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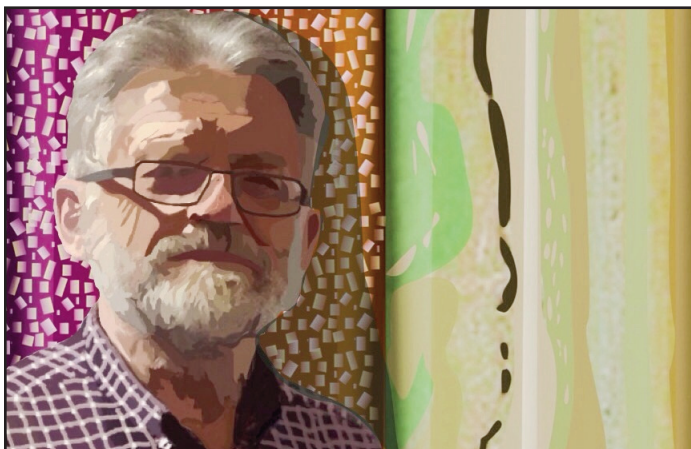
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Résumé de l'article

Des granites silicifiés ont été utilisés pour construire les monuments romans dans la ville d'Ávila, en Espagne. Les pierres de construction comprennent deux types de granite selon leurs propriétés techniques et leur couleur : Bleeding Stone (Piedra sangrante) et Ochre Granite (Caleño). Ils ont été utilisés comme pierre de revêtement de monuments romans du 12<sup>ème</sup> siècle de la ville (par exemple la cathédrale et de l'église de San Pedro), et pour les célèbres remparts de la ville qui constituent le meilleur exemple de l'architecture espagnole romane militaire. Durant les périodes gothique et Renaissance des 13<sup>e</sup> et 15<sup>e</sup> siècles, les granites silicifiés ont été utilisés principalement pour construire des croisés d'ogives, des vousoirs d'arcs et des éléments de fenêtres des monuments d'Ávila. Les granites silicifiés se trouvent dans la partie intermédiaire et supérieure d'une zone complexe de paléo-altération ou de manteau développée sur le socle ibérique hercynien qui supporte une grande partie de la péninsule ibérique occidentale. La silicification s'est produite dans des conditions tropicales au Mésozoïque. Le matériau mantélique altéré a été tronqué par des mouvements tectoniques alpins au cours du Tertiaire, et ses restes ont été recouverts en discordance par des sédiments plus récents dans la partie ouest et sud du bassin de Duero, et le long de la bordure nord de la vallée en graben d'Amblés. L'ancienne carrière, maintenant protégée, est située dans un village appelé La Colilla, à environ 5 km de la ville d'Ávila. Actuellement, cette pierre est exploitée uniquement pour les travaux de restauration effectués dans la ville, par exemple les murs d'Ávila, et l'église de San Pedro. La ressource est limitée et en voie d'épuisement, de sorte que la pierre sera rare dans un proche avenir. Par conséquent, ces granites silicifiés devraient être reconnus en tant que pierre du Patrimoine mondial des ressources en pierre. Les propriétés techniques spécifiques de ces pierres et leur valeur historique, leurs modes de désintégration, leur durabilité et leur pertinence pour la conservation patrimoniale justifient leur désignation en tant que roche du Patrimoine mondial des ressources en pierre.

# SERIES



## Heritage Stone 5. Silicified Granites (Bleeding Stone and Ochre Granite) as Global Heritage Stone Resources from Ávila, Central Spain\*

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### SUMMARY

Silicified granites were used to build the Romanesque monuments in the city of Ávila, Spain. The building stones comprise two types of granite based on their technical properties and

colour: *Bleeding Stone* (Piedra Sangrante) and *Ochre Granite* (Caleño). They were used as a facing stone in the city's Romanesque monuments of the 12<sup>th</sup> century (e.g. the cathedral and church of San Pedro), and the famous city walls that constitute the best example of military Romanesque Spanish architecture. During the Gothic and Renaissance periods of the 13<sup>th</sup> and 15<sup>th</sup> centuries, silicified granites were used mainly to build ribbed vaults, the voissiors of the arches, and elements of the windows in the monuments of Ávila.

Silicified granites are found in the intermediate and upper part of a complex palaeoweathering zone or mantle developed on the Iberian Hercynian Basement which underlies much of the western Iberian Peninsula. The silicification occurred during tropical conditions in the Mesozoic. The weathered mantle was truncated by Alpine tectonic movements during the Tertiary, and its remnants were unconformably overlain by more recent sediments in the western and southern part of the Duero Basin and along the northern edge of the Amblés Valley graben. The historical, and now protected, quarry is located in a village called La Colilla, about 5 km from the city of Ávila. Currently, this stone is exploited only for restoration work performed in the city, for example the Walls of Ávila, and the church of San Pedro. The resource is limited and being depleted, so the stone will be scarce in the near future. Consequently, these silicified granites should be recognized as a Global Heritage Stone Resource.

The specific technical properties of these stones and their historic use, decay patterns, durability, and suitability for conservation treatments combine to support its designation as a Global Heritage Stone Resource.

### RÉSUMÉ

Des granites silicifiés ont été utilisés pour construire les monuments romans dans la ville d'Ávila, en Espagne. Les pierres de construction comprennent deux types de granite selon leurs propriétés techniques et leur couleur : *Bleeding Stone* (Piedra sangrante) et *Ochre Granite* (Caleño). Ils ont été utilisés comme pierre de revêtement de monuments romans du 12<sup>ème</sup> siècle de la ville (par exemple la cathédrale et de l'église de San Pedro), et pour les célèbres remparts de la ville qui constituent le meilleur exemple de l'architecture espagnole romane militaire. Durant les périodes gothique et Renaissance des 13<sup>e</sup> et 15<sup>e</sup> siècles, les granites silicifiés ont été utilisés principalement

\*This article is part of a set of papers dedicated to the memory of Anders Wikström published in Geoscience Canada Special Issue: Heritage Stone; a new series that is guest edited by Dolores Pereira and Brian R. Pratt.

pour construire des croisés d'ogives, des vousoirs d'arcs et des éléments de fenêtres des monuments d'Ávila.

Les granites silicifiés se trouvent dans la partie intermédiaire et supérieure d'une zone complexe de paléo-altération ou de manteau développée sur le socle ibérique hercynien qui supporte une grande partie de la péninsule ibérique occidentale. La silicification s'est produite dans des conditions tropicales au Mésozoïque. Le matériau mantélique altéré a été tronqué par des mouvements tectoniques alpins au cours du Tertiaire, et ses restes ont été recouverts en discordance par des sédiments plus récents dans la partie ouest et sud du bassin de Duero, et le long de la bordure nord de la vallée en graben d'Amblés. L'ancienne carrière, maintenant protégée, est située dans un village appelé La Colilla, à environ 5 km de la ville d'Ávila. Actuellement, cette pierre est exploitée uniquement pour les travaux de restauration effectués dans la ville, par exemple les murs d'Ávila, et l'église de San Pedro. La ressource est limitée et en voie d'épuisement, de sorte que la pierre sera rare dans un proche avenir. Par conséquent, ces granites silicifiés devraient être reconnus en tant que pierre du Patrimoine mondial des ressources en pierre.

Les propriétés techniques spécifiques de ces pierres et leur valeur historique, leurs modes de désintégration, leur durabilité et leur pertinence pour la conservation patrimoniale justifient leur désignation en tant que roche du Patrimoine mondial des ressources en pierre.

*Traduit par le Traducteur*

## INTRODUCTION

The Global Heritage Stone Resource program aims to emphasize the need for international agreements for the care of those natural stones and quarries that are recognized for their importance in architecture and historical heritage (Pereira et al. 2015). Ávila, located northwest of Madrid, is famous for its medieval city walls and historical stone buildings, and was designated a UNESCO World Heritage Site in 1985. Two types of silicified granite, *Bleeding Stone* and *Ochre Granite*, so-called because of their technical properties and colour, crop out in nearby hills where the quarries were developed. These granites were widely used to build the main Romanesque monuments during the 12<sup>th</sup> century, including the apse of Ávila Cathedral (Fig. 1a), and churches such as San Pedro (Fig. 1b) that were built into the interior and exterior of the Walls of Ávila. During the Gothic period in the 15<sup>th</sup> century they were used mainly to build ribbed vaults such as in El Real Monasterio de Santo Tomás (Fig. 1c) and Ávila Cathedral (Fig. 1d, e), and in the vousoirs (wedge-shaped stones that allow curvature in arches or vaults) of the arches and elements of the windows. The historical quarry, which is now a protected site, is located in a village called La Colilla, about 5 km from the city (Fig. 2a, b). Currently, this stone is exploited only for restoration work performed in the city, such as for the medieval walls (Fig. 1f–h) and for a few new buildings (Fig. 1i). Resources are limited and the stone will be depleted in the near future.

The aim of this work is to focus on the *silicified granite's* resources, technical properties, historic use, decay patterns (pathologies), durability, and suitability for conservation treatments. In view of these aspects, we urge its designation as a Global Heritage Stone Resource.

## GEOLOGICAL SETTING OF BLEEDING STONE AND OCHRE GRANITE

Most of the western half of the Iberian Peninsula is underlain by the Iberian Hercynian Massif (IHM) in which granite outcrops are widespread (Fig. 2a). During the Mesozoic, the IHM underwent long periods of tropical weathering, giving rise to the development of an alteration mantle tens of metres in depth, accompanied by ca. 15–30% volume reduction. The following sequence of processes is evident at the top of these palaeoweathering zones (García-Talegón et al. 1994a; Molina-Ballesteros et al. 1997): 1) generation of clays by alteration of the parent minerals; 2) redistribution and concentration of oxyhydroxides released during alteration; 3) precipitation of silica as opal-CT (a variety of opal consisting of packed microscopic spheres made up of tiny microcrystalline blades of cristobalite and tridymite, and water content as high as 10 wt%) cementing the products of the weathered rock; and 4) generation of alunite–jarosite group minerals. These processes took place before the Alpine tectonism that affected the IHM during the Tertiary.

Three levels can be defined in the weathering profiles (Fig. 2a–f): 1) lower level (biotite granodiorite/porphyry and aplite dykes); 2) intermediate level (Ochre Granite; Caleño); and 3) upper level (Bleeding Stone; Sangrante). The lower level, Ávila Grey Granite, has been much used as a source of dimension stone from Roman ages until the present time, except for the Romanesque religious architecture. The porphyry and aplite dykes were mainly used to build the Walls of Ávila. The weathering that gave rise to Ochre Granite, (known as Caleño or Alterites), at the intermediate level produced petrophysical and mineralogical changes (in 2:1 and 1:1 layered phyllosilicates) and a decrease in the content of the most mobile cations. The Ochre Granite is several metres thick, and the parent minerals have released various elements (Ca, Na, Fe, K, etc.) during alteration to clay minerals (Fig. 2f). The upper level has received several names besides Bleeding Stone: Red Granite, White Granite, and Silcrete or Alterites. It was formed through a silicification process by precipitation of opal-CT, kaolinization, and remobilization of iron oxyhydroxides. The upper level is characterized by its hardness (a result of opal cementation), drastic changes in hues because of the mobilization of iron oxyhydroxides, and indistinct bioturbation at the top caused by pedological activity on the palaeosurface prior to cementation by opal-CT. It appears today as an undulating surface that is locally buried by younger sediments.

The generation of opal-CT, dissolution of clays (e.g. kaolinite) and precipitation of minerals of the alunite–jarosite group, all point to acidic conditions at the end of this evolution. Evidence for this is present both in the weathered Hercynian basement and the siderolithic sedimentary cover, whose outcrops are adjacent to many of the studied profiles and quarries (e.g. profiles I, II; Fig. 2e, f).

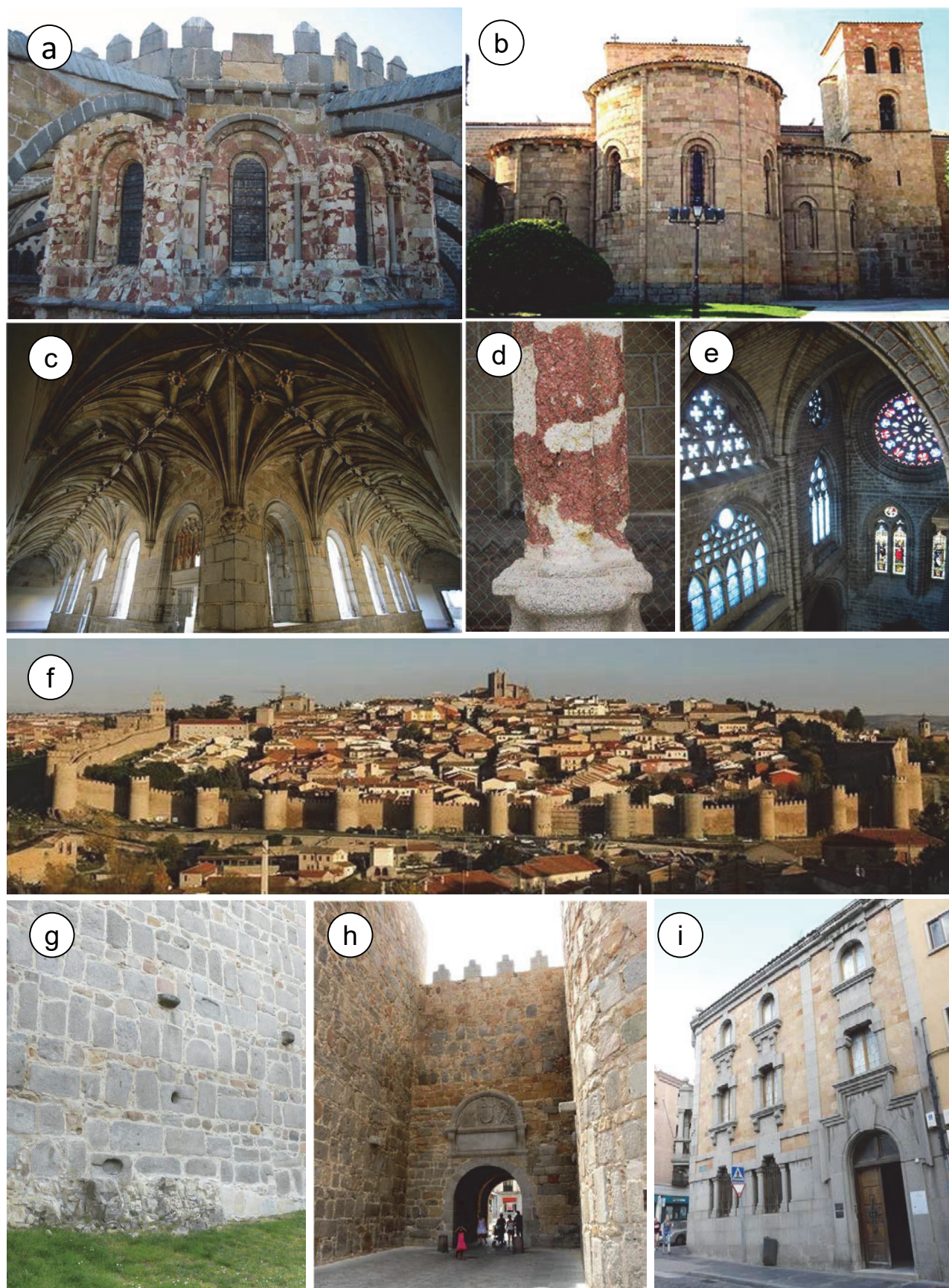
## CONSERVATION OF BLEEDING STONE AND OCHRE GRANITE

### Intrinsic Properties

#### *Mineralogical and Chemical Characterization*

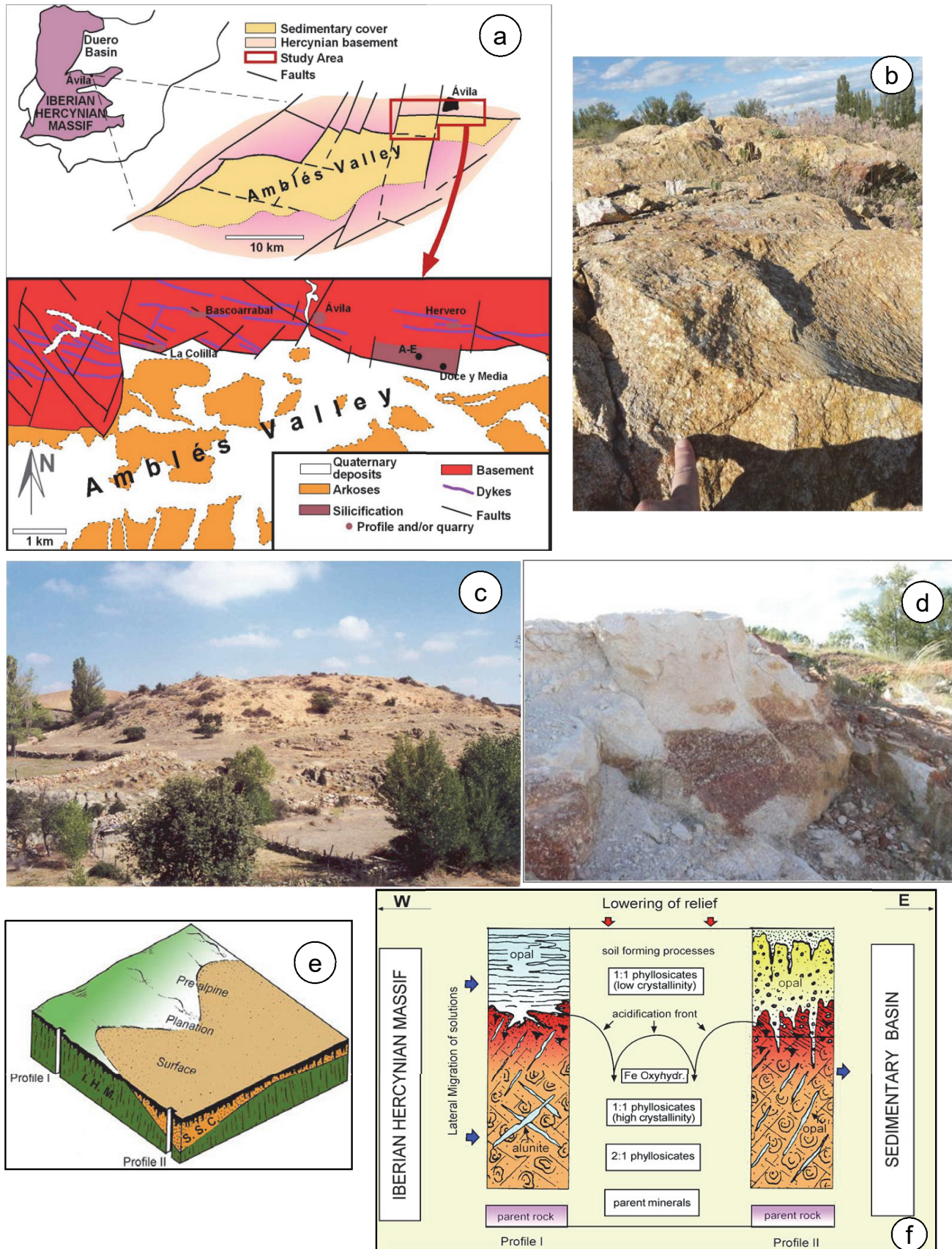
Three varieties of silicified granite were analyzed: Ochre Granite and two types of Bleeding Stone, namely Red Granite and





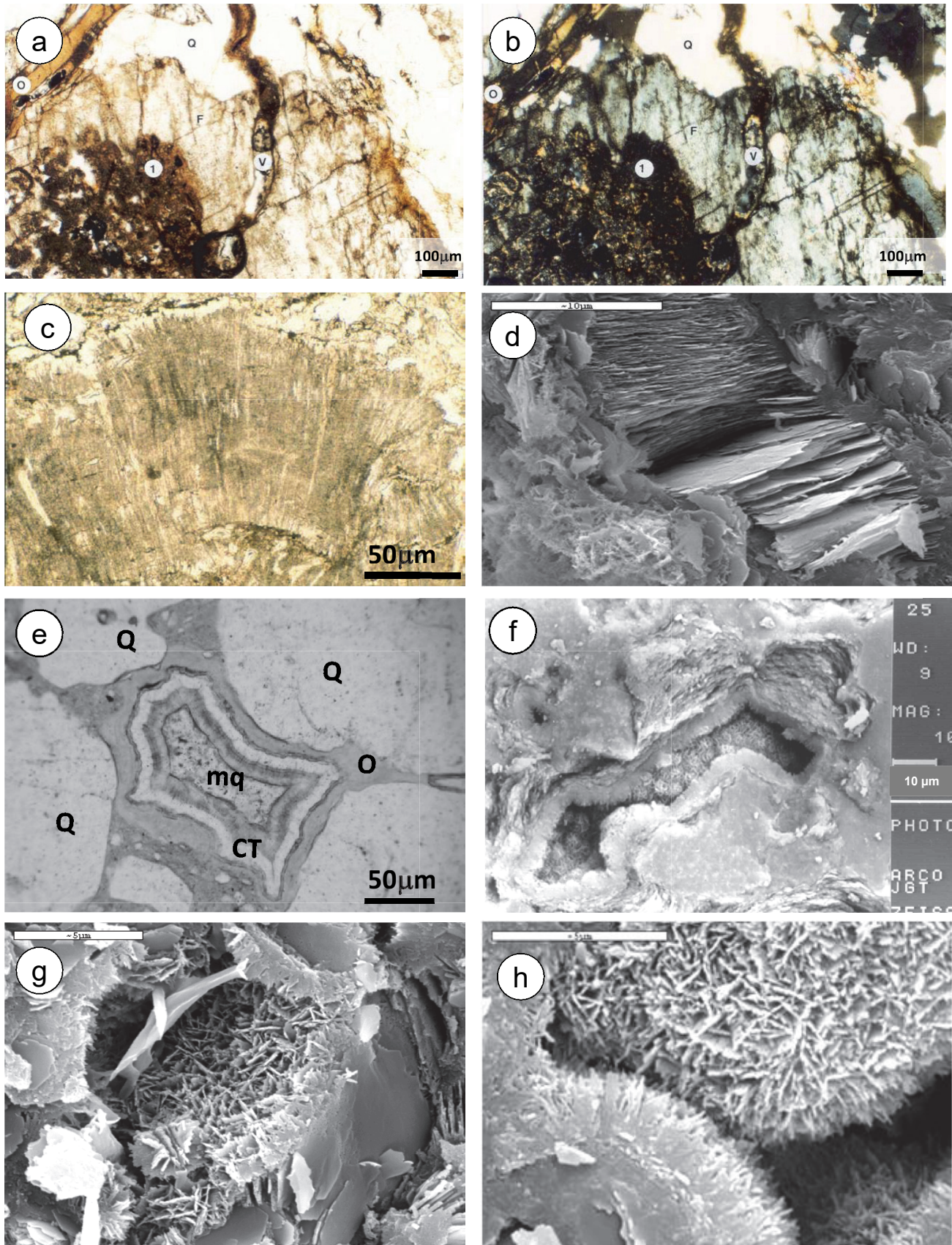
**Figure 1.** Bleeding Stone and Ochre Granite used in monuments in Ávila. a) Apse of the Ávila Cathedral (Romanesque, 12<sup>th</sup> century); the fortress-like cathedral was built into the Walls of Ávila; b) apse of the church of San Pedro (Romanesque, 12<sup>th</sup> century) in the exterior of the medieval walls; c) El Real Monasterio de Santo Tomás (Gothic, 15<sup>th</sup> century); d) column of the cloister; e) roof of the central nave, Ávila Cathedral; f) panorama of Ávila; g) Roman elements reused for the Walls, including cists that once held cremated remains; h) restorations of the Walls of Ávila; i) new buildings.





**Figure 2.** Geology and historical quarries of Bleeding Stone and Ochre Granite. a) Location and geological framework of the study area; b) middle level (Ochre Granite) of the main historical quarry, La Colilla; c) outcrop in the vicinity of La Colilla quarry; d) upper level (Bleeding Stone) of La Colilla quarry; e) 3D diagram showing the pre-Alpine planation surface on the Iberian Hercynian Massif (IHM), the overlying Tertiary siderolithic sedimentary cover (SSC), and location of profiles I and II; f) schematic representation of the main weathering processes that affected the Iberian Hercynian Massif.





**Figure 3.** Mineralogical characterization of the Bleeding Stone and Ochre Granite. a) and b) Thin section photomicrographs (plane- and cross-polarized light, respectively) of a level in the middle of the palaeoweathered zone, Ochre Granite. Feldspar (F) is weathered and cracks are filled mainly by opal-CT (O) and clays (1); V= residual void space; Q = quartz; c) thin section photomicrograph of kaolinite; d) SEM photomicrograph of kaolinite; e) thin section photomicrograph of opal-CT (O) lining a cavity; CT= opal-CT lepispheres; mq = chalcedony microcrystalline quartz; Q = quartz; f) SEM photomicrograph of opal-CT lepispheres (spherical rosettes of authigenic silica formed during low-temperature diagenesis) lining a cavity; g) SEM photomicrograph of opal-CT and 1:1 phyllosilicates; h) SEM photomicrograph of opal-CT lepispheres.



White Granite. Transformation to Ochre Granite involved alteration of the most labile (unstable) mineral species of the basement granite, the disappearance of chlorite, biotite and feldspar (Fig. 3a, b), and the appearance of 2/1 layer silicates (interstratified illite/smectite) and iron oxyhydroxides (goethite). However, the texture of the fresh granite is conserved. The formation of Red Granite and White Granite involved kaolinization (Fig. 3c, d), the formation of opal-CT (Fig. 3e–h), and later the redistribution, under hydromorphic conditions, of iron oxides that were then concentrated in Red Granite. (Hydromorphy is a permanent or temporary state of soil water saturation associated with reducing conditions). The percentage of SiO<sub>2</sub> is high, followed by Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, the content of Al<sub>2</sub>O<sub>3</sub> does not vary appreciably among the varieties of quarry granites. Similarly, there are few significant changes in Fe<sub>2</sub>O<sub>3</sub> except for its scarcity in White Granite, which in the quarry has undergone hydromorphic leaching of iron that was then concentrated in the Red Granite (García-Talegón et al. 1994b). Hence, in both the Ochre and Red granites, the greater quantity of iron is due to the presence of iron oxyhydroxides. Alkalis and alkaline earth elements decrease in abundance dramatically as the Grey Granite passes into the weathered versions in the quarry (Table 1). The trace element composition of Ochre Granite and Bleeding Stone (Table 1) differs among the silicified granite varieties, and is also specific to the location of the historical quarries (García-Talegón et al. 1999a).

### Physical and Mechanical Properties

The physical characteristics (measured in water) of three varieties of Bleeding Stone and Ochre Granite (Table 2) show that the permeability to steam, total porosity in water, and the coefficient of imbibitions (the absorption of water by porous rock, while totally immersed, under the force of capillary attraction and without pressure) are lower in the Bleeding Stone and higher in the Ochre Granite; furthermore, the Red Granite has lower values than the White Granite because of the infilling of pores in the former by iron oxyhydroxides. The porosity of all three varieties of granite is quite high, leading to sharp differences in real and apparent densities; this is most pronounced in the Ochre Granite. With respect to free porosity and capillary absorption coefficient, the Ochre Granite has the highest values, whereas Red Granite has intermediate values and White Granite the lowest values.

Mercury porosimetry measurements for Bleeding Stone and Ochre Granite (Table 3) show that the Ochre Granite has the highest porosity, followed by the red and white varieties; White Granite is least porous because it has undergone silicification that filled some of the pores. In the Ochre Granite, 58.77% of the porosity is free and the rest trapped, whereas in the red variety the percentages of free and trapped porosity are similar, and in the White Granite the free porosity is clearly predominant because the pores have not been filled by iron oxyhydroxides. Specific surface area (a property of solids defined by the total surface area of material per unit of mass, derived by Hg injection) is also much higher in the Ochre Granite.

Pore network characteristics of the three varieties of granite were also determined with the mercury porosimeter (Fig. 4a–c). The Ochre Granite has pores with a radius between 3  $\times$

**Table 1.** Major element (wt%) and trace element (ppm) composition of the Grey Granite (G), Ochre Granite (O), Red Granite (R) and White Granite (W).

	G	O	R	W
SiO <sub>2</sub>	66.6	69.6	73.2	73.6
Al <sub>2</sub> O <sub>3</sub>	16.1	14.1	13.8	15.2
Fe <sub>2</sub> O <sub>3</sub>	3.7	5.7	3.1	0.9
CaO	3.4	0.1	0.1	0.1
MgO	1.2	0.1	0.1	0.1
Na <sub>2</sub> O	3.1	0.1	0.2	0.1
K <sub>2</sub> O	3.7	0.1	0.2	0.2
SO <sub>3</sub>	0.1	0.1	0.1	0.1
TiO <sub>2</sub>	0.5	0.4	0.4	0.5
MnO	0.1	0.0	0.0	0.1
P <sub>2</sub> O <sub>5</sub>	0.3	0.2	0.2	0.1
S	120	333	297	411
Zr	130	78	122	110
Cr	180	363	252	336
Sr	10	195	199	280
Zn	60	48	35	25
Ba	320	91	79	67
Nb	60	14	34	20

**Table 2.** Physical properties (measured in water) of Ochre Granite (O), Red Granite (R) and White Granite (W).

	O	R	W
Kv	0.476	0.256	0.356
CI	12.78	7.92	8.25
n <sub>t</sub>	28.40	20.13	21.04
DR	2.47	2.48	2.37
DA	1.77	1.98	1.87
n <sub>o</sub>	74.31	66.70	60.48
CA	1.40	0.80	0.70

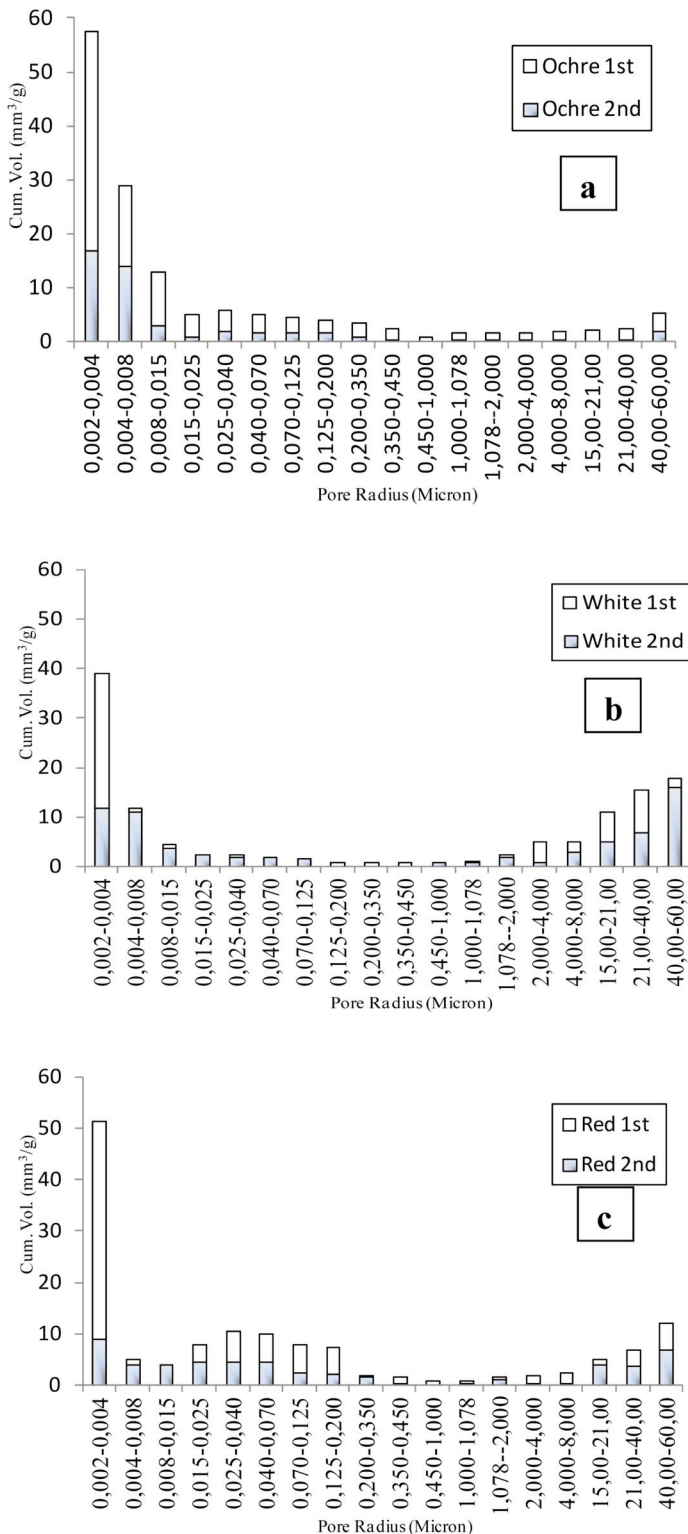
Kv = permeability  $\times 10^{-7}$  (kg/m<sup>2</sup>s), CI = coefficient of imbibition by total immersion (%), n<sub>t</sub> = total porosity (%), DR = real density (g/cm<sup>3</sup>), DA = apparent density (g/cm<sup>3</sup>), n<sub>o</sub> = percentage of water absorbed present in free form (%), CA = capillary absorption coefficient (g/cm<sup>2</sup>/sec  $\times 10^3$ ).

**Table 3.** Physical properties (measured in mercury) of Ochre Granite (O), Red Granite (R) and White Granite (W).

	O	R	W
n <sub>t</sub>	19.55	17.45	13.18
n <sub>o</sub>	11.49	9.94	9.18
n <sub>a</sub>	8.06	7.51	4.00
S <sub>c</sub>	18.09	8.04	7.51

n<sub>t</sub> = total porosity (%), n<sub>o</sub> = free porosity (%), n<sub>a</sub> = trapped porosity (%), S<sub>c</sub> = specific surface area by injection (m<sup>2</sup>/g).

$10^{-3}$   $\mu$ m and  $9 \times 10^{-3}$   $\mu$ m, and essentially no pores with a radius greater than  $5 \times 10^{-1}$   $\mu$ m. In the White Granite, free porosity predominates, and there are two ranges of pore radius: 3–8  $\times 10^{-3}$   $\mu$ m and 8–40  $\mu$ m. In the Red Granite, there are three pore size ranges: 5–40  $\mu$ m, 1–20  $\times 10^{-2}$   $\mu$ m and 3–5  $\times 10^{-3}$   $\mu$ m. There is a striking similarity between the white and red varieties of the rock in terms of pore radii greater than 5  $\mu$ m; however, the



**Figure 4.** Pore characteristics determined by mercury porosimetry: a) Ochre Granite, first and second injection; b) White Granite, first and second injection; c) Red Granite, first and second injection.

Red Granite possesses greater trapped porosity in the medium ( $1-20 \times 10^3 \mu\text{m}$ ) and small ( $<5 \times 10^3 \mu\text{m}$ ) pore size ranges.

The Ochre Granite has a high but intricate porosity of a type referred to as ‘bottle-neck’ (referring to pore throat diameter, and the ease or difficulty of water flow), and has a high trapped porosity (Table 3). The Red and White granites pos-

**Table 4.** Mechanical properties of three varieties of granite employed in the Ávila Cathedral. O = Ochre Granite; R = Red Granite; W = White Granite.

	O	R	W
$V_X$	2585	3156	2985
$V_Y$	2633	3180	3412
$V_Z$	2497	3344	3350
T	281	485	428
$f_{ii}$	59	48	36
$T_{teórica}$	461	688	689

$V_X$ ,  $V_Y$  and  $V_Z$  = Velocity of ultrasound propagation (m/s); T = Resistance to compression ( $\text{kg}/\text{cm}^2$ );  $f_{ii}$  = Resistance to indirect traction ( $\text{kg}/\text{cm}^2$ );  $T_{teórica}$  = Theoretical resistance to compression deduced from the velocity of ultrasound propagation ( $\text{kg}/\text{cm}^2$ ).

sess a low percentage of macroporosity and, especially in the White Granite, the porosity shows more connection to the surface at atmospheric pressure (i.e. there is greater open porosity). Mechanical properties (Table 4) indicate that resistance to compression and to indirect traction is higher in the two Bleeding Stone granites than in the Ochre Granite. The variation in the velocity of ultrasound propagation is high in all three, but highest in the White Granite. It will be noted that the values for resistance to compression are always less than the theoretical values obtained directly from the velocity of ultrasound propagation.

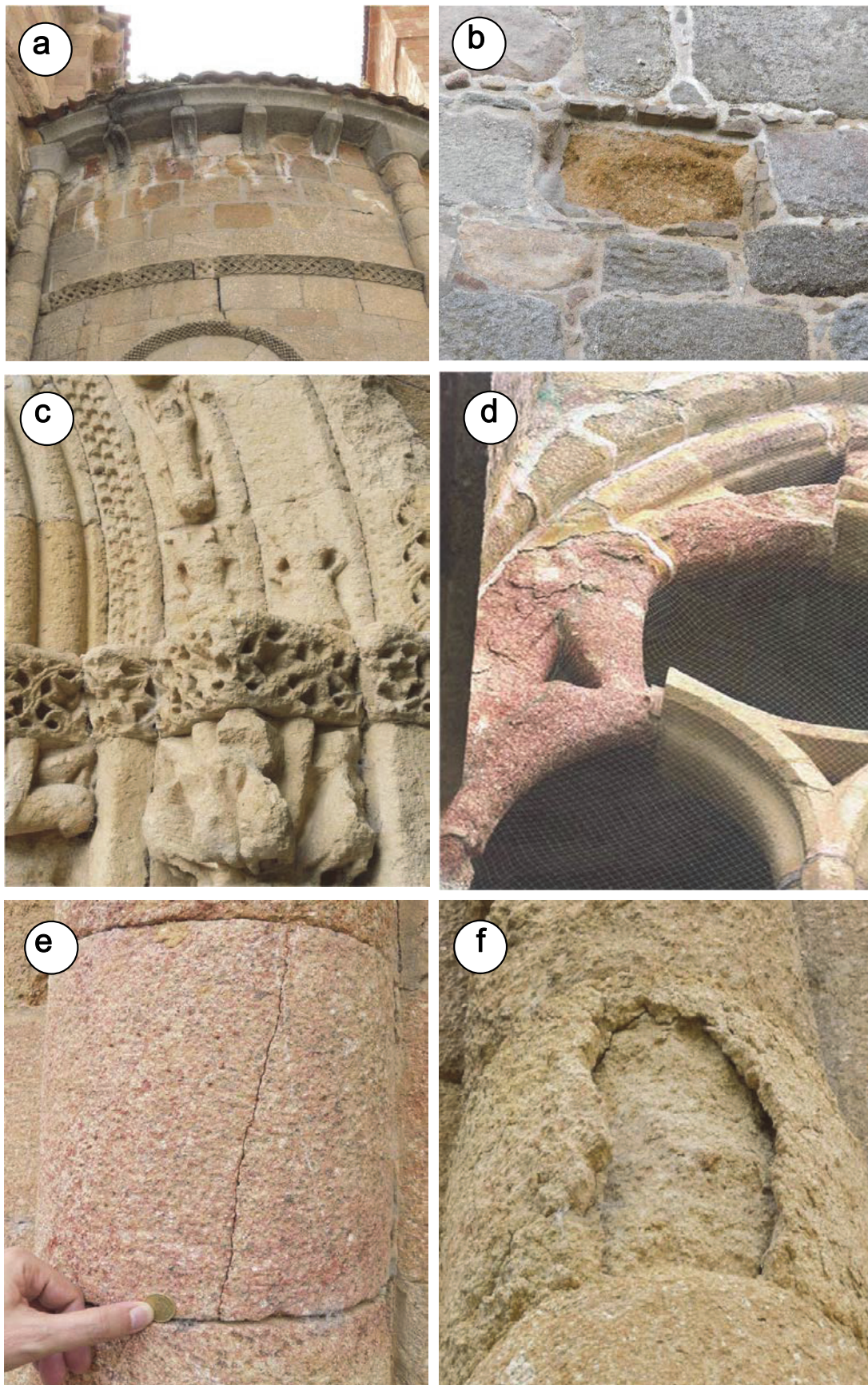
**Decay Patterns of Bleeding Stone and Ochre Granite**

Building stones suffer decay processes, depending on intrinsic factors such as the composition of the material itself, and extrinsic factors like environmental conditions (climate and pollution), where the monument is located, and even the ‘microclimate’ produced by the specific architectural elements where it is employed (Rives and García-Talegón 2006; García-Talegón et al. 2015). The pathologies observed most often in the monuments of Ávila are plaques, scales and granular disintegration (Fig. 5a–f). Efflorescence of soluble salts is present locally, in places affected by damp, both from creeping and from filtrations from roofs and terraces (Fig. 5a). The most labile mineralogical component in the Bleeding Stone (Red and White granites) and Ochre Granite is opal-CT, followed by phyllosilicates (smectite and kaolinite) and iron oxyhydroxides, which show strong surface reactivity and susceptibility to change due to the conditions of the medium (pH, redox potential, etc.) and the pore network of the silicified granites (García-Talegón et al. 1999b). The decay of the outer and upper parts of monuments is the result of physical weathering caused by thermal processes (thermoclasty) and freezing and thawing (gelifraction). These processes lead to fissuring and granular disintegration, giving rise to the erosion of exposed areas (Fig. 5a–f).

**Alteration by Freezing/Thawing and Thermal Shock**

The city of Ávila is located on the Castilian plateau at an elevation of 1100–1200 m, with a semi-arid continental climate and low atmospheric pollution. The minimum and maximum annual temperatures are  $-20^\circ\text{C}$  and  $39^\circ\text{C}$ , respectively; on average, there are 60 days of subzero temperatures and annual pre-





**Figure 5.** Pathologies of Bleeding Stone and Ochre Granite. a) Salt efflorescence in the upper part of the apse of the church of San Pedro (12<sup>th</sup> century); b) material loss of Ochre Granite in the Walls of Ávila; c) material loss of the main door of the church of San Mateo (12<sup>th</sup> century); d) scaling of Bleeding Stone in the cloister of Ávila Cathedral; e) crack in Red Granite; f) scaling of Ochre Granite.



precipitation of ~400 mm (Trujillano et al. 1995). Given this climate, the silicified granites are vulnerable to damage caused by frost weathering (gelifraction). Resistance to this kind of damage depends upon the porosity, pore size and pore connectivity to the surface.

Extreme changes in temperature cause differential expansion between mineral grains in building stones. This expansion, which may also occur when water freezes (about a 9% volume increase), induces tensile stresses that generate micro- and macroscopic discontinuities, allowing the circulation of fluids (water, dissolved salts, etc.). The intrinsic properties of the silicified granites (porosity, pore size distribution and mineral content) have a great influence on deterioration. It is well known that pores in the diameter range of microporosity (<7.5  $\mu\text{m}$  by Hg injection) play an important role in degradation processes such as gelifraction and haloclasty (physical weathering caused by growth of salt crystals) (Camuffe 1996; Putnis and Mauthe 2001; Ruedrich and Siegesmund 2007; García-Talegón et al. 2015).

To quantify the resistance of the various stones to changes in temperature, 6 cm cubes were aged through 25 cycles of freezing/thawing and thermal shock (-20 to 100°C) in a simulation chamber (Iñigo et al. 2013). Colour characterization before and after this artificial ageing (Table 5) was determined with a MINOLTA colourimeter (Chroma Metra) (Iñigo et al. 2014). The  $L^*$  value refers to lightness (or darkness), while  $a^*$  and  $b^*$  are the chromaticity coordinates. The  $a^*$  coordinate values range between positive, identified with red, and negative, identified with green. The negative values of the  $b^*$  coordinate are associated with blue and the positive values with yellow. Changes in each of the chromatic coordinates for each of the tests are recorded as the difference in coordinate magnitude between the aged sample and the original sample (Table 5). Ochre Granite becomes less red (<  $a^*$ ) and yellow (<  $b^*$ ); Red Granite is clarified (>  $L^*$ ) and becomes more red and yellow (>  $b^*$ ); and White Granite darkens (<  $L^*$ ).

### Effectiveness and Sustainability of Conservation Treatments

The various granites were subjected to application of conservation treatments, which are meant to improve the durability and appearance of the stone. The conservation treatments used in this study were H224, RC70 and RC80 from Rhône-Poulenc, and supplied by Siliconas Hispania. H224 waterproofer is a colourless alkylpolysiloxane oligomer; RC70 consolidant is a colourless organic silicate having a viscosity of 0.86 mPa/s, a density of 0.890 g/cm<sup>3</sup>, and a silicone content of 70%. RC80 consolidant and waterproofer is a colourless, catalyzed organic silicate with a methyl resin. It has a viscosity of 1.13 mPa/s, a density of 0.905 g/cm<sup>3</sup>, and a silicone content of 68%. The solvent in all treatments is a white spirit. Two successive coats of the H224 waterproofer were brushed on to the surface of the stone, the second 24 hours after the first (Esbert et al. 1991). The application of the RC70 and RC80 products was carried out, with slight modification from the recommendations (García-Talegón et al. 1998; Iñigo et al. 2006), by immersing the sample in 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

**Table 5.** Colour changes in silicified granite of Ávila when subjected to artificial aging caused by freeze/thaw cycles. O = Ochre Granite, R = Red Granite and W = White Granite.

	O	R	W
$L^*$	67.30	63.88	73.14
$a^*$	5.53	8.22	4.53
$b^*$	22.16	19.85	16.68
$L_{F/T}^*$	67.37	66.61	71.63
$a_{F/T}^*$	4.92	7.26	4.41
$b_{F/T}^*$	18.61	26.11	16.65

$L^*$ ,  $a^*$  and  $b^*$  = Chromatic coordinates of silicified granite at quarry;  $L_{F/T}^*$ ,  $a_{F/T}^*$  and  $b_{F/T}^*$  = Chromatic coordinates of silicified granite aged by repeated freeze/thaw cycles.

out by immersing the samples in white spirit for 30 minutes, followed by immersion in white spirit solutions of the conservation products at three levels of concentration: (i) 8 hrs in a 5% solution; (ii) 24 hrs in a 40% solution; and (iii) 40 hrs in a 75% solution. Table 6 shows that all treatments had a significant effect on the physical properties of the Bleeding Stone and Ochre Granite, producing a decrease in values of imbibition capacity, open porosity and capillary absorption coefficient, the main criteria used for evaluating treatment effectiveness and therefore the quality of the materials before and after treatment. Furthermore, the application of RC80, a combined consolidant and water repellency treatment, is more effective than when only a consolidant or waterproofing product (i.e. RC70 and H224, respectively) is used, at least in terms of the physical properties studied.

### CONCLUSIONS

Bleeding Stone and Ochre Granite (silicified granites) have been used to build the Romanesque monuments in the 12<sup>th</sup> century city of Ávila (a 1985 UNESCO World Heritage Site). Silicified granites were used as facing stones in the city's 12<sup>th</sup> century cathedral, other churches, and the city walls. During the Gothic and Renaissance periods, silicified granites were used mainly as an ornamental natural stone in the monuments of Ávila. Silicified granites are found in the intermediate and upper part of a complex palaeoweathering mantle developed on the Iberian Hercynian Basement. Three levels are defined; from bottom to top: 1) lower level (Grey Granite, including biotite granodiorite/porphyry and aplite dykes); 2) intermediate level (Ochre Granite, formed from the previous level through a tropical weathering process); and 3) upper level (Bleeding Stone, formed through an opal-CT silicification process, kaolinization, remobilization of iron oxyhydroxides, and later processes of hydromorphy).

A study of the physical properties (permeability to steam, total porosity in water, free porosity, the capillary absorption coefficient and the coefficient of imbibition by total immersion) of the respective stones demonstrates that the values of these parameters are lower in the Bleeding Stone (Red and White granites) and very high in the Ochre Granite. Mercury porosimetry data show that the Ochre Granite has a high porosity that is quite intricate ('bottle-neck') and includes significant trapped porosity, whereas the Red and White granites have lower values. The percentage of macroporosity in the



**Table 6.** Values of the physical properties of Ávila granites before and after application of conservation treatments H224, RC70 and RC80 (see text). O = Ochre Granite; R = Red Granite; W = White Granite.

Samples	TP	FP	AC	RD	AD	IC	CAC	WVP
O	27.20	20.70	75.55	2.46	1.84	13.70	0.001520	0.0000017
OH224	26.81	6.66	24.61	2.43	1.78	10.18	0.000705	0.0000011
ORC70	26.33	11.48	42.59	2.45	1.80	11.61	0.000730	0.0000013
ORC80	24.17	5.68	23.91	2.48	1.88	6.78	0.000396	0.0000011
R	24.03	10.95	45.59	2.32	1.99	7.64	0.000631	0.0000010
RH224	21.35	3.55	16.66	2.48	1.95	5.40	0.000443	0.0000006
RRC70	20.03	5.14	26.29	2.49	1.99	6.93	0.000510	0.0000009
RRC80	20.55	1.83	8.90	2.45	1.95	3.05	0.000395	0.0000007
W	22.51	13.36	59.60	2.42	1.88	10.12	0.001227	0.0000020
WH224	20.15	4.65	23.23	2.38	1.91	6.18	0.000582	0.0000012
WRC70	19.02	5.47	28.46	2.39	1.93	7.31	0.000620	0.0000014
WRC80	19.03	2.64	13.83	2.36	1.91	3.75	0.000438	0.0000011

TP = total porosity (%); FP = free porosity (%); AC = absorption coefficient (%); RD = real density (g/cm<sup>3</sup>); AD = apparent density (g/cm<sup>3</sup>); IC = imbibition coefficient (%); CAC = capillary absorption coefficient (g/cm<sup>2</sup>/sec); WVP = water vapour permeability (Kg/m<sup>2</sup>/sec).

Red and White granites is lower than in the Ochre Granite. Decay processes (salt crystallization, thermoclasty and gelifraction) occur in both the Ochre Granite and the Bleeding Stone, but are more pronounced in the former because of its high clay mineral content. Conservation treatments using H224, RC70 and RC80 produce a decrease in measured values for imbibition capacity, open porosity and the capillary absorption coefficient, vital parameters for evaluating treatment effectiveness and therefore the quality of the materials before and after treatment. The application of RC80 is more effective than when RC70 or H224 is used separately.

A historical and protected quarry is located in the village of La Colilla (Ávila, Spain). Currently, only silicified granite (Bleeding Stone and Ochre Granite) is used for restoration work in the city. Quarry reserves of the 'silicified granite' in the quarry are limited and being rapidly depleted. Taking such points into account, it is suggested that the Bleeding Stone and Ochre Granite of Ávila be recognized as a Global Heritage Stone Resource.

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