Quantification of color change of building limestone due to humidity variations

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Colorimetry is a Non Destructive Technique (NDT) commonly used in cultural heritage. It allows quantifying the subjective nature of color in order to characterize, identify or distinguish materials or to control their weathering stage. Indeed, whether it is by biocolonisation, salt crystallization or pollutant accumulations, the weathering processes often lead to a color change. This technique is then often used directly on the field on buildings, or in the laboratory. But climatic conditions (temperature, relative humidity and even rain) can be quite different from the field and the laboratory, and in the field, from one day to another. It is well known that color is highly dependent on humidity. A wet stone has often a different color than a dry stone. So, when using this technique to compare color data from one day to another, for example during monitoring campaigns, it is hard to have the same climatic conditions and to know if the color variations are significant. Color change of materials due to humidity is mainly related to mineralogy, porosity, pore distribution and specific area. All materials will not have the same behavior.

In order to quantify color change due to humidity, 4 building stones were sampling, characterized and submitted to different humidity conditions before color measurements.
Materials were building stones used in monuments of North-Eastern Paris (France): one building limestone (Bj) from the Bajocian layer of the Paris Basin (France) and one reconstituted stone made with debris this limestone (Rs) and that was used as substitution stone during restoration works; one limestone from de Lutetian layer of the Paris basin (Cv) and one limestone from the Portlandian layer usually used to replace the Lutetian (Sv). All of them have light color with yellowish tendency.
Each material were characterized by microscopy, water and mercury porosity and adsorption-desorption kinetics were measured. Results showed similar characteristics of the four materials, especially between the pairs.

Color was measured on 6 samples (5x5x1 cm^3) of each stone at different states: dry, after adsorption at 33%, 75% and 97%, wet and during drying. The colorimetry was set up with a Minolta CR400 chromameter.
Results showed that the parameter that changed the most with humidity was the Luminance (L*).
Maximum adsorption of stone was around 1% in weight except for the reconstituted stone that was around 2.5%. Even the maximum of weight increase at 97% of RH was for the RS, only the Bajocian limestone showed a color variation ΔE up to 3, meaning that the color change was visible to the naked eye.
Color change (ΔE) after immersion showed that the wet restoration stones (Rs and Sv) had a higher change of color ($\Delta E > 15$) than the original stones (Bj and Cv).
During drying, the value of luminance was directly correlated to the saturation. ΔE was significant (>3) until the saturation reached 15% for Bj, Rs and Cv and 5% for Sv.

This study showed that stones with close petrophysical properties could have different color change behavior enough to distinguish them on a building. It also showed that stones were highly sensitive to humidity, but that this change was related to how this humidity is located in the porous network (adsorption-desorption or absorption-drying). Further experiments would test color variation with humidity of stone contaminated with salts.

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