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Colour and ultrasound propagation speed changes by different ageing of freezing/thawing and cooling/heating in granitic materials

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A B S T R A C T

In the present work we determined the chromatic coordinates (L^*, a^*, b^*) and ultrasound propagation speeds on the three spatial planes (V_x, V_y, V_z) of three ornamental granites (Aqueduct of Segovia, Spain) before, during, and after being subjected to 70 cycles of two types of accelerated ageing (typical of cold regions): a) freezing/thawing and cooling/heating (T1), and b) freezing/thawing and cooling/heating + salt crystallization (T2). A multivariate technique (Canonical Biplot) was applied to the data obtained, with the observation of significant variations between the two types of accelerated artificial ageing as compared with those obtained in quarry rock in the three chromatic coordinates (L^*, a^*, b^*). With regard to the ultrasound propagation speed, we only detected differences in the results of the T2 artificial ageing treatment with respect to those of quarry rock. This fact is confirmed by the estimated data of resistance to compression.

1. Introduction

In Segovia, located in the Regional Community of Castilla y León (Spain), with a Mediterranean climate with a continental trend [cold region, characterized by sharp and sudden thermal oscillation (up to as much as 40 °C between the day and the night) give rise to the so-called thermoclastic phenomena and weathering through freezing appears in humid areas, where the temperature is fairly low. Where permanent humidity exists, weathering is also produced by precipitation and crystallization of salts in pores], the mechanisms that have most frequently given rise to degradation due to climate are as follows (García-Talegón et al., 2006a, 2006b; Iñigo et al., 2000a, 2003; Rives and García-Talegón, 2006; Vicente, 1996):

a) Freezing/thawing and cooling/heating (T1)
b) Freezing/thawing and cooling/heating + salt crystallization (T2)

These methods of artificial ageing were used under controlled conditions in a simulation chamber.

Extreme changes in temperature cause differential expansion between mineral grains in granitic materials. These expansions generate micro-discontinuities, allowing the circulation of fluids (water, dissolved salts, etc.) (Takarli et al., 2008). The fluids react in the rock-fluid interface, producing solutions and/or precipitation reactions (Sausse et al., 2001).

When water freezes, it produces a volume increase generating micropores (about 9% of original volume). This expansion induces stress concentration and tensile damage in micropores (Iñigo et al., 2000b). When the rock thaws, the water flows through the micropores causing new fractures (Chen et al., 2004; Hori and Morihiro, 1998; Matsuoka, 1990; Tan et al., 2011).

The properties of the granites (initial porosity, the pore size distribution and mineral content) have a great influence on deterioration (Iñigo et al., 2000a, 2000b). These authors used the nitrogen adsorption technique to study the specific surface area and the pore size distribution of five types of granites. This method allows detection of pores with a diameter < 1 μm. It is well known that pores in this diameter range play an important role in degradation processes such as haloclasty and gelifraction (Camuffo, 1996).

Colour is a parameter that must be currently controlled to monitor the quality a quarry rock when it is used in a monument, both as regards its deterioration due to environmental (Sebastián-Pardo and Zezza, 1998; Zezza, 2002a) and microenvironmental factors in certain zones of buildings (Zezza, 2002b) and after the application of conservation treatments (García-Talegón et al., 1998; Iñigo et al., 1997, 2004).

Additionally, another important variable to be controlled both in ageing and in the application of conservation treatments is measurement of the ultrasound propagation speed, which for example indicates a

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Table 1
Mineralogical composition of the different granites studied.

Sample	Q	Fk	Pl	I/M
Ortigosa del Monte	xxx	xx	xx	xx
La Granja	xxx	xxx	xxx	x
Magullo	xxx	xx	xx	xx

Q: quartz, Fk: potassium feldspar, Pl: plagioclase, I/M: micas
xxx: dominant, xx: abundant, x:present

decrease of cohesion of minerals as a result of T1 an T2 ageing (Chen et al., 2004; Matsuoka, 1990), or an increase in this parameter due to application of a conservation treatment (consolidation).

The main objective of this work was to investigate the influence of freeze–thaw cycles, with (T2) or without (T1) the presence of salts in water (sulphates), on the chromatic coordinates (L^*, a^*, b^*) and ultrasound propagation speeds on the three spatial axes (V_x, V_y, V_z). This variations in the colour and ultrasound propagation speeds were studied applying a multivariate method (Canonical Biplot) to the data obtained concerning these variables to 3 of the granites most widely used in the construction and successive interventions of the Roman Aqueduct in Segovia (Ortigosa del Monte, La Granja and Magullo) before, during, and after subjection to 70 cycles of the two types of ageing used. Additionally, we determined possible weight losses by ANOVA analysis after the application of the two types of ageing applied in the controlled cycle. We propose also a linear regression model between the resistance to compression and the ultrasonic propagation speed in granites.

2. Materials and methods

The granite materials most used in construction and later interventions on the Aqueduct in Segovia are from Ortigosa del Monte, La Granja, and Magullo. Their mineralogical composition was determined by X-ray diffraction. As expected, the main minerals were quartz (Q), potassium feldspars (Fk), plagioclase (Pl) and micas (I/M) (Table 1).

Using the results of the chemical analysis of the major elements (Table 2), we classified the three varieties according to the CIPW normative calculation (Q'-ANOR') (Streckeisen and Le Maitre, 1979), observing that the Ortigosa del Monte material corresponded to a sienogranite; that from La Granja to a monzogranite, and that from Magullo to a granodiorite (Fig. 1). This classification confirms the microscopy observations. Magullo was the variety with the most calcic plagioclases (anorthite) and the Ortigosa del Monte material had the most sodic plagioclases.

The stones were cut in cubic samples (5×5×5 cm) and were subjected to 70 cycles of the following accelerated ageing treatments in a simulation chamber under controlled conditions:

T1: Freezing/thawing and cooling/heating (−20 to 110 °C). After a drying period at 60 °C until constant weight was reached, the blocks were submerged in distilled water for 16 hours (rocks are saturated), after which they were cooled to −20 °C and kept at that temperature for 3 hours. Following this, temperature was raised to 110 °C (rate = 2 °C/min), and the blocks were held at that temperature for 3 hours. Finally, the blocks were left for 2 hours at room temperature and the process was started again (Iñigo et al., 2000a; Tiano and Pecchioni, 1990).

T2: The experiment was carried out over a combined freezing/thawing and cooling/heating treatment with sulphate crystallization. We used the method T1, but the samples are immersed in a 14% solution of hydrated sodium sulphate ($Na_2SO_4•10H_2O$) instead of distilled water.

The chromatic coordinates (L^*, a^*, b^*) were measured with a MINOLTA model CR-310 colorimeter for solids during cycles 0 (before starting each of the artificial ageing treatments) 20, 40, 60 and 70.

Ultrasound propagation speed was measured in the same number of cycles as colour during the ageing treatments. To accomplish this, an ULTRASONIIC Tester BP-5 from STEINKAMP was used.

To study the influence of the number of ageing cycles (freezing/thawing and cooling/heating, and freezing/thawing and cooling/heating + salt crystallization) on the quarry samples, the multivariate technique known as Canonical Biplot (Amaro et al., 2008; Varas et al., 2005) was used.

The Canonical Biplot is equivalent to MANOVA analysis (Multivariate Analysis of Variance), but it includes all the characteristics of the Biplot method (Gabriel, 1971, 1972, 1995), which is aimed at discriminating the set of groups of previously established populations. This technique was later developed and completed (Amaro et al., 2004; Galindo, 1986; Vicente-Villardón, 2012), and applied to the field of cultural heritage conservation (Iñigo et al., 2004; Varas et al., 2005; Vicente and Vicente-Tavera, 2001).

The results are summarized on several factor planes, where the variables are represented as vectors that start out from a hypothetical origin and the means of the different groups as stars surrounded by confidence circles in the same reference system. If two variables are represented with a very small angle then the variables are highly correlated: if they are opposite their correlation is inverse. Additionally, if the angle is close to perpendicularity, their correlation is minimum. On projecting all the star markers perpendicularly onto the directions of any of the variables, the order of the projections in the direction of those variables is equivalent to the value that the population means take on that variable. If two confidence circles are projected perpendicularly on one of the variables and the intervals of both projections do not overlap, this is tantamount to saying that there are differences between both means (Student's t test); the amplitudes of the circles will depend on the significance, α, determined (MSD, Bonferroni corrections, etc.). These interpretations are subject to a series of measurements of the quality of representation for the different planes (inertia absorption of the planes, the goodness of the projections of the measurements on the variables for the dimensions selected, etc.).

In our case, we started out from a matrix formed by 900 rows and 6 columns (variables). The rows were divided into 27 groups (populations) with specific characteristics:

Varieties of granite (V): Ortigosa del Monte (O), La Granja (G) and Magullo (M).
Types of ageing (T): freezing/thawing and cooling/heating (TI) and freezing/thawing and cooling/heating + salt crystallization. (T2).
Number of cycles (C): 0, 20, 40, 60 and 70.

Table 2
Chemical composition of the major elements of each of the granite varieties studied.

Sample	SiO_2[a]	Al_2O_3[a]	TiO_2[a]	Fe_2O_3[a]	MnO[a]	MgO[a]	CaO[a]	Na_2O[a]	K_2O[a]	P_2O_5[a]	V.M.[a]
Ortigosa del Monte	71.33	14.14	0.24	1.99	0.03	0.3	1.19	3.47	5.32	0.15	1.34
La Granja	72.73	14.16	0.27	1.85	0.03	0.18	1.54	3.30	3.98	0.11	1.35
Magullo	69.64	15.55	0.47	2.9	0.06	0.73	2.5	3.58	3.19	0.13	0.75

V.M.: Volatile material
[a] % oxides of major elements.