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## Relationships between natural color, mineralogy, and decay of the ashlar of the Palace of the Popes (Avignon, France)

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### ABSTRACT

The Palace of the Popes exhibits yellow limestone ashlar on its façades and alternating yellow and grey ashlar on the tower edges, bays, and vaults. However, the grey type systematically displays a significant loss of stone plates. The intensity of this decay pattern, called spalling, spans from aesthetic disorder to actual threat to the structure stability. As the natural color of geological materials is intimately related to their mineralogical composition, we experimentally compared the two stone types to pinpoint the mineral components explaining the sensitivity to spalling. The results highlight an interesting relationship between natural color, swelling clay minerals content, and hydromechanical behavior which corroborate the decay intensity. We thus extended this study to a large ensemble of sedimentary stones quarried in Provence, Switzerland, and Italy to identify the best candidates for integration plates or replacement of the grey ashlar in the ongoing restoration campaign.

### KEYWORDS

building limestones | natural color | spalling decay | clay minerals | hydric dilation

### INTRODUCTION

The architectural technique of alternating ashlar of light and dark colors originates from the Byzantine empire and has spread across the Mediterranean basin during the middle ages through Islamic, Romanesque, and Gothic architecture. The Palace of the Popes (Avignon, France), witness of the cultural exchanges of the 14<sup>th</sup> century (Vingtain 2015), exhibits yellow limestone ashlar on its façades and alternating yellow and grey ashlar on the tower edges, bays, and vaults. However, the grey type systematically displays a significant loss of stone plates (Figure 1A). The intensity of this decay pattern, called spalling, spans from aesthetic disorder preventing the reading of the alternation of colors, to actual threat to the structure stability. The ongoing restoration campaign, recognizing the stratified cultural and material values of the edifice, aims at maximizing the preservation of its materiality by paying close attention to the knowledge of the building materials and their evolution. A multidisciplinary team, led by Pierre-Antoine Gatier (ACMH), currently seeks to map the Old Palace's ashlar and decay evolution from the origins to the last restoration that took place in the late twentieth century (Bernardi and Hartmann-Virnich 2005) through direct survey and archives researches. The identification of the grey ashlar's provenance, the understanding of their decay mechanism, and the choice of integration or replacement stones are therefore at the heart of the scientific questions.

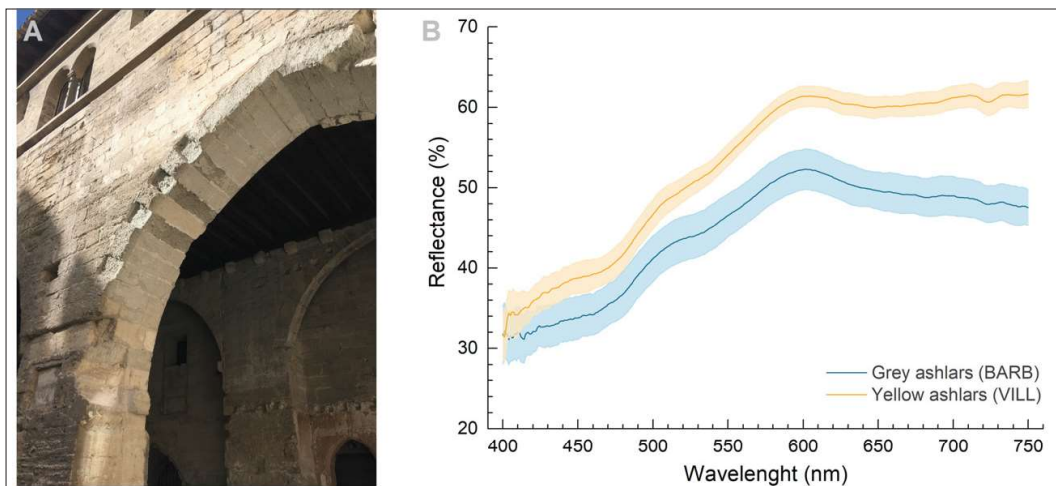


Figure 1: Chromatic contrast of alternating yellow and grey limestone ashlar of the Palace of the Popes (Avignon, France). A/ Vault of the cloister courtyard with alternating yellow and grey ashlar displaying various sensitivity to spalling decay. B/ Corresponding reflectance curves measured on the stone surfaces.

The spalling decay pattern affects numerous stone types in Europe and is currently explained by the presence of swelling clay minerals within the mineralogical composition of the stones (Franzini *et al.* 2007; Colas *et al.* 2011; Berthonneau *et al.* 2016; Tiennent *et al.* 2019). As the natural color of geological materials is intimately related to their mineralogical composition, we designed an experimental study to understand the contrasting sensitivity to spalling of the alternating ashlar. The chromatic attributes of the two types of ashlar were first evaluated by spectroradiometry. Their mineralogical composition was then fully characterized with a focus on the quantification of the clay mineral species, especially those displaying swelling properties. In the meantime, the mechanical behavior was followed along water content variation by recording their dynamic deformation. Our results highlight an interesting relationship between natural color, swelling clay minerals content, and hydromechanical behavior corroborating the decay intensity. We therefore extended this study to the colorimetric, mineralogical, and hydromechanical properties of a large group of “Pierre du Midi” samples quarried in Provence, as well as some sedimentary stones from Switzerland and Italy. We thus compared the natural color and expected spalling sensitivity of these stones to identify the best candidates to be used as integration plates or replacement of the grey ashlar, i.e. those displaying comparable natural colors but with a lower expected sensitivity to spalling.

## EXPERIMENTS

The nature and provenance of the two types of ashlar identified on the Palace were determined by a petrographic and mineralogical comparison with the stone collection of the institute. Macroscopic blocks were then sampled in their respective extraction quarries. As these two types of limestone belong to the “Pierre du Midi” lithotype originating from Burdigalian (20-16 Ma) sedimentary deposits extensively used for building in the Provence region since antiquity, a large ensemble of samples was constituted from the main documented quarries. This set of samples was completed with fragments of some sedimentary stones of comparable texture from Switzerland (Moliere, Magenwiller) and Italy (Maremma) in order to identify potential candidates for the integration or replacement of the decayed grey ashlar.

Color measurements were carried out on each stone surfaces with a Photon Lines NCS-RUBY contactless spectroradiometer, using the color-system CIE L\*a\*b\* 1976. The variation in lightness L\* and chromatic coordinates a\* and b\* were specifically characterized. These parameters were used to define the attributes of chroma C\* and hue h\*. In addition, the percentage of light reflectance of the considered surface was measured between 400 and 750 nm from the accumulation of 99 curves with a 1 nm resolution (Figure 1B).

The overall mineralogical composition of the stones was defined by coupling calcimetry (NF X31-105) with X-ray diffraction (XRD, Bruker D8 Focus) on total and acid insoluble residue powders. As a noticeable clay fraction composes these stones, a clay mineral identification and quantification was performed. The procedure resulted from the combination of transmission electron microscopy (TEM, JEOL JEM 2011) coupled with an energy-dispersive X-ray spectrometer (EDX, X-Flash Silicon Drift Detector 5030, Bruker) and profile modelling of X-ray diffractograms. The crystal chemistry of each clay mineral composing the clay fraction was defined by TEM-EDX and their relative proportions were deduced from the fitting of the diffractograms acquired on oriented preparations after air drying at room temperature (AD) as well as after a 24h exposition to ethylene glycol (EG) vapor. The quality of the simulation, and thus the error associated with the quantitative data, was estimated with an unweighted parameter of fit quality  $R_p$ . The obtained clay minerals contents were compared with the methylene blue adsorption tests adapted from Yukselen and Kaya (2008).

The main petrophysical properties (density, effective porosity, Hirschwald coefficient, capillarity, and evaporation) were measured on three cores drilled perpendicularly to the bedding plane according to the French and European standards (NF B10-503, EN 13755, and NF B10-502). The hydric dilation experienced by the samples along capillary water intake was followed through time inside a climatic chamber ( $23.0 \pm 0.1^\circ\text{C}$ ) by LVDT sensors (Solartron® LE/12S,  $\pm 0.2 \mu\text{m}$ ). The ultrasound velocities were calculated from the propagation of P waves through both dry and water saturated core samples.

Eventually, the correlations linking the 21 experimental parameters to one another were evaluated by the computation of the Pearson algorithm. This set of variables was then reduced by principal component analysis (OriginPro® 2016). The components displaying the maximal Eigenvalues were finally plotted against each other to evidence the main trends linking the variables.

## RESULTS AND DISCUSSION

### Contrasting spalling sensitivity of the alternating ashlar

The comparative petrographic and mineralogical study of the ashlars sampled on the Palace of the Popes with the stones collection of the institute allowed to identify their geological nature and respective extraction quarries, in agreement with the historical documentation (Gagniere 1966). Thereby, both types are bioclastic limestones belonging to the "Pierre du Midi" lithotype. While the bioclastic fragments are cemented by a calcareous matrix in the yellow type, a greyish marl matrix, some glauconites, and ferruginous coatings are noted in the grey type. The yellow type comes from the quarries of Villeneuve-lez-Avignon (VILL) located in front of the Palace, across the Rhone river, whereas the grey ashlars were extracted near Barbentane (BARB), a few kilometers south of Avignon.

The chromatic attributes measured on the respective surfaces (Table 1) denote the slight change in color, mainly expressed by higher values of lightness ( $L^*$ ) and chroma ( $C^*$ ) on the yellow type (VILL). This colorimetric variation may be compared with the overall mineralogical composition (Figure 2A), and specifically the variation of their carbonates (BARB: 89.5 and VILL: 94.7 wt. %) contents. In addition, the grey type presents a higher clay minerals content (5.80/1.32 wt. %) which, together with the presence of glauconite and ferruginous coatings, contributes to the attenuation of  $L^*$  and  $C^*$ .

Stone sample	$L^*$	$a^*$	$b^*$	$C^*$	$h^*$ (°)
BARB	73.9	1.8	14.5	14.6	83.1
VILL	78.5	2.8	16.6	16.8	80.3

Table 1: Mean values of the chromatic attributes measured on the grey (BARB) and yellow (VILL) ashlars.

Because the nature and the quantity of the clay minerals impact the sensitivity to spalling decay (Berthonneau *et al.* 2016; Tiennot *et al.* 2019), we applied a quantification procedure based on profile modelling of the X-ray diffraction patterns (Figure 2B). It allowed identifying various phases among which swelling clay minerals were always present within mixed layers phases. Yet, their absolute proportions varied greatly between  $1.7 \pm 0.2$  wt. % for BARB and  $0.3 \pm 0.1$  wt. % for VILL. We further noted that these absolute values are rightfully sensed by the methylene blue absorption test (VBS =  $9.9 \pm 1.6$  and  $3.2 \pm 1.8$  mg.g<sup>-1</sup> for BARB and VILL, respectively).

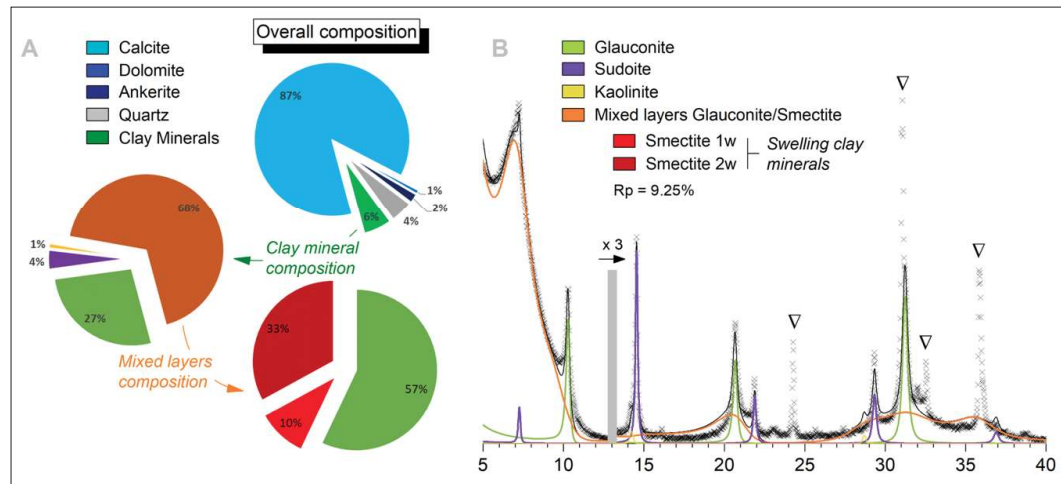


Figure 2: Quantitative mineralogy of the grey ashlar (BARB). A/ Quantitative representations of the mineralogical composition. B/ X-ray diffraction profile modelling allowing for the clay mineral quantification (Swelling clay mineral content =  $5.80 \times 0.68 \times 0.43 = 1.7 \pm 0.2$  wt. %).

Eventually, the differences in natural color and mineralogy lead to contrasting hydromechanical behavior (Figure 3). In fact, for comparable water adsorption coefficients ( $C = 0.20 \pm 0.02$  g.cm<sup>-2</sup>.h<sup>-1/2</sup> for BARB and  $C = 0.33 \pm 0.11$  g.cm<sup>-2</sup>.h<sup>-1/2</sup> for VILL), the two stone types display drastically different hydric dilation ( $\Delta_{\text{hyd}} = 1.34 \pm 0.16$  mm.m<sup>-1</sup> for BARB, see Figure 3A, and  $\Delta_{\text{hyd}} = 0.21 \pm 0.06$  mm.m<sup>-1</sup> for VILL, see Figure 3B). Numerous studies previously evidenced the impact of hydric dilation of stones on the development of the spalling decay (Franzini *et al.* 2007; Colas *et al.* 2011). Therefore, the contrasting natural color, mineralogy, and hydromechanical behavior corroborate the different decay intensity of the two types of ashlar of the Palace of the Popes (Figure 1A).

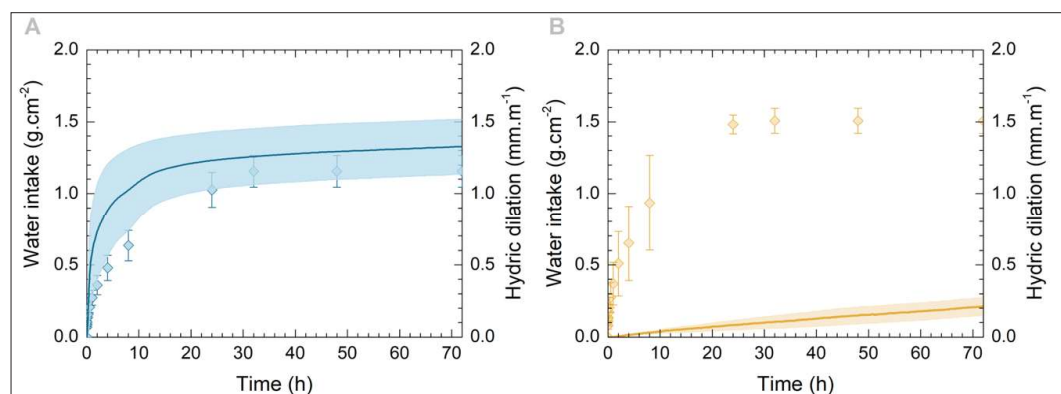


Figure 3: Hydric dilation (solid lines) of the grey (A/ BARB) and yellow (B/ VILL) limestone ashlar along water intake from capillary imbibition (diamonds).

### Mechanistic relationship leading to spalling decay of the Pierre du Midi

The experimental procedure applied on the ashlar of the Palace of the Popes was extended to a large ensemble of 24 samples belonging to the “Pierre du Midi” lithotype. This ensemble contains 2 grey types extremely sensitive to spalling (e.g. BARB) and 22 yellowish (e.g. VILL) to whitish types displaying a moderate to low sensitivity to spalling on historical buildings. The statistical relationships between the experimental parameters measured on these stones were explored by computing the Pearson correlation coefficients (Figure 4A). Based on the results, the main colorimetric, mineralogical, and petrophysical parameters were identified (in bold on Figure 4A) and reduced by principal component analysis (Figure 4B). The first two principal components clearly evidence a mechanistic relationship between natural color, mineralogy, and hydromechanical behavior of the “Pierre du Midi” lithotype. In brief, the stones presenting low  $L^*$  and high VBS contain a high swelling clay minerals content and experience significant hydric dilation. As a result, they are sensitive to the spalling decay.

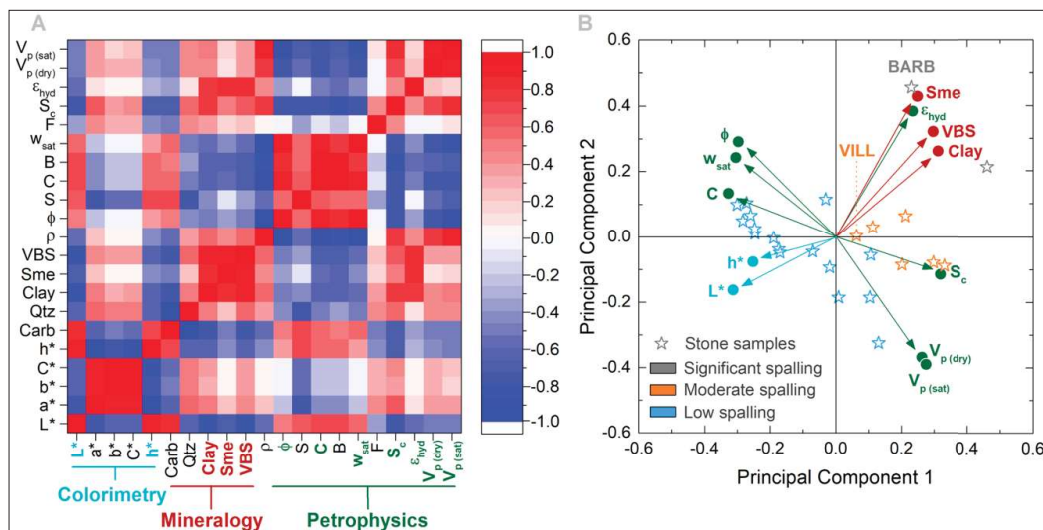


Figure 4: A/ Heatmap of the Pearson correlation coefficients linking the colorimetric, mineralogical, and petrophysical variables. B/ Projection of the variables and the studied samples (with their spalling sensitivity) on the first two principal components (PC1 + PC2 = 83.1 % of the total variance).

### Insights for the on-going restoration campaign

The original quarries of the decayed grey ashlar are no longer accessible (Gagniere 1966). However, the mechanistic relationship presented above may provide insights for the selection of stones to be used as integration plates or replacement in the ongoing restoration campaign. In brief, the best candidates should display comparable macroscopic texture and colorimetric attributes (similar  $L^*$ , for example), while having as low swelling clay content as possible (low VBS). Accordingly, the stones belonging to the “Pierre du Midi” lithotype must be considered with caution (i.e. in this case, a low  $L^*$  would generally lead to a high swelling clay mineral content, see Figure 4). We therefore measured the  $L^*$  and VBS of some sedimentary stones still quarried in Switzerland (yellow and blue facies of Moliere and Mägenwiller stones) and Italy (Maremma stone). We found that some of these facies interestingly present colorimetric attributes close to BARB together with a low swelling clay mineral content (VBS < 4 mg.g<sup>-1</sup>). This approach seems promising and could easily be extended to a greater set of stones.

## CONCLUSION

This comparative study of stones displaying contrasting spalling decay sensitivity allowed to draw an interesting relationship between natural color, swelling clay minerals content, and hydromechanical behavior. Collectively, our results evidence that the “Pierre du Midi” limestones exposing a natural grey color have lower  $L^*$ , contain a high swelling clay mineral content, experience high hydric dilation, and are sensitive to the spalling decay. By extension, this relationship provides insights to identify the most durable materials for the integration or replacement of the decayed ashlars in the ongoing restoration campaign aiming at maximizing the preservation of the Palace of the Popes’ materiality.

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