durability of a stone. In general, higher porosity corresponds to lower durability and higher density to higher durability [9]. The distribution of pore size has great importance to know the durability of the rocks [10,11].

## 2. Materials and Methods

A visual inspection has been performed on the four fountains stones, focusing on fossils and forms of decay. Two small chips of the basal pylon (SE fountain) have been obtained. One from an original ashlar and another of a replacement ashlars. Two thin sections of these samples were made and characterized under a polarized light microscope Olympus BX 51 equipped with a digital DP coupled camera (6 V/2.5 Å) Olympus DP-Soft software Olympus (version 3.2).

A mosaic was constructed with thirty microphotographs and an approximate surface area of 1 cm<sup>2</sup>.

Once the sample was characterized, a following study has been conducted in historical archives and cartography of cabinet and field, following the methodology proposed by to locate the quarries that have provided the building stones.

A stone block was obtained in the historic quarry from which seven cubic specimens of 5 cm of side were cut for petrophysical analysis and a cylinder for analysis of porosimetry by mercury intrusion. Specimens were cut at low speed (120 rpm) and low strain.

A thin section of a sample obtained in *Redueña* quarry and a mosaic of photomicrographs was made, the procedure used for its study was the same as for the samples obtained in the basal pylon of the SE fountain.

A visual inspection has been made at the sculptures located in the *San Isidro. Los orígenes de Madrid* museum.

For the XRD analysis A Philips analytical PW 1752 diffractometer operated at 40 KV and 30 mA was used with copper anode tube, graphite monochromator and PC-ADP Diffraction software. The dust samples were analyzed with Cu $\alpha$  radiation. The measurements were performed in a range between 2 and 68 with an interval of 0.02 and 2 /min in continuous mode.

A Niton Series XL3t portable X-ray fluorescence kit has been used to identify the elements present in *Redueña dolostone* and *Colmenar de Oreja* limestone. This portable elemental analysis technique is non-destructive and fast. Ten measurements were made on the both fresh surfaces stones and the average for each stone has been calculated.

Effective porosity test (Pe) was performer using the natural stone method described in European

standard UNE-EN, 1936, 2007 in the seven cubic samples of *Redueña* dolostone. After the samples had reached a constant weight, they were placed in a vacuum chamber at 2 kPa for 2 h and they were slowly submerged in water (room temperature) and then stored at atmospheric pressure for 24 h, reaching water saturation. The  $P_e$  values were calculated from Equation 1:

$$P_e (\%) = ((W_s - W_d) / (W_s - W_h)) \times 100 \quad (\%) \quad (1)$$

$W_s$  is the weight of 24-h water-saturated sample,  $W_d$  is the sample dry weight, and  $W_h$  is the submerged in water sample weight.

The bulk density ( $\rho_b$ ) mean of the same samples was also found as per European standard UNE-EN, 1936, 2007 as the ratio between specimen mass and its bulk volume, from equation 2:

$$\rho_b (\%) = ((W_d) / (W_s - W_h)) \times 1000 \quad (\text{kg/m}^3) \quad (2)$$

Ultrasonic pulse velocity ( $V_p$ ) was measured for each of the seven cubic specimens of *Redueña* dolostone in the three orthogonal directions, using the mean of four consecutive measurements of each face of the cube as the accepted value.  $V_p$  was taken with CNS Electronics PUNDIT equipment (precision:  $\pm 0.1 \mu\text{s}$ ) following European standard UNE-EN, 14579, 2007. The 1 MHz transducers (11.82 mm in diameter) were affixed to the surface with Henkel Sichozeil Kleister (a carboxymethyl cellulose) paste and water to enhance the transducer-stone contact.

The anisotropy indices  $dM$  and  $dm$  were obtained [12] for *Redueña* dolostone following equations 3 and 4:

$$dM = [1 - (2 V_{pmin} / (V_{pmean} + V_{pmax}))] \times 100 \quad (3)$$

$$dm = [2 (V_{pmax} - V_{pmean}) / (V_{pmax} + V_{pmean})] \times 100 \quad (4)$$

( $V_{pmax}$ ,  $V_{pmin}$  y  $V_{pmean}$ ) refer to the  $V_p$  in the three orthogonal directions of space. In this way,  $V_{pmax}$  is the maximum value,  $V_{pmin}$  is the minimum value and  $V_{pmean}$  is the average value of the ultrasonic pulse velocity.

Mercury intrusion porosity (MIP) is an indirect and relatively fast and simple method for determining the distribution of pore size diameter [10].

MIP was conducted on a single prismatic specimen ( $12 \pm 2$  mm in diameter and  $20 \pm 2$  mm high) cut from a *Redueña* quarry specimens. The analysis was run on a sample oven-dried at  $70^\circ\text{C}$  to a constant weight. A Micromeritics Autopore IV 9520 porosimeter with maximum pressure of 414 MPa (60000 psi); pore throat diameter measuring range 0.001 to 400  $\mu\text{m}$ . The pore distribution is divided between macroporosity (diameter  $> 5\mu\text{m}$ ) and microporosity (diameter  $< 5\mu\text{m}$ ) [13,14].

Five measurements of color have been made on each side of the seven dry samples of *Redueña* dolostone and one of the *Colmenar de Oreja* limestone. The mean of these measures was calculated for each stone. The same number of measurements were made on the wetted surface with water from the same specimens.

The CIELAB parameters,  $L^*$ ,  $a^*$  and  $b^*$ , and the European standard UNE-EN, 15 886, 2011 were used: The lightness ( $L^*$ ), chromatic coordinate from red to green ( $a^*$ ), chromatic coordinate from blue to yellow ( $b^*$ ), yellow index ( $YI^*$ ) and white index ( $WI^*$ ) [15,16].

The spectrophotometer used was a Minolta CM-700D, with a CM-S100W DATA Software SpectraMagic COLOR NX. The measure of change in visual perception of two given colors,  $\Delta E^* = \sqrt{(L^*_1 - L^*_2)^2 + (a^*_1 - a^*_2)^2 + (b^*_1 - b^*_2)^2}$ , has been calculated in relation to the dry and wet sample with water. This value establishes a numerical comparative value between the color variation in the dry and wet samples.

Surface optical micro-roughness was measured with a portable TRACEiT rugosimeter on the four fountains preserved in *San Isidro. Los orígenes de Madrid* museum.

This non-destructive and portable equipment allows the analysis of topography in 3D with high precision, with a resolution of 1 micron in height (Z axis) and 2.5 micrometers in the X/Y axis. The measurement field is 5 mm  $\times$  5 mm. And the number of data points measured on the X/Y axes are 2000. The micro-roughness parameters were calculated by the software as stipulated in DIN EN ISO 4287. Five micro-roughness measurements were performed on the surface of each stone spout and the mean of three micro-roughness parameters ( $R_a$ ,  $R_q$  and  $R_z$ ) was calculated.  $R_a$  is the arithmetic mean of the absolute values of the deviations of the midline profile;  $R_q$  represents the square root of the deviation of the evaluated profile, and  $R_z$  is the sum of the vertical distances between the five highest peaks and the five deepest valleys within the sampling length.

### 3. Results

Due to difficulties in financing of Carrara marble for the fountains, Ventura Rodríguez proposed the use of *Redueña* dolostone (Figure 2), a village located approximately 50 km North of Madrid, which would reduce costs and speed up works. The master builder *Pedro de Paliza* won the concession and the *Gorrachategui* brothers, from the municipality of Berriz (Basque Country), were the stonecutters who extracted the stone in the quarry located at the coordinates 40.80208, -3.59141. The construction of the fountains was slow and difficult due to the thickness of dolostone strata that do not exceed 1.5 meters as shown in figure 3.

The SE fountain, located next to the botanical garden, was bombed (Figure 4) during the Spanish Civil War, in 1936 (Figure 4A) and was recovered in 1944. Three ashlar of the basal pylon, the column, small pylon and the sculpture with the spout were replaced by *Colmenar de Oreja* limestone, while the rest of the elements remain *Redueña* dolostone.



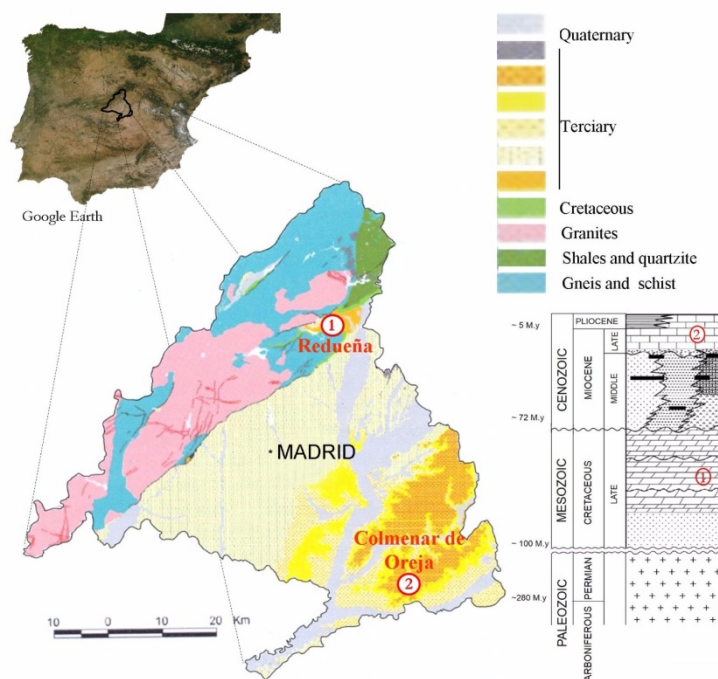


Figure 2. Location of the stones analyzed.

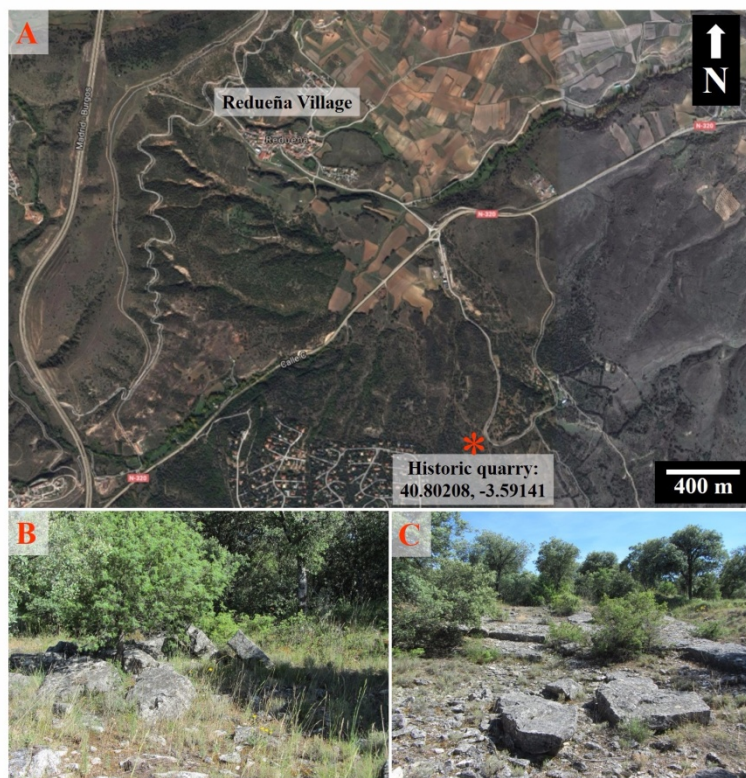
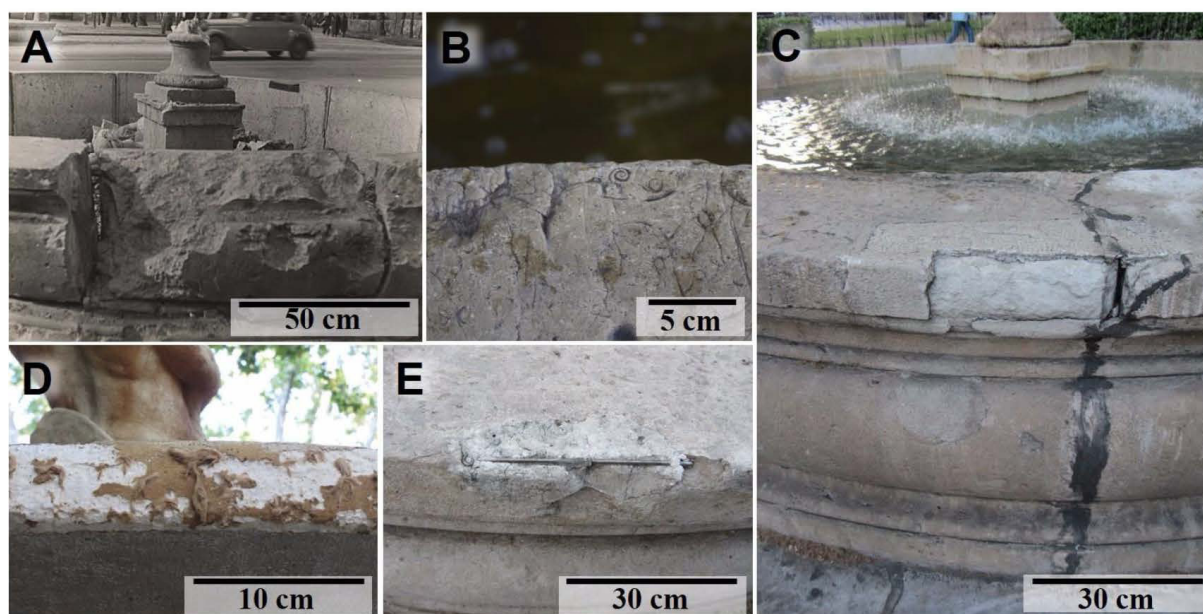


Figure 3. A. Redueña area in satellite view. The asterisk indicates the location of the historic quarry. B and C detail of the historic quarry with remains of extraction (40.80208, -3.59141).



**Figure 4. Fountains decay. A. SE fountain 1934. Source: General Administration Archive of Spain (AGA). B. Dissolution of the calcite filling fossils and microcracks. C. Biological colonization and use of Portland mortar. D. Break of epoxy resin. E. Metal staple.**

The Department of Building Conservation of the City of Madrid restored the four fountains in 1996, the work consisted of the cleaning, consolidation, sealing, obtaining molds from the sculptures of the tritons holding a dolphin which were replaced with epoxy resin replicates. Also the granite and porphyry cobblestones of the paving between the four fountains were replaced by asphaltic pavement.

The sculptures were sent to the *San Isidro. Los orígenes de Madrid* museum. Dependent of the City council of Madrid.

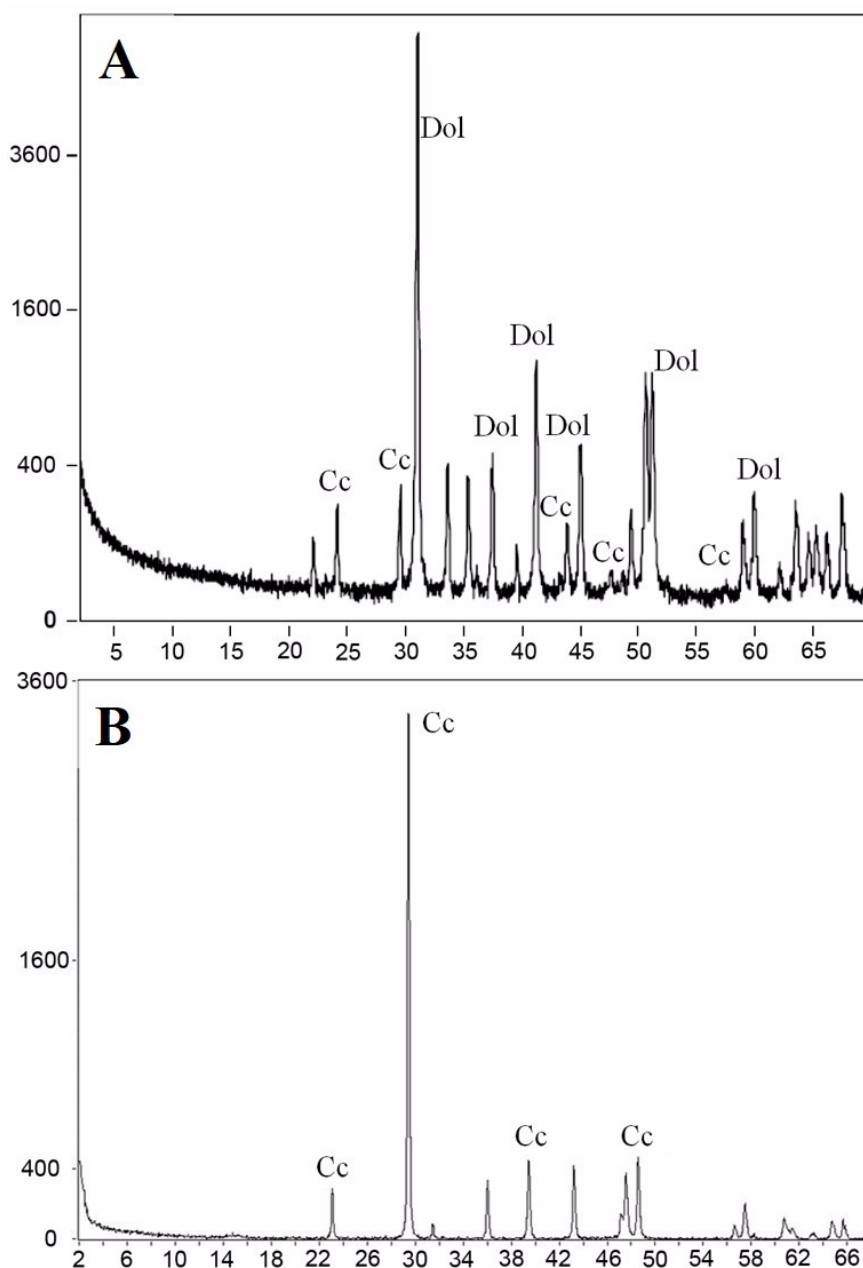
*Redueña* dolostone is a massive dolostone formed by rhombic dolostone crystals. And the fossils are mainly composed of gastropods and fragments of bivalves. These fossils are found as molds filled with calcite. The thickness of their shells can reach 3 mm thick, which probably represents the adult stage of the same species. Remnants of their original depositional texture are preserved, generally disposed fossils aligned longitudinally to the lamination. Geopetal structures appears and microcracks filled with calcite are also observed [17]. The matrix crystals are microcrystalline, equigranular ( $< 50 \mu\text{m}$ ) and dark, with few mottled colors and poikilotopic and blocky mosaic cements predominate. Incipient dedolomitization can be observed. The dolostone correspond to the *Montejo* member that forms part of the *Castrojimeno* Formation (Santonian). This member has a level of *Trochactaeon Lamarcki* specie gastropods located in the around *Redueña* Village.

*Colmenar de Oreja* limestone is a biomicrite/biosparite stone containing Upper Miocene fossils of oysters and gastropods [18] from the Madrid sedimentary basin. It is classified as a lacustrine



biomicrite/biosparite formed by a bioclast skeleton (40% characeae, ostracods and gastropods) and cryptocrystalline micrite matrix (20–30%), calcitic in composition and dark-colored, alternates with sparitic cement (30–40%). The sparitic cement sometimes appears as drusy mosaic. The existence of geopetal structures (matrix/cement) is indicative of significant phreatic-vadose conditions in the sedimentary medium.

The XRD allows identifying the constituent mineralogy. *Redueña* dolostone with gastropods has a higher dolomitic content than calcite (Figure 5).

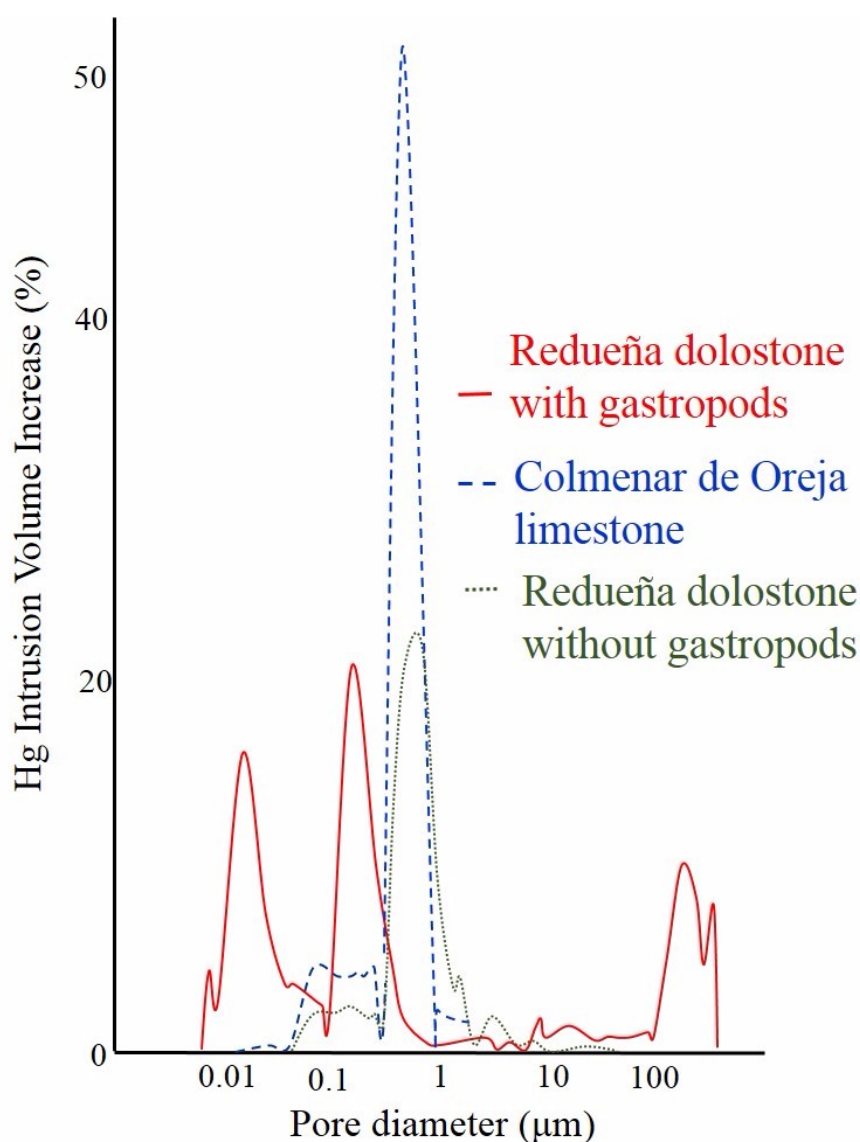


**Figure 5. XRD results. (A) *Redueña* dolostone with *Trochactaeon Lamarcki* gastropods B. *Colmenar de Oreja* limestone.**

The elements in which the *Redueña* dolostone differs with *Colmenar de Oreja* limestone are mainly Ti, Fe and Mg as shown in Table 1.

In Table 2, the petrophysical properties of the *Redueña* dolostone analyzed are similar or even better than those of *Colmenar de Oreja* limestone. *Redueña* dolostone presents higher porosity,  $V_p$  and lower porosity due to mercury intrusion and less anisotropy.

The pore diameter distribution of *Colmenar de Oreja* limestone and *Redueña* dolostone without gastropods is concentrated at a pore diameter range of approximately 0.5 to 1  $\mu\text{m}$  [2]. The pore diameter ranges of the *Redueña* dolostone with gastropods are between 0.01 and 1  $\mu\text{m}$  and 100 to 400  $\mu\text{m}$ . As can be seen in figure 6.



**Figure 6: Pore-size distribution curves of *Colmenar de Oreja* limestone [2] and *Redueña* dolostone, with and without *Trochactaeon Lamarcki* gastropods.**

**Table 1. XRF results. Minor elements of *Colmenar de Oreja* limestone and *Redueña* dolostone, with and without *Trochactaeon Lamarcki* gastropods.**

	<i>Sr (%)</i>	<i>Cu (%)</i>	<i>Fe (%)</i>	<i>Ti (%)</i>	<i>Al (%)</i>	<i>Si (%)</i>	<i>Cl (%)</i>	<i>S (%)</i>	<i>Mg (%)</i>
Colmenar de Oreja Limestone	0.01	0	0.02	0.20	0	0.94	0.56	0.53	0
Redueña dolostone (without gastropods)	0.01	0.01	0.07	0	0.49	1.39	0.05	0.20	9.21
Redueña dolostone (with gastropods)	0.01	0	0.09	0	0	0.91	0.11	0.37	9.52

**Table 2. Mean values of bulk density, open porosity, porosity accessible to mercury (micro-and macroporosity), ultrasound velocity transmission ( $V_p$ ) and anisotropy indices for *Colmenar de Oreja* limestone and *Redueña* dolostone. The data of the petrophysical properties of *Colmenar de Oreja* limestone are from [2].**

<i>Property</i>	<i>Colmenar de Oreja limestone</i>	<i>Redueña dolostone (With Trochactaeon Lamarcki gastropods)</i>
Density ( $\text{g cm}^{-3}$ )	$2579 \pm 30$	$2722 \pm 43$
Porosity accessible to water (%)	$3.8 \pm 1.2$	$3.8 \pm 1.0$
Porosity accessible to Hg (%)	3.9	2.9
% Microporosity	84	67
% Macroporosity	16	33
$V_p$ ( $\text{m s}^{-1}$ )	$5941 \pm 111$	$6135 \pm 92$
$\Delta dM$ (%)	3.1	2.0
$\Delta dm$ (%)	1.2	1.2

**Table 3. Color parameters of *Colmenar de Oreja* limestone and *Redueña* dolostone.  $L^*$ : lightness;  $a^*$ : chromatic coordinate from red to green;  $b^*$ : chromatic coordinate from blue to yellow; WI: white index; YI: yellow index;  $\Delta E^* = \sqrt{(L^*_1 - L^*_2)^2 + (a^*_1 - a^*_2)^2 + (b^*_1 - b^*_2)^2}$  global color change.**

<i>Samples</i>		$L^*$	$a^*$	$b^*$	<i>WI</i>	<i>YI</i>	$\Delta E^*$
Colmenar de Oreja limestone	Dry	$83.5 \pm 1.6$	$1.9 \pm 0.2$	$9.8 \pm 0.6$	$21.8 \pm 3.8$	$16.5 \pm 1.2$	4.6
	Wet	$81.3 \pm 1.2$	$2.5 \pm 0.2$	$13.9 \pm 0.6$	$4.5 \pm 3.1$	$23.2 \pm 1.2$	
Redueña dolostone (With <i>Trochactaeon Lamarcki</i> gastropods)	Dry	$77.5 \pm 1.0$	$3.0 \pm 0.3$	$11.3 \pm 0.8$	$10.5 \pm 3.1$	$20.0 \pm 1.4$	16.6
	Wet	$66.9 \pm 1.0$	$5.3 \pm 0.3$	$18.5 \pm 0.4$	$14.5 \pm 1.0$	$34.7 \pm 0.8$	

**Table 4. Micro-roughness parameters in the surface of the four sculptures preserved in the museum. (Three correspond to *Redueña* dolostone and one to *Colmenar de Oreja* limestone).**

	<i>Ra</i>	<i>Rq</i>	<i>Rz</i>
Colmenar de Oreja limestone	$3.2 \pm 0.9$	$4.3 \pm 1.3$	$12.9 \pm 2.9$
Redueña dolostone (With <i>Trochactaeon Lamarcki</i> gastropods)	$8.4 \pm 2.4$	$10.6 \pm 3.0$	$34.1 \pm 7.8$

*Redueña* dolostone and *Colmenar de Oreja* limestone show similar chromatic coordinates.  $L^*$  indicates the lightness and  $a^*$  indicates the red/green coordinates (+a indicates red, -a indicates green) and  $b^*$  indicates yellow/blue coordinates (+b indicates yellow, -b indicates blue) in Table 3.  $L^*$  has in general high values, between 66.9 and 83.5, being more light *Colmenar de Oreja* limestone. Both stones experience a reduction of the light when getting wet.  $a^*$  and  $b^*$  lower for *Colmenar de Oreja* limestone, indicating that this rock is whiter than the *Redueña* dolostone, whose colors are closer to the red and yellow. *Redueña* dolostone experiences greater change of total color when wet.

The micro-roughness varies considerably according to the type of stone from the sculptures located in the museum. The three original sculptures, carved from *Redueña* dolostone around 1782, have greater micro-roughness than the fountain of *Colmenar Viejo* limestone installed in 1944, seen in Table 4.

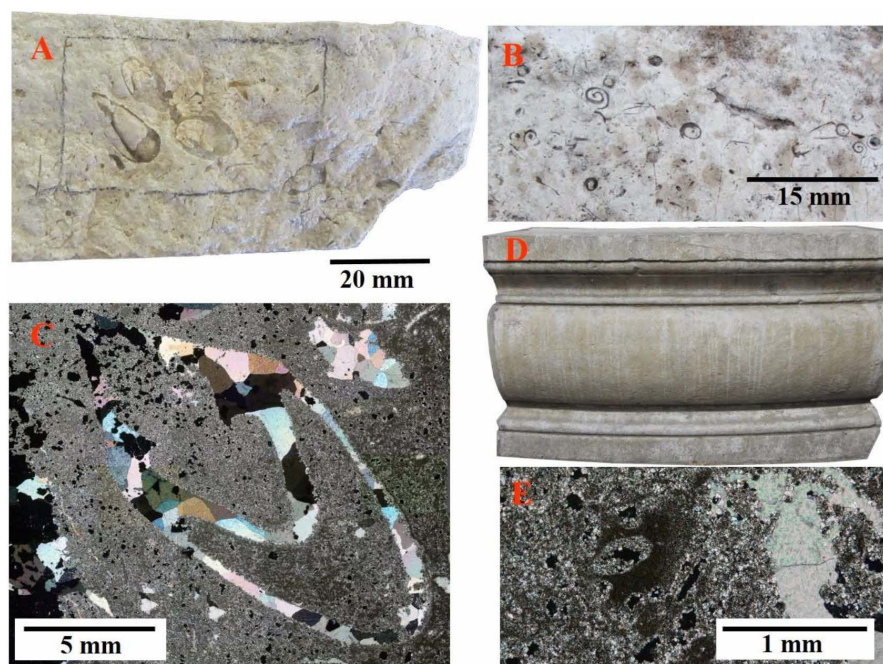
$R_a$  is the arithmetic mean of the absolute values of the deviations from the mean;  $R_q$  is the square root of the deviation and  $R_z$  is the sum of the vertical distances between the five highest peaks and five lowest valleys found in the sample.

#### 4. Discussion

The four fountains preserve original building stones of *Redueña* dolostone. The use in construction of *Montejo* member of *Castrojimeno* Formation with *Trochactaeon Lamarcki* gastropods is the first time being described in a scientific literature. Although *Redueña* dolostone has been studied in previous scientific articles [19–21] as a building stone. For example, in [2] and [19] the petrophysical characteristics of *Redueña* dolostone without *Trochactaeon Lamarcki* gastropods are described. The level with gastropods shows a lower porosity and highest ultrasound velocity [2] that makes it more resistant to the decay.

Geological history, petrophysical and petrographic characteristics, use, environmental conditions such as humidity, temperature, presence of salts and contamination, in conjunction with other factors, determine the durability of building stones [22,23]. Madrid has a climate with frequent frosts [26]. An important point related to the decay (figure 4C) is the action of mechanical strength due to low temperatures. A study on the response to freeze–thaw of *Redueña* dolomite is necessary. The basal pylons present large fractures, with loss of material. Also biological colonization [20], black crusts [24], use of Portland mortar, metal staples and improper coatings on fractures (Figure 4). In addition, these stones are susceptible to decay due to exposure to aggressive agents [25], mainly due to them being located in one of the most touristic areas of the city of Madrid with heavy vehicular traffic.

As indicated in petrography, fossils and fractures are filled with calcite (Figure 7) and the matrix of *Redueña* stone is dolomitic. Fossil molds are visible on the top horizontal surface of the basal pylon ashlar (Figure 7B). The calcite has greater dissolution in these horizontal pylon surface ashlar because drops of water fall on them and remain for a few minutes until their evaporation. However, in the basal pylon outer surfaces (vertical planes), no differential dissolution is observed (Figure 7D) because the exposure to water is minimal.



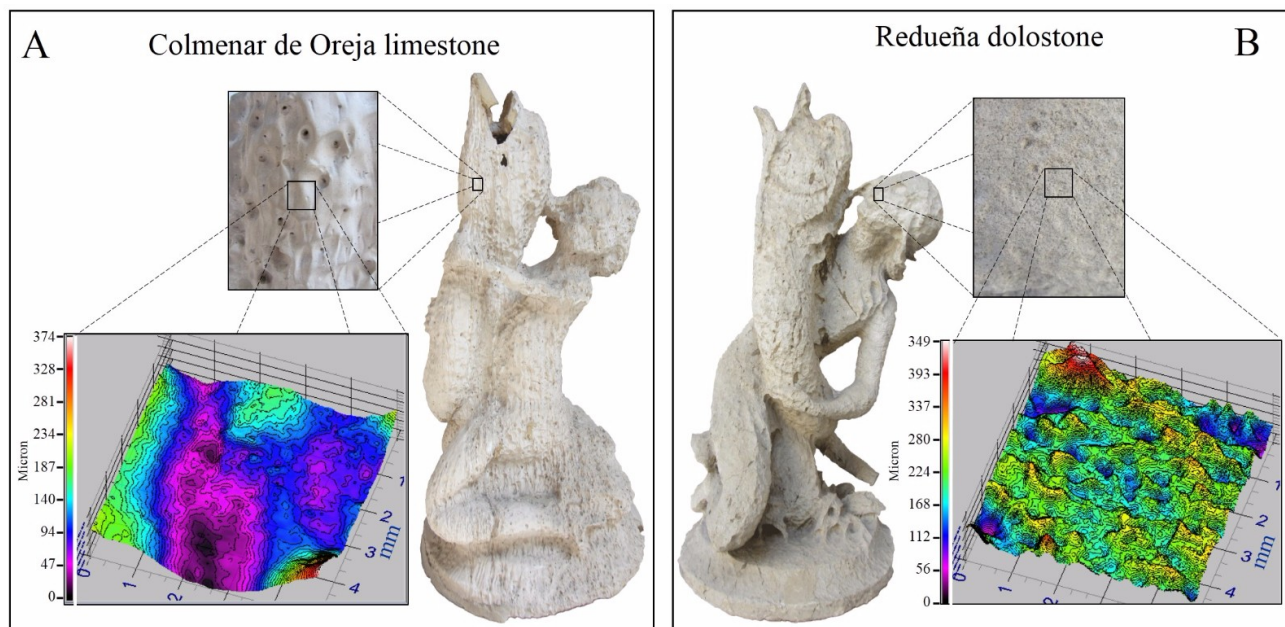
**Figure 7. A. Sample extracted in the quarry located in the coordinates (40.80208, -3.59141). B. Aspect of the horizontal surface of basal pylons. C. Micromosaic (with thirty microphotographs) with crossed nicols showing a gastropod of the *Trochactaeon Lamarcki* specie. D. Aspect of the lateral surface of a basal pylon ashlar from which a small chip has been extracted. E. Photomicrograph with crossed nicols of the chip extracted in the basal pylon (D).**

There are different techniques for measuring the weathering of the stones [27]. Dissolution by water is the most important decay in the sculptures with water spouts preserved in the *San Isidro. Los orígenes de Madrid* museum. *Colmenar de Oreja* limestone has a higher degree of dissolution and it has less micro-roughness than *Redueña* dolostone, since *Colmenar de Oreja* limestone is mostly composed by calcium carbonate [18] (Figure 5). The flow of water forms vertical dissolution grooves 1 cm [28] (Figure 8A) in *Colmenar de Oreja* limestone. *Redueña* dolostone is not as soluble as *Colmenar de Oreja* limestone and the water flow encounters the dolostone microcrystals that act as insoluble obstacles. The calcite crystals are smaller and their dissolution produces very narrow valleys (Figure 8B).

The 3D image showed a very smooth topography in *Colmenar de Oreja* limestone, with very open valleys, compared with the *Redueña* dolostone, which presents more closed valleys. In carbonate stones, greater micro-roughness modifies specific surface in ways favoring the accumulation of water and hence the action of other agents of decay that accelerate its alteration [29]. Nevertheless, this does not happen when there is a difference in solubility between the carbonate stones. Both sculptures have lost their original shape (Figure 8A and B) and they have a similar appearance. Even though the spouts of *Colmenar de Oreja* limestone sculpture (Figure 8A) has been in use for 52 years compared to the 214 years that have been in use the spouts of the *Redueña* dolostone sculpture (Figure 8B). The



micro-roughness is greater in *Redueña* dolostone, and the macro-roughness is greater in *Colmenar de Oreja* limestone. These data are consistent with those obtained with the MIP, the *Redueña* dolostone analyzed in this work has smaller micropores than *Colmenar de Oreja* limestone.



**Figure 8.** Sculptures with water spout (mouth of the dolphin) preserved in the *San Isidro. Los orígenes de Madrid* museum. Surface relief has obtained with portable TRACEiT rugosimeter. Vertical units are  $\mu\text{m}$  and horizontal units in mm. A. Sculpture carved in 1944. *Colmenar de Oreja* limestone. B. Sculpture carved in 1981. *Redueña* dolostone.

The gastropods level of *Redueña* dolostone has similar petrophysical properties than *Colmenar de Oreja* limestone (Table 2) and better than *Redueña* dolostone without gastropods [2].

The sedimentary structures can cause anisotropy in carbonate stones [30], which in turn influences in the durability. It is observed that the anisotropy is lower in the *Redueña* dolostone analyzed in this study than in *Colmenar de Oreja* limestone.

$a^*$  and  $b^*$  parameters are higher in *Redueña* dolostone with *Trochactaeon Lamarcki* gastropods than in the other two stones (Table 3). It may be due to the greater presence of iron in *Redueña* dolostone obtained with XRF (Table 1), this Fe gives reddish color to the stone.

It is important for urban planners and policy makers to focus on projects aiming to maintain and restore the traditional stones [31–34]. The maintenance or cleaning [35] that should be applied to the building stones used in heritage will be conditioned by the type of decay [36,37], polishing, finishing and mineralogy [38]. Non-destructive techniques are an excellent tool for diagnosing decay in building stones.

The main type of the fountain pylons decay is due to the use of incorrect mortars, staples and conservation treatments. These treatments have different durability and color than the original stone (Figure. 4C, D and E). The chromatic parameters of *Redueña* dolostone are provided in this study. The color of restoration treatments should be similar to the original stone color.

## 5. Conclusions

The petrography has provided us with additional information to the historical data and allowed to determine the historical quarry of the four fountains of the Plaza Murillo in Madrid (Spain).

The original carbonate stone used in the four fountains come from a *Redueña* quarry. It is located at the coordinates 40.80208, -3.59141. In this place, the dolostone of the *Montejo* member of *Castrojimeno* Formation presents *Trochactaeon Lamarcki* gastropods and greater cementation than in other levels of the same formation. Which generates a different porosity and increases its durability or resistance to decay.

The four stone sculptures with water spout of the studied fountains are preserved in the *San Isidro. Los Orígenes de Madrid* museum. The study of their petrophysical properties allowed to determine that three of them are carved out of *Redueña* dolostone and one out of *Colmenar de Oreja* limestone.

The analysis of micro-roughness was employed to define that the dissolution effect on the sculptures is different between *Redueña* dolostone and *Colmenar de Oreja* limestone. Dolostone is more resistant to dissolution effect than limestone. The micro-roughness is greater in the *Redueña* dolostone, and however, macro-roughness is greater in *Colmenar de Oreja* limestone.

*Redueña* dolostone with gastropods has good quality, with low porosity and with good durability, carving, polishing and degree of dissolution that are adjusted to the needs of a carbonate stone to be used in places with the presence of water.

The SE fountain presents replacement stones (*Colmenar de Oreja* limestone) in three of the ashlar that constitute its basal pylon, in part of the central column, in the small pylon and in the sculpture with the water spout (Now in the *San Isidro. Los Orígenes de Madrid* museum). Now days the four water spout sculptures are epoxy resin replicas in the four fountains of the Plaza Murillo.

The petrographic characteristics of building stones give good petrophysical properties and also provide very useful scientific data for other disciplines such as history, archeology, restoration, fine arts and architecture.

It is necessary to carry out petrophysical studies with non-destructive techniques to detect fractures in the four fountains and their materials added should be removed on future conservation and restoration works. The stones must be from the original quarries to ensure their durability and compatibility of materials.

## Acknowledgments

This study has been funded by the Community of Madrid under the program GEOMATERIALES-2CM (S2013 / MIT-2914). The authors are members of the research group of the Complutense University of Madrid (UCM): “Alteration and Conservation of Heritage Materials” (ref. 921349).

Petrographic analyzes and thin sections have been carried out in the Department of Petrology and Geochemistry of the Faculty of Geological Sciences of the UCM and in the Petrophysics laboratory of the Institute of Geosciences IGEO (CSIC-UCM), affiliated to the network of laboratories of the Heritage (RedLabPat), Campus of International Excellence Moncloa (UCM-UPM).

Thanks to the *San Isidro. Los orígenes de Madrid* museum, especially to María Victoria López Hervás, for her collaboration and availability for the measurement of color and micro-roughness. Thanks to the General Administration Archive of Spain (AGA) for the photographs of the Spanish Civil War.

## Conflict of Interest

All authors declare no conflicts of interest in this paper.

## References

1. Bednarik M, Moshhammer B, Heinrich M, et al. (2014) Engineering geological properties of Leitha Limestone from historical quarries in Burgenland and Styria, Austria. *Eng Geol* 176: 66-78.
2. Fort R, Alvarez de Buergo M, Pérez-Monserrat E.M, et al. (2013) Evolution in the use of natural building stone in Madrid, Spain. *Q J Eng Geol Hydrogeol* 46: 421-429.
3. Cardell C, Benavente D, Rodríguez-Gordillo J (2008) Weathering of limestone building material by mixed sulfate solutions. Characterization of stone microstructure, reaction products and decay forms. *Mater Charact* 59: 1371-1385.
4. Sajid M, Coggan J, Arif M, et al. (2016) Petrographic features as an effective indicator for the variation in strength of granites. *Eng Geol* 202: 44-54.
5. Yavuz H, Altindag R, Sarac S, et al. (2006) Estimating the index properties of deteriorated carbonate rocks due to freeze-thaw and thermal shock weathering. *Int J Rock Mech Min Sci* 43: 767-775.
6. Sajid M, Arif M (2015) Reliance of physico-mechanical properties on petrographic characteristics: consequences from the study of Utla granites, north-west Pakistan. *Bull Eng Geol Environ* 74: 1321-1330.

7. Vasconcelos G, Lourenço PB, Alves CAS, et al. (2008) Ultrasonic evaluation of the physical and mechanical properties of granites. *Ultrasonics* 48: 453-466.
8. Martínez-Martínez J, Benavente D, García-del-Cura MA., (2011) Spatial attenuation: The most sensitive ultrasonic parameter for detecting petrographic features and decay processes in carbonate rocks. *Eng Geol* 119: 84-95.
9. Vázquez P, Alonso FJ, Carrizo L, et al. (2013) Evaluation of the petrophysical properties of sedimentary building stones in order to establish quality criteria. *Constr Build Mater* 41: 868-878.
10. Ordoñez S, Fort R, del Cura MA. (1997) Pore size distribution and the durability of a porous limestone. *Q J Eng Geol* 30: 221-230.
11. Benavente D, García del Cura MA, Fort R, et al. (2004) Durability estimation of porous building stones from pore structure and strength. *Eng Geol* 74: 113-127.
12. Guydader J, Denis A (1986) Propagation des ondes dans les roches anisotropes sous contrainte évaluation de la qualité des schistes ardoisiers. *Bull Eng Geol Environ* 33: 49-55.
13. Russel SA (1927) Stone preservation committee report (Appendix I). H.M. Stationary Office, London.
14. Rodríguez C, Sebastián E (1994) Técnicas de análisis del sistema poroso de materiales pétreos ornamentales: usos y limitaciones. *Ing Civ* 96: 130-142.
15. Sassoni E, Naidu S, Scherer GW (2015) The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones. *J C Herit* 12: 346-355.
16. García O, Malaga K (2012) Definition of the procedure to determine the suitability and durability of an anti-graffiti product for application on cultural heritage porous materials. *J C Herit* 13: 77-82.
17. Anders MH, Laubach SE, Scholz CH. (2014) Microfractures: A review. *J Struct Geol* 69: 377-394.
18. Fort R, Varas-Muriel MJ, Alvarez de Buergo M, et al. (2015) Colmenar Limestone, Madrid, Spain: considerations for its nomination as a Global Heritage Stone Resource due to its long term durability. Geological Society, London, Special Publications 407: 121-135.
19. Fort R, Fernandez-Revuelta B, Varas MJ, et al. (2008) Effect of anisotropy on Madrid-region Cretaceous dolostone durability in salt crystallization processes. *Mater Constr* 58: 161-177.
20. Cámara B, De los Ríos A, Urizal M, et al. (2011) Characterizing the microbial colonization of a dolostone quarry: implications for stone biodecay and response to biocide treatments. *Microb Ecol* 62: 299-313.

21. Varas-Muriel MJ, Pérez-Monserrat EM, Vázquez-Calvo C, et al. (2015) Effect of conservation treatments on heritage stone. Characterisation of decay processes in a case study. *Constr Build Mater* 95: 611-622.
22. Jamshidi A, Reza-Nikudel M, Khamsehchiyan M. (2013) Predicting the longterm durability of building stones against freeze–thaw using a decay function model. *Cold Reg Sci Technol* 92: 29-36.
23. Cassar J (2016) The Historic and Archaeological Heritage: Pollution and Non-Urban Sites. In: Urban Pollution and Changes to Materials and Building Surfaces, 255-290, P. Brimblecombe (ed). Imperial College Press.
24. Silva B, Aira N, Martínez-Cortizas A, et al. (2009). Chemical composition and origin of black patinas on granite. *Sci Total Environ* 408: 130-137.
25. Liu C, Huang S, Kang Y, et al (2015) A prediction model for uniaxial compressive strength of deteriorated rocks due to freeze–thaw. *Cold Reg Sci Technol* 120: 96-107.
26. Freire-Lista DM, Fort R., Varas-Muriel MJ (2015) Freeze-thaw fracturing in building granites. *Cold Reg Sci Technol* 113: 40-51.
27. Moses C, Robinson D, Barlow J. (2014) Methods for measuring rock surface weathering and erosion: A critical review. *Earth–Sci Rev* 135: 141-161.
28. Goodchild MF, Ford DC (1971) Analysis of scallop patterns by simulation under controlled conditions. *J Geol* 79: 52-62.
29. Urosevic M, Sebastian E, Cardell C. (2013) An experimental study on the influence of surface finishing on the weathering of a building low-porous limestone in coastal environments. *Eng Geol* 154: 131-141.
30. Garcia-del-Cura MA, Benavente D, Martinez-Martinez J, et al. (2012) Sedimentary structures and physical properties of travertine and carbonate tufa building stone. *Constr Build Mater* 28: 456-467.
31. Compitello MA (2003) Designing Madrid, 1985–1997. *Cities* 20: 403-411.
32. Whitehand J.W.R, Gu K. (2010) Conserving urban landscape heritage: A geographical approach. *Proced-Soc Behav Sci* 2: 6948-6953.
33. Freire-Lista D.M, Fort R. (2017) Stone provenance and conservation of the Trinitarias Descalzas and San Ildefonso convent, Madrid (Spain). *Geo-Conservación* (In press).
34. Rukavina M (2015) Archaeological heritage and urban planning in Mérida (Spain), In: Obad Šćitaroci, M. Author, *Heritage urbanism: Urban and Spatial Models for Revival and Enhancement of Cultural Heritage*. Zagreb: 496-501. ISBN 978-953-8042-10-2.
35. Kronlund D, Lindén M, Smått J.H (2016) A polydimethylsiloxane coating to minimize weathering effects on granite. *Constr Build Mater* 124: 1051-1058.

36. Casal Porto M, Silva Hermo BM, Delgado Rodrigues J (1991) Agents and forms of weathering in granitic rocks used in monuments Science, Technology and European. *Cult Herit* 439-442.
37. Pérez-Monserrat E, Varas-Muriel MJ, Fort R, et al. (2011) Cleaning methods assessment for the limestone's façades of formerly workers Hospital of Madrid, Spain. *Stud Conserv* 56: 297-312.
38. Pozo-Antonio JS, Rivas T, Fiorucci MP, et al. (2016). Effectiveness and harmfulness evaluation of graffiti cleaning by mechanical, chemical and laser procedures on granite. *Microchem J* 125: 1-9.



AIMS Press

© 2017 David M. Freire-Lista, et al., licensee AIMS Press. This is an open access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>)