Cofinanciado por:

Multi-cycle statistical analysis of laboratory salt weathering tests

Carlos Alves [1], Carlos Figueiredo [2]

[1] LandS/Lab2PT (Landscape, Heritage and Territory Laboratory), UID/AUR/04509/2013; POCI-01-0145-FEDER-007528, and Earth Sciences Department, School of Sciences, University of Minho, Portugal.

[2] CERENA - Centro de Recursos Naturais e Ambiente, UID/ECI/04028/2013, DEcivil, Instituto Superior Técnico, University of Lisbon, Portugal.

Soluble salts are important pollutants in the built environment (having both anthropogenic and geogenic sources) and salt weathering is the most widespread erosive hazard to stone materials in the cultural heritage (also affecting some contemporaneous stone works).

While end-term erosive effects are well-established, the evolution along time has been much less studied. This temporal aspect is nonetheless frequently very important in an applied perspective when it is necessary to assess whether a given observed decay situation is at equilibrium or will evolve in the sense of further erosion (hence requiring interventions to avoid that kind of evolution).

This study is based on the results of salt weathering laboratory tests on three Portuguese limestone types: two grainstones (Semi-rijo and Moca Creme) and a travertine.

These rock types are detailed described in Alves et al. 2010 but it will be useful to refer here that the grainstones have diverse allochemical components with a sparry cement (being the allochemical components coarser in Moca Creme than in the Semi-rijo) and that the travertine (presents) is dominated by compact portions but presents diverse more friable (detritic-rich) portions with an irregular distribution (at the specimen scale).

Salt weathering tests were performed on cubic specimens of these rock types following the indications of the European Standard (EN 12370) by 15 cycles of immersion in sodium sulphate solutions and oven-drying, being the final mass measured after throughout washing of the specimens.

These salt weathering tests showed higher mass losses in the grainstones than in the travertine (higher in Moca than in Semi-rijo). Our previous studies showed that the mass increase phase and mass decrease phase separated the travertine from the grainstones and the parameters of the mass decrease phase present a good correlation with the final mass loss value (unlike the results of the mass increase phase).

It will also relevant to refer for these rock types what Angeli et al. 2007 refer as **weathering patterns**.

grainstone specimens present a homogeneous weathering pattern, with rounding of edges and corners (being generally similar among the different specimens)

travertine specimens presented a heterogeneous weathering pattern, with marked differences in different zones of the same specimen with an irregular distribution.

In this work will be presented a multivariate study of the results of the different cycles, as mass differential between successive cycles as a percentage of initial mass.

Standardized values (obtaining by subtracting the mean and dividing by the standard deviation) were used in cluster analyses, PCA and multivariate tests to avoid the undue effect of differences in variance of the considered variables (cycles).

In the hierarchical cluster analyses were used the following available classification procedures: single linkage, complete linkage, unweighted pair-group average, weighted pair-group average, unweighted pair-group centroid, weighted pair-group centroid (median) and Ward’s method.

Matrix plot (allowing the presentation as coloured areas of the results of the differences between successive cycles for each specimen and cycle)

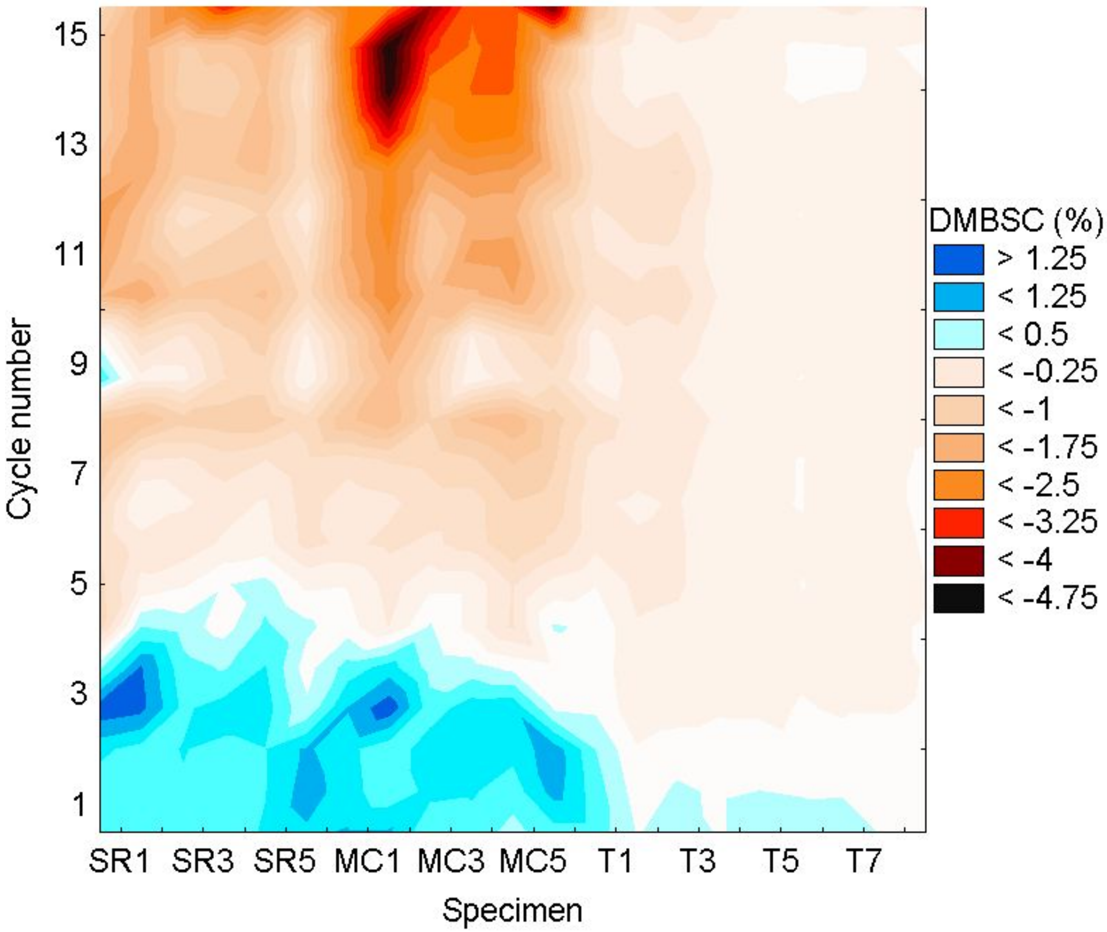
Cluster analyses (both K-means and hierarchical analyses)

Principal Component Analysis (PCA)

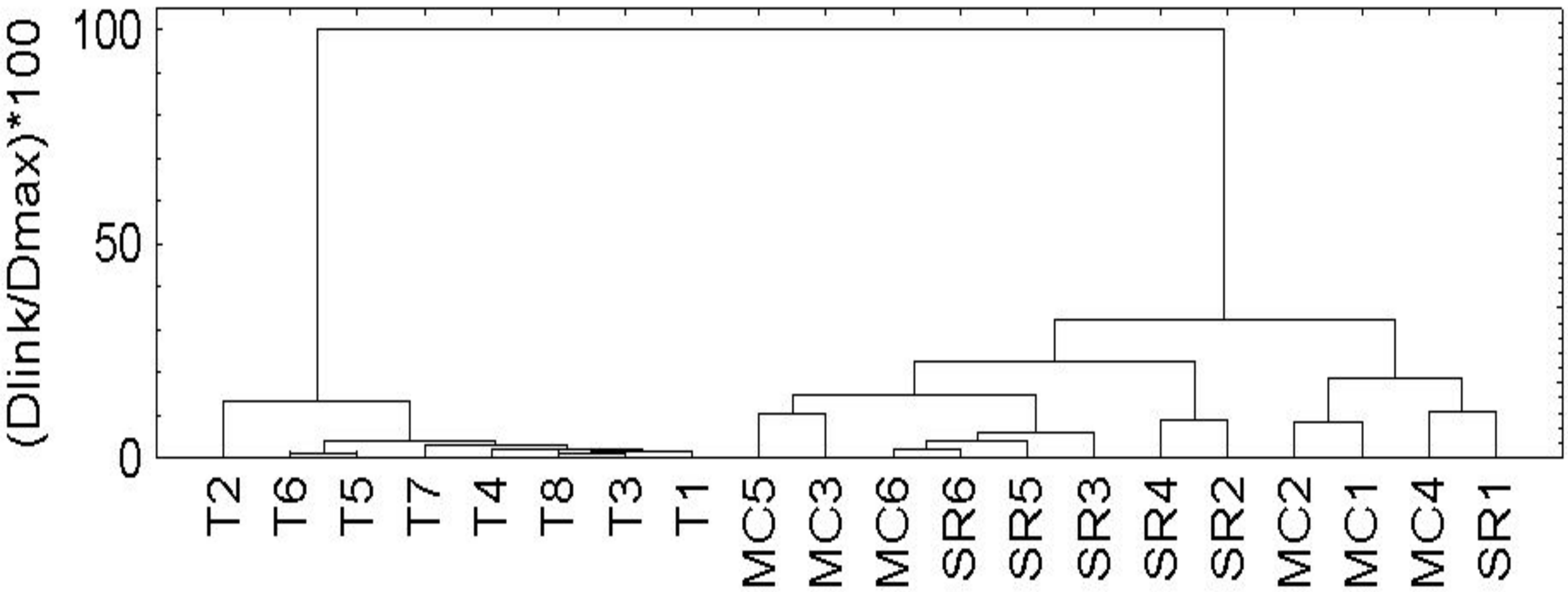
Multivariate statistical tests for comparison of groups (one-way ANOSIM and one-way PERMANOVA)

Page's test - Not strictly a multivariate test but based on diverse measurements on the same subject; considered the last ten cycles to assess whether there is a trend towards increasing mass loss between cycles.

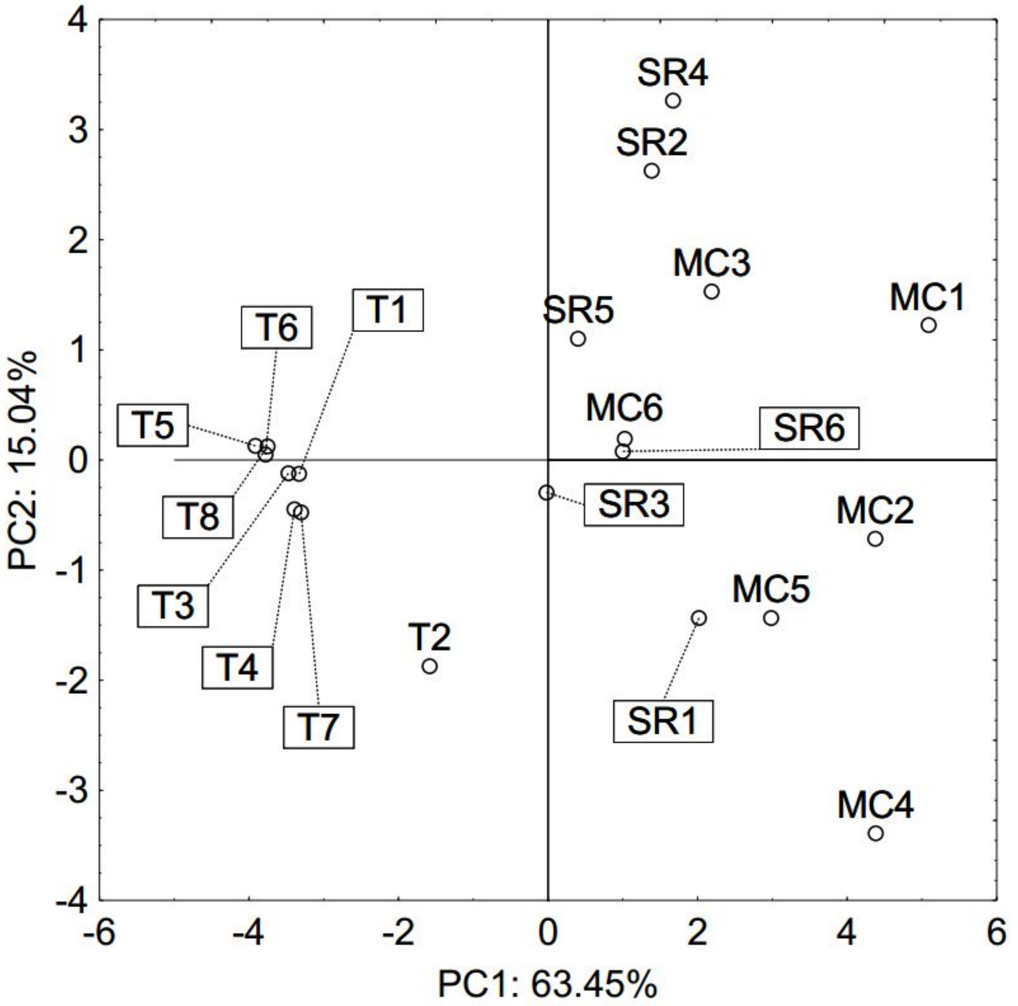
Matrix plot.
More marked variations in Semi-rijo and Moca Creme specimens at the beginning and end of the salt crystallization tests, especially end Moca Creme specimens.
There is a certain irregularity in the intermediate portions of grainstone tests (much harder to detect with the more usual cumulative curve of mass variation).



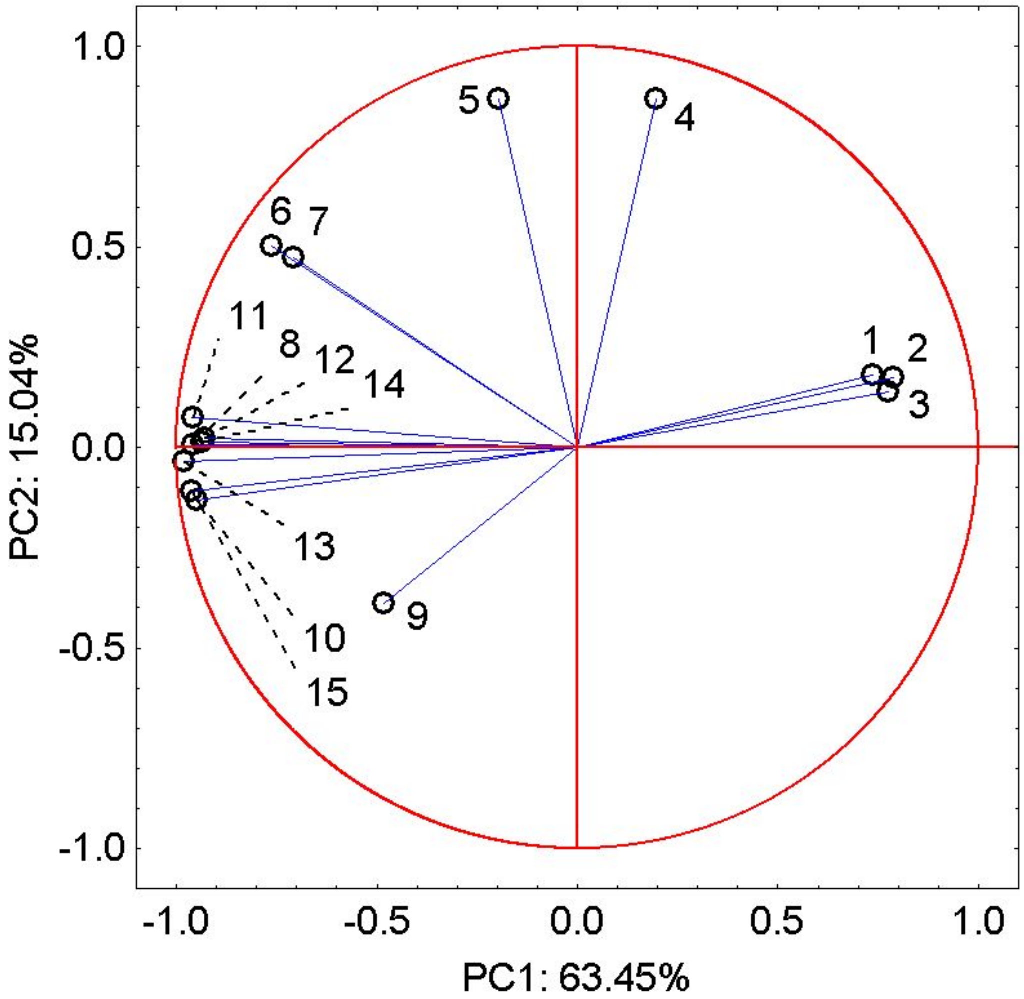
All the hierarchical cluster analyses put all travertine specimens (T) in a cluster separated from the grainstones(Semi-rijo, SR; Moca Creme, MC).



Travertine specimens separated from grainstones by PC1 (T2 almost in an intermediate position between other travertine specimens and grainstones).
PC1 dispersion is much higher for Moca Creme specimens.
PC2 dispersion is clearly higher for the grainstones



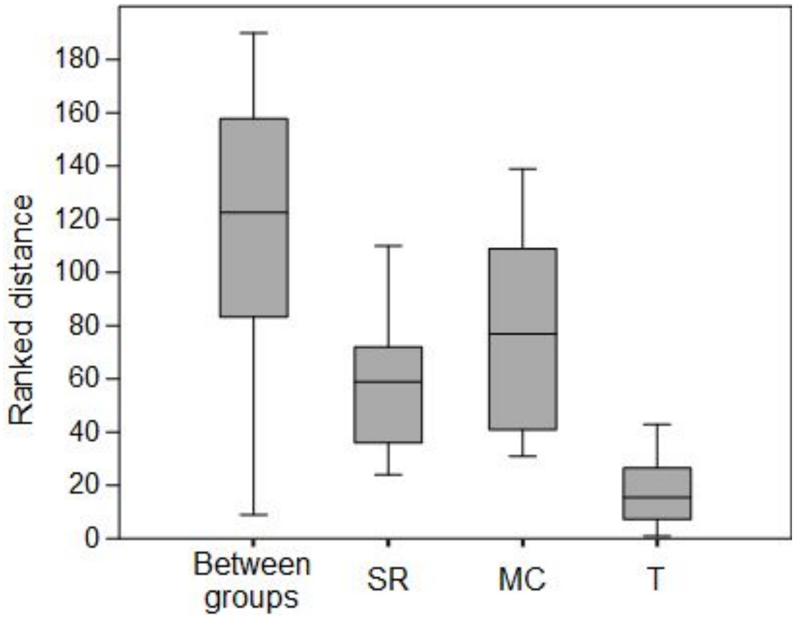
Positive association of PC1 with the initial cycles and a strong negative association with the final cycles. PC2 is related to most of the intermediate cycles; could be related to the phase referred by Angeli et al. as corresponding to a balance between mass gain and the beginning of the erosive breakdown.



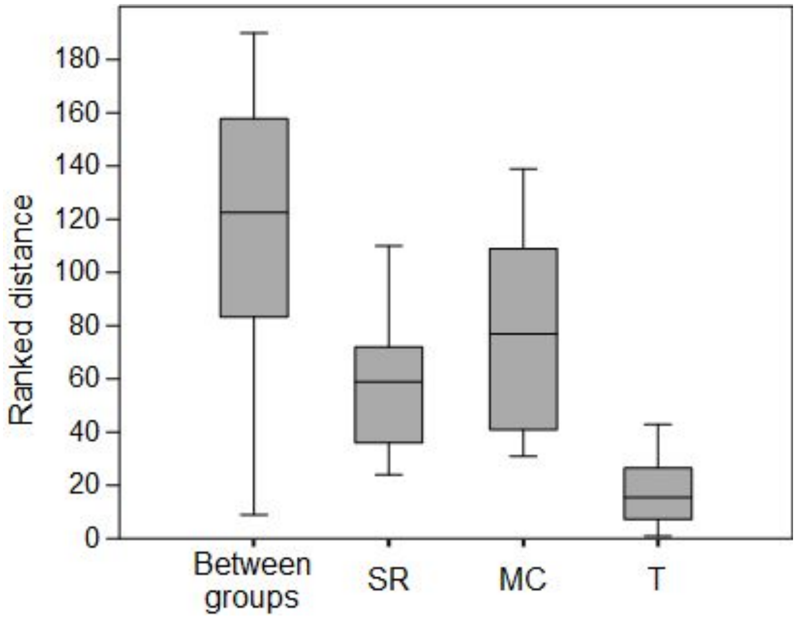
Results of one-way ANOSIM and one-way PERMANOVA multivariate tests (10^7 permutations) on specimens of the two grainstone types (Semi-rijo, SR, and Moca Creme, MC) and travertine (T).

Statistical test	*p*-value same	SR vs. MC	SR vs. T	MC vs. T
4×10^{-7}	0.04986	0.0003383	0.0003223	4.00E-07
2×10^{-7}	0.03685	0.0003405	0.0003298	2.00E-07

Boxplot of ranked distance obtained in ANOSIM test between groups and for the groups considered - two grainstone types (Semi-rijo, SR, and Moca Creme, MC) and travertine (T)



Boxplot of ranked distance obtained in ANOSIM test between groups and for the groups considered - two grainstone types (Semi-rijo, SR, and Moca Creme, MC) and travertine (T)



Page's L statistic (2144 for Semi-rijo and 2237 for Moca Creme) are above the critical value for 6 subjects, 10 measurements and $p = 0.001$ (meaning p-value < 0.001)

For the travertine the L statistic (2424) is below the critical value for 8 subjects, 10 measurements and $p = 0.05$ (meaning p-value > 0.05).

If the grainstones are considered together, the L statistic will be 4381, which is above the critical value for 12 subjects, 10 measurements and $p = 0.001$ (meaning p-value < 0.001)

Conclusions

The detailed analysis of the results of mass differences between successive cycles of salt weathering laboratory tests separates clearly the travertine from the grainstones. The usefulness of this tool is largely proved and underpinned by the generally convergent results obtained by applying the panoply of multivariate analysis procedures that were tried in this study in an alternative perspective to more traditional analyses based on the final mass loss and could help to discuss the behaviour along time of the stones under salt weathering.

Conclusions

The petrographical model of salt weathering can help to understand the different behaviour of these rock types under salt weathering conditions. While in the travertine specimens, salt weathering will be limited to the more susceptible zones of the specimens, given the heterogeneous character of this rock, in the grainstones salt weathering proceeds through the development of fissures along the edges of the specimens and further cycles seem to promote further fissures. After the initial cycles and due to higher erosion, the results from the Moca Creme begin to diverge from those of the Semi-rijo given the coarser textural heterogeneities in this rock type. The presence of coarser grains will imply a higher mass loss in Moca Creme and possibly fissures that penetrate deeper (given that the interface grains/cement is deeper on account of coarser grains), but the behaviour along time will be essentially similar.

Conclusions

In a lay terms synthesis, one could say that the grainstones are being "peeled off" along the successive cycles (Moca Creme with coarser layers). In the travertine the erosive process goes on "nibbling" the more susceptible zones (the ones that are more affected by the salt weathering and that our previous studies suggest are the detritic enriched portions) while salt penetration is limited by the contrast with the more compact portions.

The results of this study of cycles could be considered relevant for the understanding of the behaviour of stones in the field along time. They suggest that, if salt weathering cycles persist, mass loss does not stop after the onset of erosion and in some cases (as in the grainstones) mass loss could increase along time even after the erosion of significant portions of the specimens.

Funding: The experimental data considered in this publication discussed were obtained in the context of the Project PORENET (POCTI/CTA/44940/2002) funded by the FCT — Fundação para a Ciência e Tecnologia (Portugal). The software and informatic equipment used in the preparation of this publication was also supported from funding of the FCT to the Centro de Investigação Geológica, Ordenamento e Valorização de Recursos of the School of Sciences of the University of Minho.

Acknowledgments: The Lab2PT, Landscape, Heritage and Territory Laboratory(UID/ECI/04028/2013) of the University of Minho and the CERENA — Centro de Recursos Naturais e Ambiente (UID/ECI/04028/2013) of the Instituto Superior Técnico, University of Lisbon are supported by the FCT — Fundação para a Ciência e Tecnologia (Portugal), with Portuguese funds and funds from the European Union (FEDER, Programa Operacional Factores de Competitividade — COMPETE 2020 — Programa Operacional Competitividade e Internacionalização, POCI, POCI-01-0145-FEDER-007528). Acknowledgments also to Eng. Teresa Luís, Eng. Sónia Pereira, and Enterprise Mármores Galrão for the rock blocks.