

Villamayor Stone (Golden Stone) as a Global Heritage Stone Resource from Salamanca (NW of Spain)

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Abstract: Villamayor Stone (VS) is an arkosic stone and is known by several names: (i) VS because the quarries are located in Villamayor de Armuña village (Salamanca, Spain); (ii) Golden Stone due to its patina, which gives the stone a ochreous/golden colour; (iii) Franca Stone is known locally and in historical documents. VS has several varieties ranging from channel to floodplain facies. In this work, we have selected three varieties. VS was quarried and used in the construction of Romanesque monuments such as the Old Cathedral, Gothic monuments including the New Cathedral and the University façade, and Baroque monuments, notably the Main Square. Also, VS was used in the reconstruction of the Roman Bridge (Salamanca, Spain). Currently, VS is quarried by a small number of family businesses, using traditional methods for cladding façades of new buildings. Unfortunately, part of the construction sector went bankrupt in the 2008 crisis. However, VS is still the main stone used in the city of Salamanca for the restoration of monuments, even though used in relatively small quantities in comparison with usage before the economic crisis. It is thus of great importance for future generations that their quarries and the craft of masonry be protected. This work proposes that VS should be designated as a Global Heritage Stone Resource.

The particular charm of a city is a product of the geological environment in which it is located. In the case of Salamanca, Spain (Fig. 1a–e), which was declared a World Heritage City by UNESCO in 1988, the singular beauty of the city is provided by the Golden Stone (Franca Stone) which is extensively used throughout the city center. Quarries in the district of Villamayor de la Armuña (located some 5 kilometres from the city) are the source of this stone.

In Salamanca, the construction of the principal religious and civil monuments maintains a fixed pattern in the use and position of the stone that is used. In the lower parts of monuments and columns (base, shaft and capital) other types of Heritage Stones have been used (Fig. 2a–f) such as silicified conglomerates (Sandstone Salamanca Formation (Tosca Stone)), monzogranite (Granite of Los Santos) and leucogranite with tourmaline from Martinamor (Stone of Vaugnerite, Pajarilla Stone) (Molina Ballesteros *et al.* 1997; López-Plaza *et al.* 2007a, b, 2009; Nespereira *et al.* 2010).

Tourists are often surprised by the excellent state of conservation of historic buildings of the city of Salamanca. Even so, the results of standardized petrophysical classification of Villamayor

stone to determine its quality and validity as Dimension stone indicate this stone would be rated as being of poor quality, and therefore its use should be discouraged for use in the facades of new buildings (Fig. 1a–e).

The growing urban sprawl of Salamanca city, as well as the creation of leisure and recreation areas, have created strong urban pressures around and within the municipality of Villamayor de la Armuña (Salamanca). These pressures have impeded the development of new quarries, as well as concealing or destroying older quarries, as is currently happening in the periphery of La Moral (Villamayor de la Armuña, Salamanca).

Furthermore, the location itself for new quarries is highly conditioned by the dynamics, dispersion, sediment accumulation, and trajectory of the river system that generated Villamayor sandstone (Alonso-Gavilán *et al.* 2006).

Villamayor Stone is an arkosic stone of Middle Eocene age and belongs to the Cabrerizos Sandstone Formation (Fig. 2a, b) that comprises braided fluvial systems and palaeosoils at the top of each stratigraphic sequence. The sandstone is known by several names: (i) It is known locally and in historical documents as Franca Stone; (ii) Villamayor

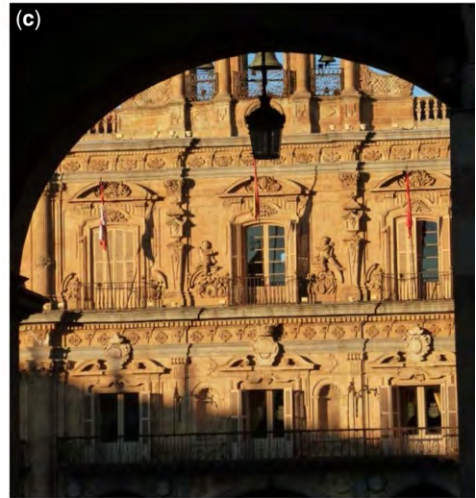


Fig. 1. (a) Golden Stone: New Cathedral (Gothic style). (b) West façade and atrium of Saint Esteban Church (15th century): (1) Villamayor Stone; (2) Leucogranite Tourmaline Martinamor; (3) Vaugnerite Stone; (4) Silicified Conglomerate (with CT opal). (c) Main Square built in Golden Stone (17th century). (d) Roman Bridge built with Granite. (e) Golden Stone: a detail of the façade of University of Salamanca (16th century).

Stone because the quarries are located in Villamayor de Armuña; (iii) the Golden Stone due to its patina that produces a ochreous/golden colour on the façades of monuments of Salamanca (World Heritage City, UNESCO 1988), which are built with this natural stone. In this paper, Villamayor Stone (Golden Stone) is presented as a candidate to be designated a Global Heritage Stone Resource.

In previous works Villamayor Stone has been characterized as it appears in the quarry (Vicente 1983; Vicente 1984; Vicente & Vicente-Hernández 1985; Vicente & Brufau 1986; Martín-Patino *et al.* 1993; Rives & Vicente 1993; Saavedra *et al.* 1993; Iñigo *et al.* 2003). The stones that have undergone important processes of decay on several representative buildings have also been analysed (Rives & Vicente 1993; Madruga *et al.* 1994; Vicente 1996). The high capacity for water absorption, together with its porous network and mineralogical composition, makes Villamayor Stone a stone that is easily workable and sculpted when wet. From this starting point, real sculptural wonders have been created in the city of Salamanca, a highlight being the façade of the old University (plateresque style) and the entrance to the New Cathedral.

Looking at the Villamayor Stone monuments, it can be deduced that on the façades exposed to the sun and the joint action of wind and rain (Rives & Vicente 1993; Vicente 1996), but without the constant humidity to produce their arenization, the patina is more intense. Two types of surface modification of the Villamayor Stone in these monumental microenvironments have been defined: (i) on vertical surfaces which have good drainage and are exposed to the sun, good conservation of the stone can be observed, and it acquires a beautiful golden patina and (ii) if the stone is located in zones of frequent humidity, water with or without salts (nitrates, chlorides, sulfates, phosphates, etc.), which is located in the lower parts of the monument, rises from the bases by capillary action. If the monument is located in an area with frequent moisture (e.g. leaking roofs in poor condition, gargoyles and spouts blocked by bird excrement), the stone crumbles and the patina effect is not produced. The patina is a symptom of the condition of the stone and contributes to its conservation (Vicente & Brufau 1986, Iñigo *et al.* 2003).

Villamayor Stone was used in the noble and upper parts of the walls of existing monuments and buildings because in areas influenced by the capillary rise of water (bases), alteration (decay) is more intense and fast due to the presence of smectites in its mineralogical composition, which produces the swelling and contraction of the same and a lack of mechanical resistance when the material is exposed to a high degree of permanent moisture. Therefore, in these areas the arenization process is very fast

and the natural patina does not develop. Today this process is being facilitated by the chloride salts that are used to prevent ice sheets developing on frosty days.

Furthermore, the façades of the monuments demonstrate a surprising uniformity in which it can be observed that the ashlar have different intrinsic characteristics, given the wide variety of types of Villamayor Stone. This fact suggests that the uniformity of the colour of the surfaces is due to chemical treatments (artificial patinas) used in order to achieve a chromatic homogeneity and to protect both the façades of new constructions (20th and 21st centuries) and in the restoration of monuments. These artificial patinas are a mixture of gypsum (a principal component) and clay soil rich in iron oxyhydroxides, feldspars and kaolinite (Sienna type) and some additives (glues, casein, etc) (Rives & Vicente 1993).

The Villamayor Stone (Fig. 1a–e) was quarried for the construction and ornamentation of Romanesque religious monuments such as the Old Cathedral and San Julian church, Gothic monuments (Spanish plateresque style) such as the New Cathedral and the Church of San Esteban, and the sculpted façade of the Salamanca University, one of the oldest Universities in Europe (it was established in 1250); and this stone was used in the galleries and arcades of the sumptuous Baroque Main Square of Salamanca (1729). Villamayor Stone was also used in the construction of palaces, walls and in the restoration of the Roman Bridge of Salamanca.

The quarry sites are family owned and thus neither the quarrying techniques nor the machinery employed have changed much over time. The transition to democracy in Spain, the adoption of different political models and several economic crises have generated large fluctuations in the labour and consumer markets, and these changes have affected the local market. For example, there was a sharp decline in production, which was caused by the economic crisis that began in 2008, and up to the present day there are still few signs of recovery.

Geological setting and quarries of Villamayor Stone

Geological setting

The study area is situated within the Iberian Peninsula (Fig. 2a), in the southwestern part of the autonomous community of Castilla y León in sheet 478 of the Spanish MTN at E/1:50,000, on the right bank of the River Tormes, and it occupies part of the periphery of the municipalities of Salamanca and Villamayor de la Armuña (Fig. 2a). The topography of this area is characterized by the absence of large

reliefs and escarpments, the minimum elevation being 768 m (roughly equivalent to the level of the River Tormes) and the maximum being 864 m (Pizarrales).

The Duero basin is the largest of all the Cenozoic basins of the Iberian Peninsula (Alonso-Gavilán *et al.* 2004) with an approximate extension of about 50 000 Km². It is a continental basin whose origins are to be found at the beginning of the Cretaceous period, gradually evolving throughout the Mesozoic and Cenozoic eras (Alonso-Gavilán *et al.* 2012). In general, sedimentation in the Duero basin was conditioned by three factors: tectonics, climate and the source zone. The interaction of these three factors and the dimensions of the sedimentary basin produced differing geodynamic and palaeogeographic features on the edges of the zone, and in consequence, the sedimentary process was different in each one of them. This allows three stratigraphic sequences to be distinguished and they are separated by discontinuities at basin-scale level (Alonso-Gavilán *et al.* 2004); the main area of study being focused on the second sequence, Eocene–Oligocene. More specifically, in the western and southwestern edges of the Duero basin, the horst and graben tectonics generated conjugate geological faults in SW–NE and SE–NW directions. This structure of high and sunken blocks, generally tilted towards the NW, interacted over time and conditioned the sedimentation at sub-basin level (Alonso-Gavilán *et al.* 2004). This process produced the location and geographical dispersion of Villamayor sandstone. In addition, the lithology of the source zone (granitoids and low-grade metamorphic rocks, greenschist facies from the Precambrian and Palaeozoic periods) determine the maturity and composition of the sediments deposited whether subarkose or arkose.

Further, the movement of the Iberian Peninsula from a latitude of roughly 30°N to 40°N during the Cretaceous, Palaeogene and Neogene periods are reflected in a change in climatic factors, as well as in the composition of the sediments. The river basin became isolated, passing from being close to the sea in the NE during the Palaeogene period to being endorheic and centripetal in the Neogene, and then open to the west to the Atlantic Ocean, at the end of the Cenozoic period, in an open basin.

The palaeoenvironmental characteristics which can be deduced from the fossils of turtles and crocodiles (Jiménez 1974) corroborate the idea that the changes were not only palaeogeographic but also palaeoclimatic, changing from a warm subtropical climate with distinct seasons (Cretaceous and Upper Palaeogene) to a continental Mediterranean climate (from the beginning of the Eocene onwards).

Villamayor Stone occupies a specific position in the general Mesozoic–Cenozoic column at the SW edge of the Duero basin (Fig. 2b–f). It forms a part of the Cabrerizos Sandstone Formation, constituting one of four lithofacies that are related laterally by changes of facies. Villamayor Sandstone is discordant on the (Upper Cretaceous) Salamanca Sandstone Formations (Fig. 2d) which make the basal deposits of the arkosic Villamayor Sandstone very porous and very frangible while the upper deposits are more silicate rich subarkoses, and metamorphic minerals are more abundant. Situated above them, and inconsistent with them, are red conglomerates of Miocene age, which give a reddish tinge to the deposits of Villamayor Stone (Fig. 2b).

Sedimentary environment

In this palaeodynamic and palaeogeographic context Villamayor Sandstone was generated by a braided river system. This river system was constituted by draining a granitoid and metamorphic source area located in the SW which flowed towards the NE. The spread of palaeocurrents indicates (Alonso-Gavilán *et al.* 2006) that the braided flow demonstrated considerable channel mobility, but there was a marked tendency for them to run in a northeasterly direction, toward where the river flowed into the sea. The sediment load, moved by saltation and traction, formed large sand deposits, overlapping megaripples, which sometimes constituted authentic sandy plains.

These active channels deposits (facies St, low angle (<10°) cross-stratified sand; and Sm, sand, medium to coarse; Miall 1977), are those which are currently exploited as Villamayor Premium Sandstone (Figs 2g, h), and having low clay content are good aquifers given the high porosity and permeability (and little or no cementation). In periods

Fig. 2. (a) Geological setting and quarries of Villamayor Stone. (b) General Stratigraphic Section of Salamanca area. (c) Detail of Leucogranite Tourmaline Martinamor (Piedra Pajarilla). (d) Silicified Conglomerate (Salamanca Fm.; Piedra Tosca) core. (e) Villamayor Stone blocks in the quarry. (f) Correlation between Natural Stone and its use in different parts of the architectural structure of the south façade of the New Cathedral of Salamanca. (g) The quarry sites of Villamayor Stone. (h) Location of Villamayor stone varieties used in this study (VAC, Villamayor carbonated; VF, Villamayor fine; VR, Villamayor network) and their correspondence to the sedimentary facies (St, low angle (<10°) cross-stratified sand; Sm, sand, medium to coarse; Fm, massive deposits silt or fine grained deposits; and P, pedogenic carbonate).

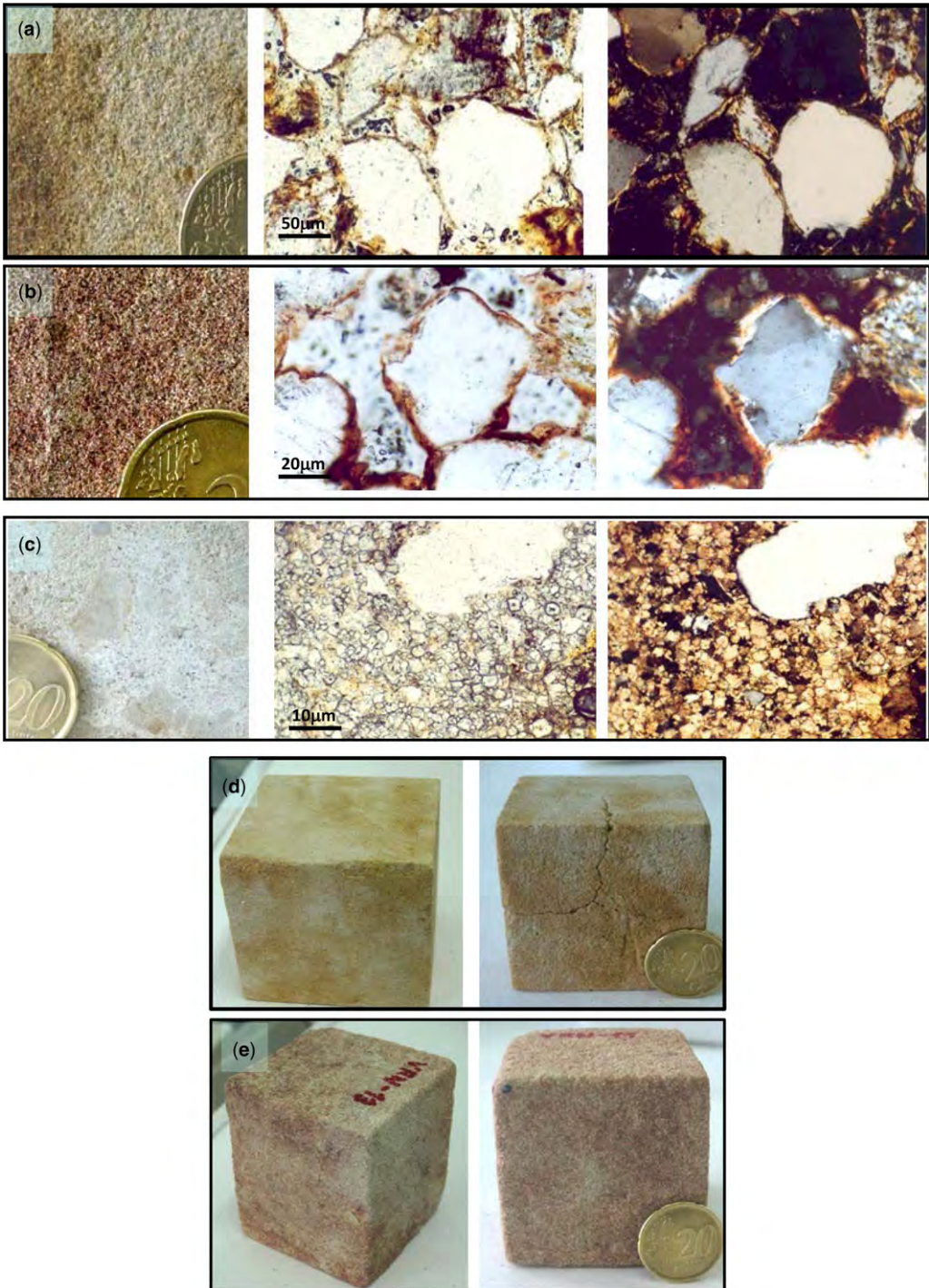


Fig. 3. Photomicrographs PPL and XPL of the varieties of Villamayor Stone. (a) Variety of Villamayor Stone (VF) contains 2:1 phyllosilicates and is fine-grained sandstone (objective: x4). (b) Variety of Villamayor Stone (VR) with oxihydroxides of iron, 2:1 phyllosilicates and is medium grained sandstone (objective: x10). (c) Variety of Villamayor Stone (VAC) with the presence of dolomite crystals as cement, or as nodules (objective: x20). (d) Natural

of flooding, the floodplains grow vertically or fill up neglected channels. In periods of drought, abandoned channels fill up, palaeosoils (Figs 2g, h) and carbonation processes are initiated (Fm, silt deposits massive or fine grained deposits; and P, pedogenic carbonate; Miall, 1977). The imperfections produced are known in the quarries by the generic name of codones.

Quarry Villamayor Sandstone. The Villamayor quarries are located in the village of Villamayor de la Armuña, a few kilometres from the city of Salamanca (Fig. 2a, b, e, g, h), and are considered the type locality of the Villamayor Stone lithofacies (Alonso-Gavilán *et al.* 2004). Localizing a Villamayor Stone extraction bank to be quarried was never an easy task, and in the beginning the choice was based on the quarryman's own experience. Digging would begin in the red conglomerate, which is the top layer of stratigraphic succession (Fig. 2g), and if underneath it traces of Villamayor Sandstone were found then digging would begin with the removal of overburden and the rubble was used to fill in cavities or former quarries. This activity is still practiced today.

The excavation would continue through the former floodplain deposits until it encountered a good quality seam of Villamayor Stone. The geometry of the former channels would determine the face to be exploited, and the thickness of the seam and the quality of the stone would determine the length of the working life of the quarry (Fig. 2g, h). The potential of the quarry face (base level of extraction) is now determined by the low elevation of the ridges, proximity to the River Tormes, and the porosity of Villamayor Stone, which can lead to flooding of the quarry. The quarry location is determined by the direction of the braided river system that was the origin of the Cabrerizos Sandstone Formation (Alonso-Gavilán *et al.* 2006).

Intrinsic properties of Villamayor Stone

Mineralogical and chemical characterization

Its mineralogical composition is determined by X-ray diffraction, polarized light optical microscope and scanning electron microscope. In this paper, three varieties of Villamayor Sandstone have been selected: carbonated variety (VAC); fine-grained variety (VF); red variety with iron oxides (VR). The varieties differ in grain size, presence of secondary minerals, the type of clays and network porosity (Fig. 3a–c). The VF consists of fine grain

size ($<100\ \mu\text{m}$), ocher tones, and is very compact with abundant clay matrix (Fig. 3a). The VR has fine–medium grain size ($>100\ \mu\text{m}$), reddish tones (Fig. 3b), no cement, low clay matrix and has iron oxides present. The VAC has very fine grain size ($<100\ \mu\text{m}$) with nodules of dolomite and clay concentrations (Fig. 3c), is white with brown patches, cemented by carbonate (crystals of dolomite) and abundant clay matrix.

The main components for all three varieties are quartz (up to 60%), feldspar, 2:1 layered silicates (smectites), palygorskite-type fibrous silicates, and small amounts of micaceous minerals (illite/mica) (Fig. 3a–c). Scanning electron microscopy reveals fibers of palygorskite lining pores and grains of quartz and feldspar (Fig. 4). The clay minerals, both inherited (illite/mica), as well as those formed by diagenetic processes (palygorskites, smectites), embedded skeletal grains (quartz and feldspar) in whole or in part which may give rise to a porous network (Fig. 3a–c and Fig. 4).

Chemical analysis of its major elements shows that the percentage of SiO_2 is high, followed by Al_2O_3 , K_2O , Fe_2O_3 , as well as H_2O . In the case of the reddish coloured samples, a greater quantity of iron can be observed, due to the presence of iron oxyhydroxides, which gives the material its superficial reddish-brown colour.

Physical characterization: hydric properties and Hg injection

Regarding the determination of hydric properties (Iñigo *et al.* 1994), the stone can be observed to be highly porous ($>30\%$) and capable of absorbing large quantities of water by capillarity (Table 1). It can be concluded from the values obtained by Hg injection (Table 2) that there are varieties of Villamayor Stone that are microporous (VAC and VF) and other varieties that are macroporous (VR).

Colour

The quarry stones come in a variety of colours ranging from white to ocher to red, and with exposure to the environment, the stone acquires a natural golden patina, as traces of iron and manganese rise to the surface of the blocks. This process is facilitated by cycles of wetting and drying, which cause these trace elements to come to the surface (Vicente 1983). It is this process that has led to Villamayor Stone being called Golden Stone.

Fig. 3. (Continued) and Aged variety of VF. (e) Natural and Aged variety of VR. After artificial ageing by freezing/thawing and thermal shock, arenization and fissuration are observed in the microporous variety (VF) and arenization in the macroporous variety (VR).

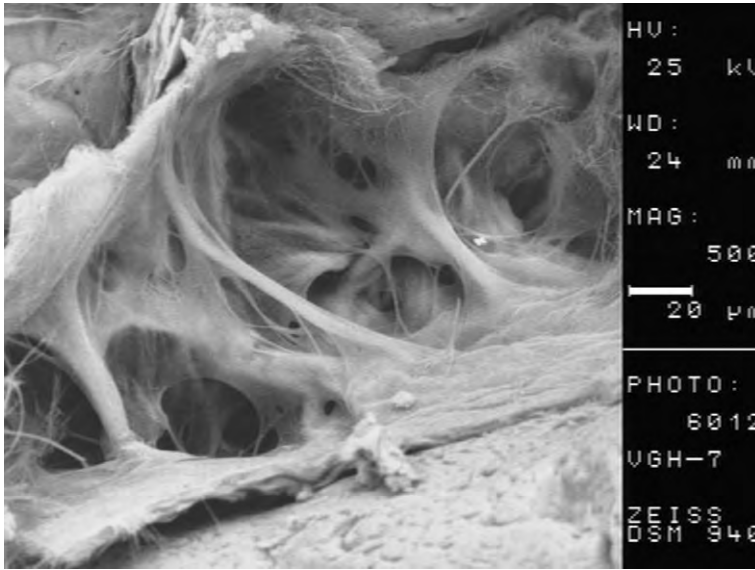


Fig. 4. SEM micrograph of the Villamayor Stone showing fibers of palygorskite lining pores and grains of quartz and feldspar. Note the network pore that originates: geometry, size and degree of connection network pore.

The chromaticity coordinates (L^* , a^* , b^*) of the colour system are presented in Fig. 5. They are used to determine colour numerically with a MINOLTA colourimeter (Chroma Metra) (García-Talegón *et al.* 1998). The L^* value refers to lightness (or darkness), while a^* and b^* are the chromaticity coordinates. The a^* coordinate range between positive values, identified with red, and negative values, identified with green. The negative values of the b^* coordinate are associated with blue and the positive ones with yellow. Changes in each of the chromatic coordinates for each of the tests correspond to the difference between the magnitude of a coordinate for the treated (or aged) sample and that of the original sample, thus obtaining parameters ΔL^* , Δa^* and Δb^* . The difference in total colour is given by the equation $\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. Stone blocks (5 cm \times 5 cm \times 5 cm) were cut and the values of the coordinates were averaged from measurements on these 5 faces.

Alterability of Villamayor Stone by artificial ageing and its conservation treatments

Alterability by artificial ageing (freezing/thawing and thermal shock) (Fig. 3d, e)

The city of Salamanca is located on the Castilian plateau at an elevation of 800 m with a semi-arid continental climate and low atmospheric pollution. The minimum and maximum annual temperatures are -17°C and 40°C , respectively, with 60 days having subzero temperatures and annual precipitation of 420 mm. Given this climate, Villamayor Stone is vulnerable to damage caused by frost weathering (cryoclastism, gelifraction). Its resistance to damage caused by frost depends upon the level of porosity and pore size distribution (network pore), which each variety possesses, and this is ultimately dependent upon the clay in which the grains

Table 1. Hydric properties of Villamayor stone: natural from the quarry

Hydric Properties	Total porosity (%)	Open porosity (%)	Real density (g/cm^3)	Apparent density (g/cm^3)	Capillary absorption coefficient ($\text{g}/\text{cm}^2\text{s}^{1/2}$) 10^{-3}
VAC	30	26	2.65	1.86	85
VF	32	25	2.66	1.80	76
VR	37	26	2.66	1.66	70

Table 2. Hg Injection properties of Villamayor stones: natural and aged

Variedad	Total Porosity %	Free Porosity %	Trapped porosity %	Macroporosity (>7.5 μm) %	Microporosity (<7.5 μm) %
VAC	15.43	7.87 (51)	7.56 (49)	1.31 (8)	14.12 (92)
VAC Aged	10.65	7.77 (73)	2.88 (27)	0.76 (7)	9.89 (93)
VF	25.68	10.60 (41)	15.08 (59)	3.57 (14)	22.11 (86)
VF Aged	20.11	4.18 (21)	15.93 (79)	1.34 (7)	18.77 (93)
VR	25.79	6.00 (23)	19.79 (77)	19.00 (74)	6.79 (26)
VR Aged	24.52	20.11 (80)	4.41 (20)	20.40 (83)	4.12 (17)

The numbers in parentheses are values based on 100% of the data and relate to the total value of mercury porosity.

are embedded, which serves to hold them together. Extreme changes in temperature cause differential expansion between mineral grains in building stones (sandstones). These expansions generate micro and macro discontinuities, allowing the circulation of fluids (water, dissolved salts, etc). When water freezes, it produces a volume increase, generating pores (about 9% of original volume). This expansion induces stress concentration and tensile damage in the pores. When the rock thaws, the water flows through the micropores causing new fractures. The intrinsic properties of the sandstones (porosity, pore size distribution and mineral content) have a great influence on deterioration. It is well known that pores in this diameter range (microporosity <7.5 μm) plays an important role in degradation processes such as haloclasty and gelifraction (Camuffo 1996; García-Talegón *et al.* 1999; Ruedrich & Siegesmund 2007; Iñigo *et al.* 2013).

The cube samples of Villamayor Stone (VAC, VF, VR) described above were aged through 25 cycles of freezing/thawing and thermal shock ($-20\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$) in a simulation chamber, following standard recommendations by Tiano & Pecchioni (1990). Hg injection properties and colour characterization before and after artificial ageing are shown in Table 2 and Figure 5, respectively.

Visually, the Villamayor Stone blocks, after the artificial aging caused by the cycles of freezing/thawing and thermal shock, demonstrate rounding of edges and vertices (Fig. 3d, e), as well as a superficial loss of grains, which produces a consequent deterioration of the smoothness of the stone. The types that are most affected have been the microporous varieties (VF, VAC), which also show signs of fissures that run through the whole block. The results of mercury porosimetry of non-aged and aged stone blocks measuring the degree of aging caused

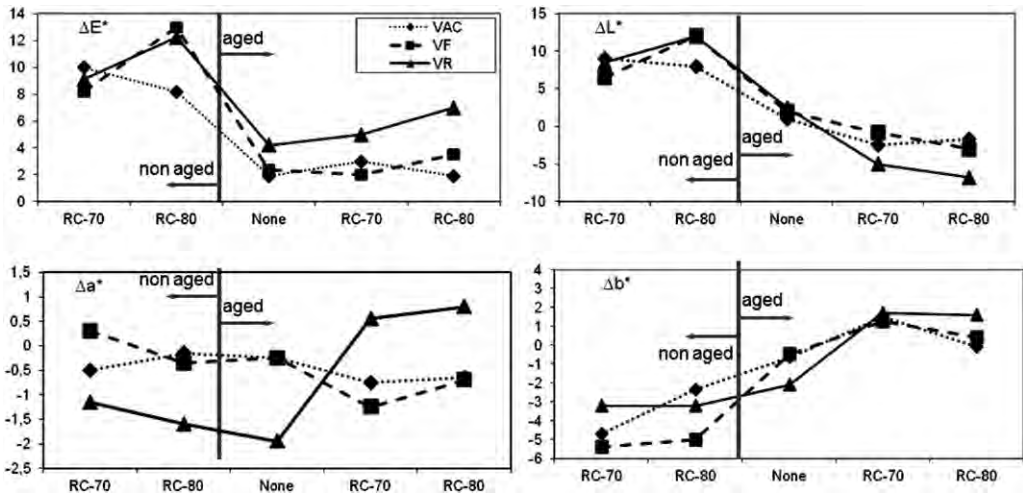


Fig. 5. Colour characterization (ΔE^* , ΔL^* , Δa^* , Δb^*) of the three varieties of Villamayor Stone (VAC, VF, VR): non-aged (natural stone from the quarry); Conservation Treatments: RC-70, RC-80; non-aged (before artificial aging); aged (after artificial aging by freezing/thawing and thermal shock).

Table 3. *Physical properties in water of Villamayor stones: natural and treated*

Sample	Apparent Density δ_{ap} , (g/cm ³)	Density δ , (%)	Total Porosity P_t , (%)	Open Porosity P_o , (%)	Water Absorption Coefficient W_{ac}
VAC	1.86	2.65	30	26	85
VAC-RC-70	1.97	2.46	20	4	22
VAC-RC-80	1.99	2.28	13	3	24
VF	1.80	2.66	32	25	76
VF-RC-70	1.94	2.50	22	4	17
VF-RC-80	1.92	2.30	17	3	18
VR	1.66	2.66	37	26	70
VR-RC-70	1.74	2.54	31	3	11
VR-RC-80	1.76	2.46	28	2	9

by freezing/thawing and thermal shock are shown in Table 2. Values based on 100% of the data relating to the total value of mercury porosity are presented in parentheses in the rest of the parameters.

Consolidation and water repellent treatments. The Conservation treatments Rhodorsil 70 (RC 70) and Rhodorsil 80 (RC80) were from Rhone-Poulenc and were supplied by Siliconas Hispania. RC 70 consolidant is a colourless organic silicate with a viscosity of 0.86 mPa/s, a density of 0.890 g/cm³ and a silicone content of 70%. The solvent is a white spirit. RC80 consolidant and waterproofer is colourless and a catalyzed organic silicate with a methyl resin in a solution of white spirit. Its viscosity is 1.13 mPa/s, it has a density of 0.905 g/cm³ and a silicone content of 68%. The application of the products was carried out slightly modified NORMAL to the recommendations (García-Talegón *et al.* 1998; Iñigo *et al.* 2006) by immersing the sample into the consolidant fluid (instead of capillary absorption) and using different concentrations (instead of a single one) in order to facilitate penetration of the product inside the stone sample. Treatment was carried out by immersing the samples in white spirit for 30 min, followed by immersion in white spirit solutions of the reagents at three levels of concentration: (i) eight hours with a 5% solution, (ii) twenty four hours with a 40% solution and (iii) forty hours with a 75% solution. The cube samples described above were age treated through 25 cycles of freezing/thawing and thermal shock (−20 to 100 °C) in a simulation chamber, following standard recommendations by Tiano & Pecchioni (1990). Hydric properties are shown in Table 3. The affect of the treatments was significant for the hydric properties determined for all varieties of Villamayor Stone: these treatments produced a decrease of all the values.

Stone blocks (5 cm³) were cut and the values of the coordinates were averaged from measurements on these 5 cm² faces. A complete three-way

experimental design was implemented: (i) type of sample; (ii) treatment; (iii) ageing. The analytical study was complemented with interaction studies, following the Analysis of Variance (ANOVA) study, and the corresponding contrasts were performed by incorporating a type-I error-correcting factor (Fig. 5). The effect of the consolidation and/or waterproofing treatments and of artificial ageing on the three varieties of Villamayor Stone shows that upon associating the variations in colour with ΔE^* , it is seen that artificial ageing alters the colour of all the natural and treated samples. However, the treatments without ageing do not modify the colour. Luminosity (ΔL^*) shows significant alterations in all samples. Chromaticity, measured with the Δa^* coordinate, is modified by ageing with colour progressively evolving towards red, except in VR, which is already reddish. Chromaticity (Δb^*) is modified by ageing in all varieties and for all treatments.

Conclusions

Villamayor Stone (or Golden Stone) lends a special aspect to the artistic and historic monuments of Salamanca, which cannot be compared to any other city in the world thanks to the golden patina which is acquired naturally with the passage of time.

On the one hand, its physical properties make it an unsuitable material for use in the foundations of historic buildings because of important phenomena related to the capillary rising of water. Its strong porosity makes it an inappropriate dimension stone in certain contexts. However, in sunny zones in which it can quickly dry, this problem is not as bad as might be expected. Arenization and roughening takes place in zones where humidity is permanent (micro-environments where buildings are in the shade, or facing north, the lower parts of walls, etc) and where the environment contains high levels of water with

dissolved salts (chlorates, sulphates, nitrates, phosphates) as, for example in the case of the basements of buildings where there is a high level of absorption of ground water that contains high saline levels.

On the other hand, the hydric and Hg injection properties and mineralogical composition of this stone render it easy to work when damp, as it offers little resistance to being sculpted, as can be observed in the case of the façade of the University of Salamanca.

The chromatic homogenization of Villamayor Stone is due to its natural golden patina and also due to artificial treatments employed for its protection and conservation, which reduce the natural diversity of this beautiful stone.

Villamayor Stone (Golden Stone) is presented as a candidate to be designated a Global Heritage Stone Resource, which can facilitate the preservation of historical quarries for use in the restoration of monuments in Salamanca. This name is recorded in an international designation of geological and heritage significance.

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