ACTA UNIVERSITATIS CAROLINAE
2000 GEOGRAPHICA, XXXV, SUPPLEMENTUM, PAG. 7–16

The Thermal Degradation of Marble

ANDREW S. GOUDIE and HEATHER A. VILES

School of Geography and the Environment, University of Oxford,
United Kingdom

ABSTRACT

The heating and cooling of Pentelicon marble through the range of temperature encountered on rock surfaces in warm deserts lead to a measurable reduction in rock strength after only a few cycles. Even though no blocks of marble suffered from visible cracking, the SEM study showed that the nature of the calcite grain interactions changed. Such changes in grain to grain contact, and in rock strength, may permit other weathering processes to be more effective, thereby accelerating the rate of desert weathering.

Key words: degradation of marble, desert weathering

1. Introduction

Many historical marble monuments provide clear evidence of degradation, which typically consists of a reduction in rock cohesion, an increase in porosity and a tendency to crumble. Even some modern buildings, such as the Amoco Building in Chicago and the Finlandia Hall in Chicago have experienced marble cladding failure (Widhalm et al. 1996). While it is possible that various mechanisms could contribute to this degradation, Rayleigh (l934) suggested that marbles that had been baked at temperatures of 100 degrees C or even less had their rigidity diminished. He suggested that this was due to the uneven way in which calcite crystals expanded on heating. Rayleigh was, therefore, advocating heating and cooling (insolation weathering or thermoclasty) as a cause of marble breakdown. On the other hand, most geomorphologists have been dismissive of the role of thermoclasty in rock breakdown. This was partly because of the experimental simulations undertaken by Tarr (l915), Blackwelder (l933) and Griggs (1936). However, these early simulations had some short-comings in terms of the cycles chosen, the nature of the rock blocks employed, and the methods used to determine whether any changes in rock properties had taken place as a result of the heating and cooling (Rice 1976).

More recently, Royer-Carfagni (l999) has used scanning electron microscopy to identify changes in marble structure on heating, and has suggested why it is that certain types of marble may be prone to the effects of quite modest heating treatments (p.119):

‘Calcite is known to expand on heating much more in the direction of its optical axis than perpendicular to it. The grains’ shapes change with temperature and a grain which fits snugly into the mosaic at a given temperature is no longer able to do so when the temperature is varied; this is because the anisotropy directions of the individual grains are oriented randomly. The result is a springing apart of contiguous grains, giving rise to a non-zero residual stress state inside the material.' Figure 1, modified after Winkler (1975), shows the nature of the response of calcite to a change in temperature, with quartz for comparison. Widhalm et al. (1997) have shown that calcite expands by 26.10^{-6} K^{-1} parallel to the crystallographic c-axis, and contracts by 6.10^{-6} K^{-1} normal to it, while Rosenholtz and Smith (l949) used dilatometry to show the high sensitivity of calcite to heating effects.

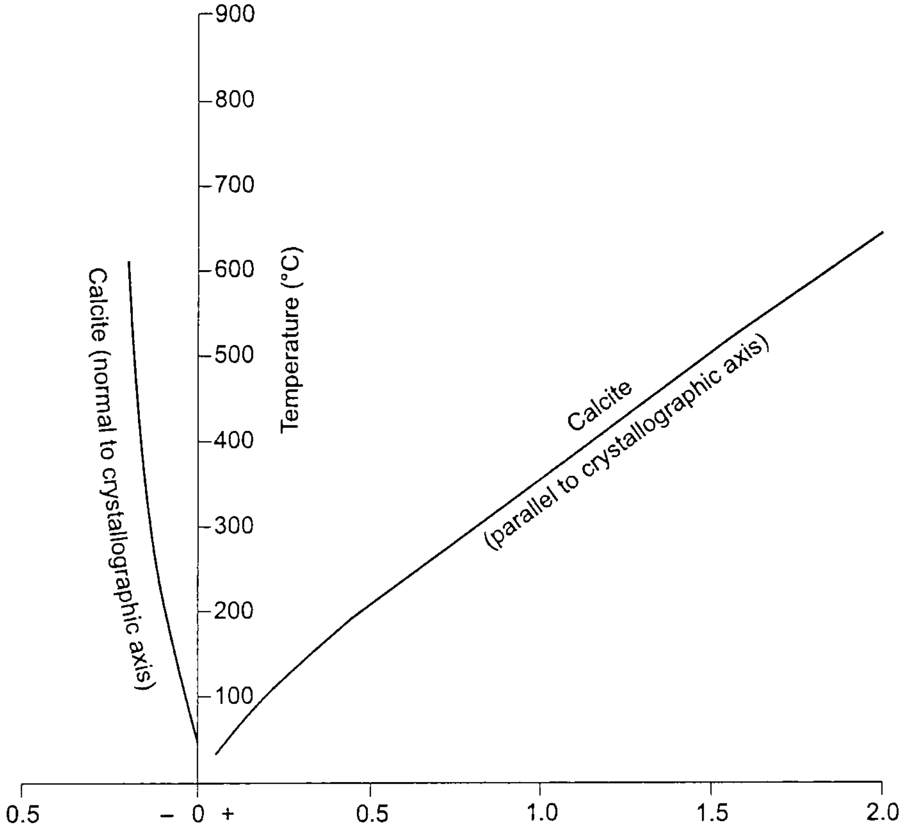


Figure 1: The linear expansion of calcite.

2. Aims

The aims of this paper are: to describe the results of two heating and cooling experiments on marble blocks; to demonstrate the use of an impulse excitation technique (the Grindosonic) for determining changes in rock properties; and to show by means of scanning electron microscopy how marble textures are changed.

3. The nature of the rock blocks

The rock blocks used in this experiment consisted of cut oblongs of Pentelicon Marble from Greece. The dimensions of the blocks were 18.5 cm x 3.5 cm x 2 cm. Pentelicon Marble, which is widely used in building, is a white marble and has the properties shown in table 1. It is composed dominantly of calcite.

Table 1: Some mechanical properties of Pentelicon Marble

Compressive strength	1680-1770 kg cm^{-2}
Water absorption	0.32 – 0.39%
Ultimate tensile strength	138-147 kg cm^{-2}
Coefficient of thermal expansion	0.0039-0.0044 mm/m degree C
Bulk density	2568-2575 kg m^{-3}

Source: http://members.tripod.com/ITALCONVOY/ITCimgC3.html

4. The Grindosonic

Before and after the marble blocks had been subjected to cycles of heating and cooling, they were subjected to Grindosonic testing. The Grindosonic measures the modulus of elasticity of a rock of known mass and dimensions by means of the impulse excitation technique. This is based on the analysis of the transient vibration of a test object following a mechanical impact. The energy thus acquired by the tested sample is dissipated in a vibratory movement, the nature of which is dependent on the geometry of the object and the density and elastic properties of the material. The Grindosonic is designed to capture this mechanical vibration, analyse it and to give an accurate measure of the natural frequency. Full details are provided, inter alia, by Allison (l988) and Prick (1997).

5. The temperature cycles

The marble blocks were subjected to heating and cooling in a Fisons FE 300 environmental cabinet, which can be programmed through its micro-processor unit to give independent cycles of temperature and humidity. Heating is by convection, and the ambient conditions with the chamber are continuously monitored by built-in sensors and chart recorders.

Two simulations were carried out. In the first of these, the Wadi Digla cycle (Figure 2), previously used by Cooke (1979) and Goudie (1993), was employed. This is based on observations of rock surface temperatures made by Williams (1923) on 9 August 1922, at Wadi Digla near Cairo, Egypt. The cycle is probably reasonably representative of ground surface environments in summer months in a warm desert, with a day-time peak of 72 degrees C. The night-time low is about 22 degrees C, so that the diurnal range is approximately 50 degrees. The humidity ranges between about 18 and 85 per cent, with

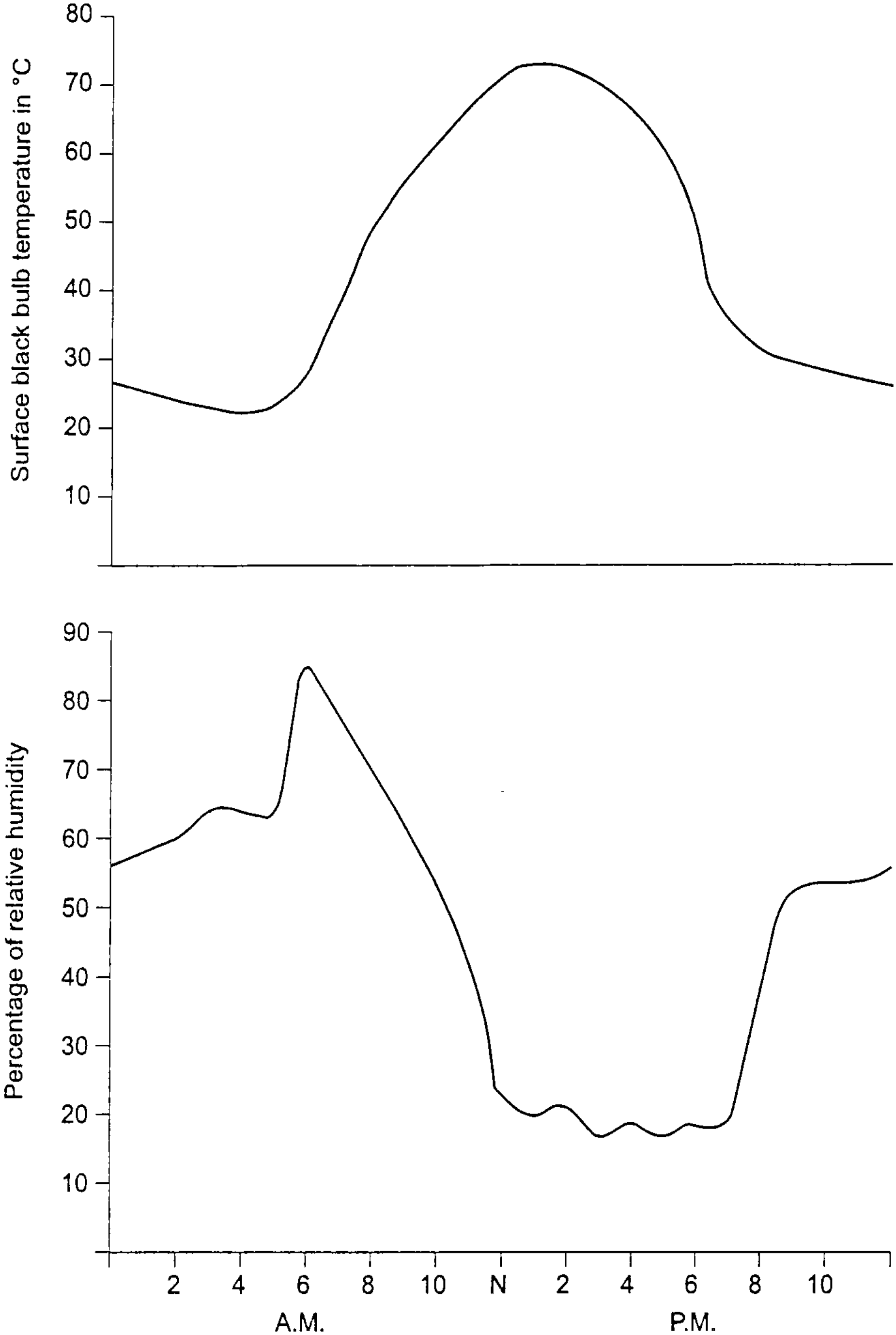


Figure 2: The Wadi Digla Temperature Cycle.

the lowest value occurring during the hottest part of the cycle. Four blocks of marble were subjected to 95 cycles of this treatment, with Grindosonic readings being taken before and after.

The second treatment used a cycle that was not a 24 hour one based on real-world temperature and humidity data. It was a 3 hour cycle in which the relative humidity was kept constant at 50%, but with the temperature cycling from 25 to 80 and back to 25 degrees C. The purpose of this was to see whether a rather faster change in temperature caused a more substantial degree of change than the more gentle real world Wadi Digla treatment. Thirteen blocks were used and each block was subjected to a certain number of cycles before being removed from the environmental cabinet. The purpose of this was to see how much the rock properties changed as the number of cycles was increased, and to enable the SEM characteristics of blocks to be examined after different numbers of cycles had elapsed. All samples were tested with the Grindosonic before the simulation, and then again after they had been subjected to their particular number of cycles. The maximum number of cycles used was 200.

6. Scanning Electron Microscope Methods

A selection of samples subjected to this second type of treatment was examined under the SEM to see whether it was possible to detect changes in the structure of the marble.

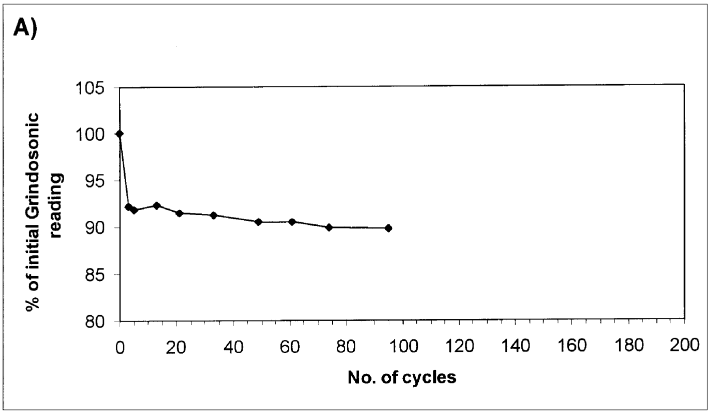
Scanning electron microscopy (SEM) provides a useful tool to investigate subtle changes in the internal structure of the marble blocks which may be responsible for the reduction in strength. Three small sub-samples were removed from marble blocks 4 (1 cycle), 7 (4 cycles), 13 (49 cycles) and 15 (65 cycles) as well as a control block which had not been used in the experiment. Sub-samples obtained by fracturing at corners using a hammer and chisel in order to minimise post-experiment disruption to the stone. The samples were then mounted with epoxy resin on standard aluminium SEM stubs and gold coated before observation in a Cambridge Stereoscan 90 SEM. Each sample was mounted so that a cross-section from the external corner inwards (covering an area of c. 1-2 cm^2) could be viewed.

Two types of analysis were carried out to investigate two possible mechanisms by which the strength of the marble blocks was reduced during the experiment. Firstly, at 20 randomly located points on the cross-section, the presence and width of any fractures or grain boundary widening were noted (using a magnification of c. x 150). Strength may be being reduced by a gradual mechanical loosening of the tightly bound minerals within the marble (as suggested by Royer-Carfagni, 1999) and thus one would expect to see an increase in fractures and crevices between grains. Secondly, 15–20 points around the edges of the stone were observed and the depth to which surface cracking penetrated was noted. Cutting the blocks with a rock saw leads to some surface disruption, especially near-surface cracks. Another possible mechanism for the reduction of block strength during the weathering experiment could be the inwards propagation of these cracks.

7. Results

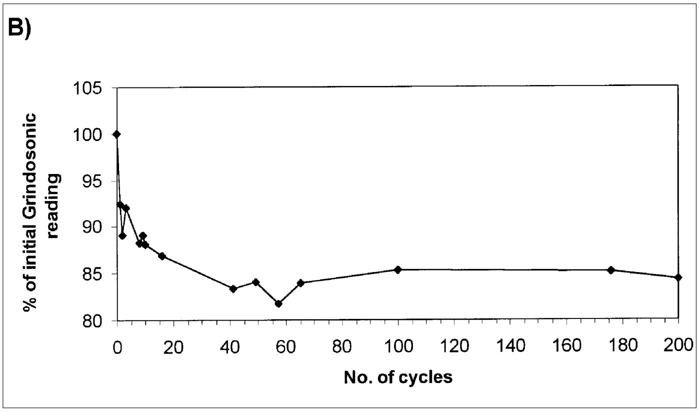
7.1. The Grindosonic

The results of the two experimental treatments are displayed in Figure 3. With the Wadi Digla treatment it is evident that after a few cycles the Grindosonic values (i.e. Young's modulus of elasticity) had fallen by about 10 per cent and that they suffered very little change after that. The other treatment also saw a rapid decline in elasticity values after just a few cycles, but with a rather greater change taking place overall. In the case of one block this amount to an 18 per cent decrease after 57 cycles. However, as with the Wadi Digla treatment, the amount of change decreased through time, and most blocks subjected to more than about 20 cycles had elasticity decreases of around 15 per cent. This response of marble to relatively modest cycles of heating, and the relatively limited changes that occur after initial cycles confirms the findings of Widhalm et al. (1996).



(A) Over 95 cycles of the Wadi Digla cycle
Marble experiment No. 2

0	100
3	92,2
5	91,8
13	92,28
21	91,51
33	91,2
49	90,47
61	90,5
74	89,88
95	89,78



(B) Over 200 cycles of the 3 hour treatment
Marble experiment No. 1

0	100
1	92,4
2	89,09
3	91,98
8	88,19
9	89,06
10	88,06
16	86,87
41	83,31
49	84,01
57	81,69
65	83,87
100	85,21
176	85,17
200	84,32

Figure 3: Changes in Grindosonic readings.

7.2. Scanning Electron Microscope

SEM observations reveal that the marble is composed of tightly interlocking calcite crystals with subsidiary amounts of Si, Al, K and Mg. Porosity appears to be very low.

A summary of the SEM observation is presented in table 2. From this table it is evident that there are no clear differences in the depth of near-surface fractures in the different blocks. This indicates that propagation of near surface cracks initially produced

Table 2: Summary data

Sample	%yes	%no	Mean w (μm)	Mean d (μm)
4C	25	75	4.3	389
4B 1 Cycle	55	45	4.2	373
4A	50	50	2.9	220
7A	63	37	4.5	362
7B 4 Cycles	65	35	5.2	328
7C	40	60	3.4	293
13A	65	35	6	566
13B 49 Cycles	80	20	4.2	431
13C	70	30	3.5	401
15A	74	26	8.2	401
15B 65 Cycles	85	15	6.6	533
15C	90	10	4.7	634
1C	50	50	4.4	601
1A Controls	30	70	3.5	
1B	40	60	7.3	

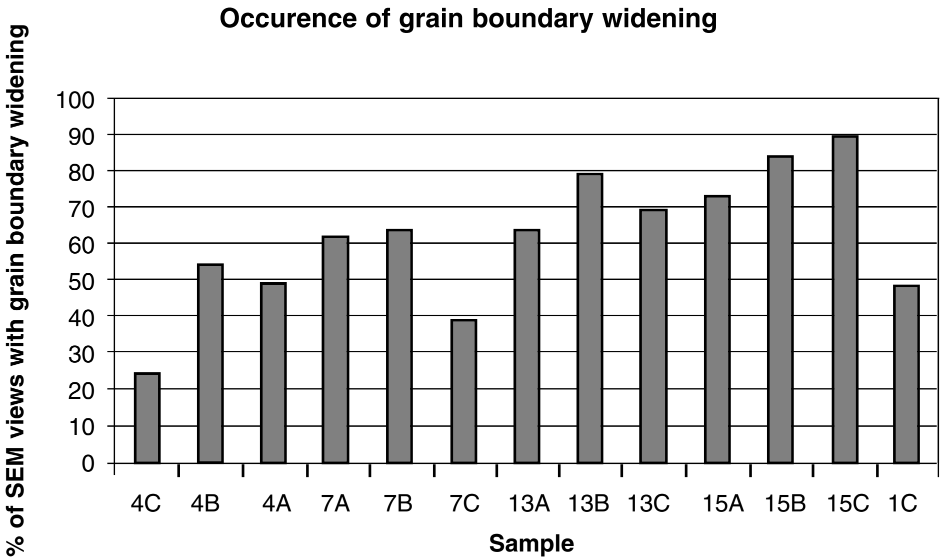


Figure 4: Observations of grain boundary widening under the SEM.

on cutting of the blocks is not occurring during the experiment. The observations of grain boundary widening and production of other sub-surface fractures and hollows are more revealing. Although it is evident from table 2 that there are no systematic trends in the width of such fractures, figure 4 illustrates a clear trend in the number of such openings. Thus, the SEM evidence backs up the hypothesis that the observed reduction in strength is caused by a gradual opening up of the internal porosity as grains are prized apart and, occasionally, fractured. This process is illustrated in Figure 5.

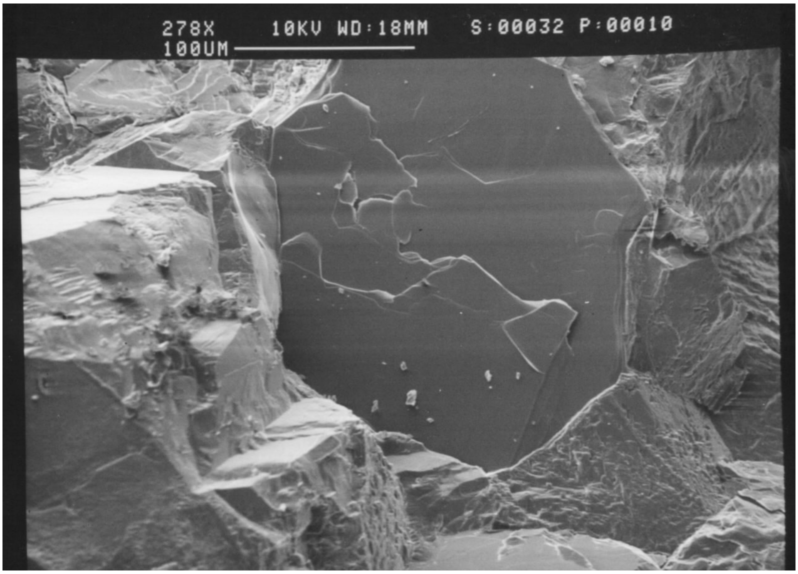


Figure 5 (A)

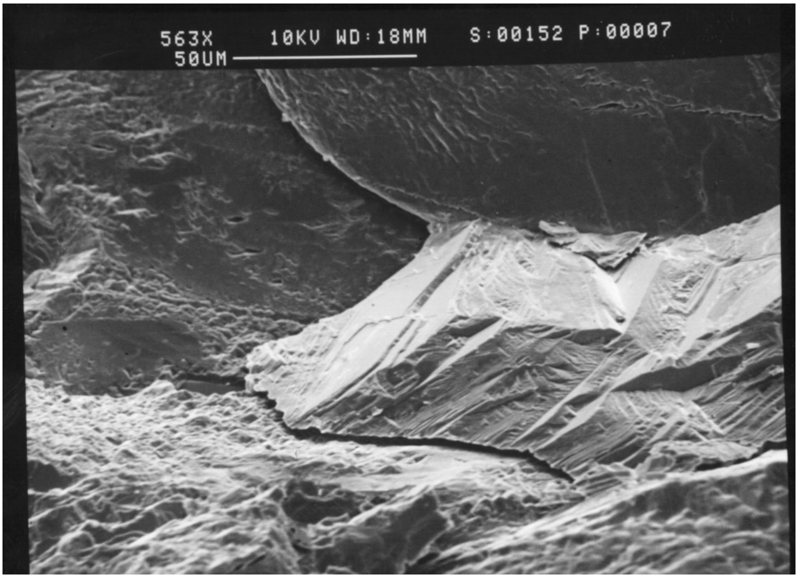


Figure 5 (B)

Figure 5 (C)

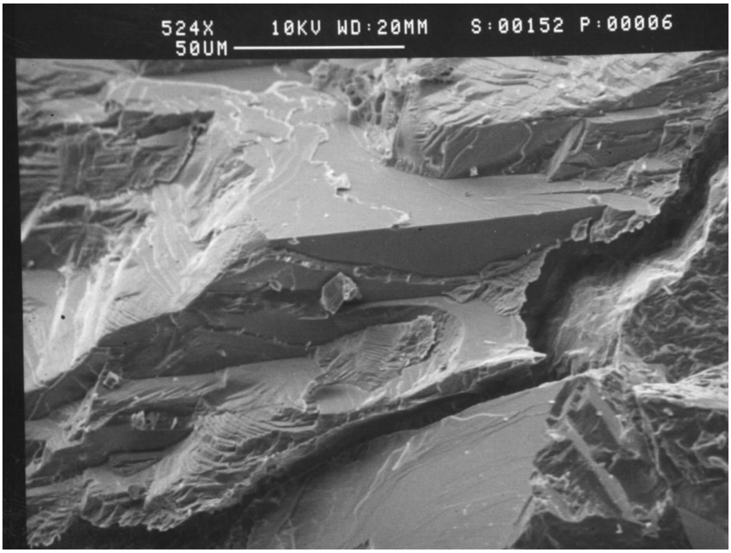


Figure 5: Scanning electron micrographs of marble samples
(A) Control sample prior to weathering. Magnification x 278, scale bar = 100 microns.
(B) Sample 15 after 65 cycles of weathering with the three hour cycle showing grain boundary widening. Magnification x 563, scale bar = 50 microns.
(C) Sample 15 after 65 cycles of weathering with the three hour cycle showing intense grain boundary widening. Magnification x 524, scale bar = 50 microns.

8. Discussion and Conclusion

The heating and cooling of Pentelicon marble through the range of temperatures encountered on rock surfaces in warm deserts, has been shown to lead to a measurable reduction in rock strength (as measured by Young's modulus of elasticity) after only a few cycles. This suggests that heating and cooling can cause marbles to degrade.

Even though no blocks suffered from visible cracking, the SEM study showed that the nature of the calcite grain interactions changed, therefore confirming the theory of Royer-Carfagni (l999) and the early observations by Rayleigh (l934). Such changes in grain to grain contact, and in rock strength, may permit other weathering processes (such as solution) to be more effective, thereby accelerating the rate of desert weathering.

References

ALLISON R. J. (l988): A non-destructive method of determining rock strength. Earth Surface Processes and Landforms 13, 729–736.
BLACKWELDER E. (1925): Exfoliation as a phase of rock weathering. Journal of Geology 33, 792–806.
COOKE R. U. (1979): Laboratory simulation of salt weathering process in arid environments. Earth Surface Processes, 4, 347–359.

GOUDIE A. S. (1993): Salt weathering simulation using a single immersion technique. Earth Surface Processes and Landforms, 18, 369–376.

GRIGGS D. (1936): The factor of fatigue in rock exfoliation. Journal of Geology, 44, 783–796.

PRICK A. (1997): Critical degree of saturation as a threshold moisture level in frost weathering of limestones. Permafrost and Periglacial Processes 8, 91–99.

RAYLEIGH A. (1934): The bending of marble. Proceedings of the Royal Society of London, 144A, 266–279.

RICE A. (1976): Insolation warmed over. Geology 4, 61–62.

ROSENHOLTZ J. L. AND SMITH D. T. (1949): Linear thermal expansion of calcite, var. Iceland Spar and Yule Marble. American Mineralogist 34, 846–854.

ROYER-CARFAGNI G. F. (1999): On the thermal degradation of marble. International Journal of Rock Mechanics and Mining Sciences, 36, 119–126.

TARR W. A. (1915): A study of some heating tests, and the light they throw on the cause of disaggregation of granite. Economic Geology, 10, 348–367.

WIDHALM C., TSCHEGG E. AND EPPENSTEINER W. (1996): Anisotrophic thermal expansion causes deformation of marble claddings. Journal of Performance of Constructed Facilities 10, 5–10.

WIDHALM C., TSCHEGG E. AND EPPENSTEINER W. (1997): Acoustic emission and anisotrophic expansion when heating marble. Journal of Performance of Constructed Facilities, 11, 35–40.

WILLIAMS C. B. (1923): A short bio-climatic study in the Egyptian desert. Bulletin of the Ministry of Agriculture, Egypt, Technical and Scientific Service, 81, 567–572.

WINKLER E. M. (1975): Stone: properties, durability in man's environment (2nd edition). Wien: Springer Verlag.

TEPELNÁ DEGRADACE MRAMORU

Résumé

Mnohé historické památky z mramoru mají nápadné projevy degradace, která je typická redukcí soudržnosti, vyšší porézností a tendencí k drobivosti. Znaky zhoršení kvality obkladového mramoru mají dokonce i některé moderní stavby. V této práci je ukázáno, že zahřátí a ochlazení mramoru z Penteliconu (Řecko) v rozmezí teplot povrchu hornin v horkých pouštích vede k měřitelné redukci pevnosti horniny již po několika cyklech. To nasvědčuje, že zahřátí a ochlazení může být příčinou degradace mramoru. I když jeho bloky nejsou postiženy viditelným rozlámáním, testy skenovacím elektronovým mikroskopem ukázaly, že původní spojení zrn kalcitu se změnilo. Takové změny na kontaktech mezi zrny a v pevnosti hornin mohou umožnit vyšší efektivitu dalších zvětrávacích procesů (např. rozpustnosti) a tím urychlovat působení pouštního zvětrávání.