

## Abstract

*This paper focuses on the effect of high temperature on the mechanical properties of a porous limestone that is widely used as dimension stone in Hungary. The changes in physical properties of 3 types of porous limestone were analyzed at 22 °C, 300 °C and 600 °C, respectively. The limestone specimens were also subjected to freeze-thaw cycles to assess the other extrinsic factor that influences the behavior. Parameters such as material density, bulk density, ultrasonic pulse velocity and tensile strength were measured and compared in different test conditions. The tests results indicate that fabric differences significantly influences the durability of tested limestones. Bioclastic grainstone is more frost resistant than ooidal grainstone or bioclastic packstone, but heating seems to reduce the pulse velocity and tensile strength of all tested limestone. It is suggested that cyclic freezing-thawing reduces the strength depending on the micro-fabric, while heating to 600 °C and the reduction of strength is less controlled by the fabric of the porous limestone.*

## Keywords

*tensile strength, ultrasonic pulse velocity, heating, freeze-thaw, porous limestone*

## 1 Introduction

Miocene limestone is one of the most common building stone in Central Europe. It is highly porous and easy to work with therefore it became one of the key construction material of the 18<sup>th</sup> and 19<sup>th</sup> century. This period is marked by emblematic monuments built from this stone, such as House of Parliament, Opera House or Citadella (Fig. 1) in Budapest, or Saint Stephan's Dom in Vienna and the Castle in Bratislava [1]. The limestone was also used for constructing bridges [2] and other stone structures from the Roman period. The stone is similar to the porous limestone of the Loire valley, France [3, 4]. Highly porous limestones are especially susceptible to weathering; gypsum crusts are formed on their surface as a result of air pollution – stone interaction [5, 6, 7]. Others studies suggest that limestone is not only sensitive to water but also salt weathering can significantly damage its structure [8,9]. The Miocene porous limestone was particularly analysed with respect to the influence of water content on its mechanical properties [10]. It has been found that water content influences the strength of this porous limestone similarly to other lithologies [11]. Limestones are important construction materials and their properties have been studied in details in recent years [12, 13,14]. Particular data set of carbonate rocks were published such as bulk density, effective porosity, ultrasonic pulse velocity and compressive strength [15]. They found that stone properties decrease after freeze-thaw cycles in wide range with respect to initial values. It was shown by Martinez et al [15] that carbonates with high open porosity (>10%) are less durable during weathering. On the basis of their microscopic observations it was stated that after a stable period when isolated micro-cracks appear the rock breakdown after a low number of cycles if micro-cracks turn into cracks and grow rapidly.

Thermal and freeze-thaw cycles also reduce the strength of carbonates [16]. The effect of high temperature on eight natural carbonate stones was also studied recently [17]. Four limestone and four marble were exposed to 200, 400, 600, 800 and 1000 °C and recorded the changes in physical properties such as colour changes, polish reception, daily physical change and variation of pH and temperature of the cooling solution.

<sup>1</sup> Department of Engineering Geology and Geotechnics  
Budapest University of Technology and Economics, H-1111 Budapest,  
Műegyetem rkp. 3., Hungary

\* Correspondent author, email: [torokakos@mail.bme.hu](mailto:torokakos@mail.bme.hu)

They found that the colour of natural stones becomes lighter in appearance with increasing temperature. Carbonate stones that are exposed to heat above 800 °C crack, fragmentize, spall and disperse.



**Fig. 1** Strongly weathered porous limestone wall, Citadella fortress (Budapest). Note the black crust formation and scaling crusts on the wall.

French soft and porous limestone called Tuffeau was particularly analysed in aspect of freeze-thaw resistance [3] and behaviour under the influence of high heat [4]. Tuffeau and Richemont limestone were subjected to freeze-thaw tests under laboratory conditions. They found that the two limestones have the same critical degree of saturation (about 85 %) and the frost damage is mostly controlled by pore-size distribution rather than the total porosity [3].

The relationship between the state of damage of stone and its non-destructive measurements results was analysed by colorimetry, too [4, 18]. Tuffeau samples were heated at different temperatures and also monitored using ultrasonic P-wave velocity methods [4]. They found that both measurements can be performed to assess the damage to building stone due to fire.

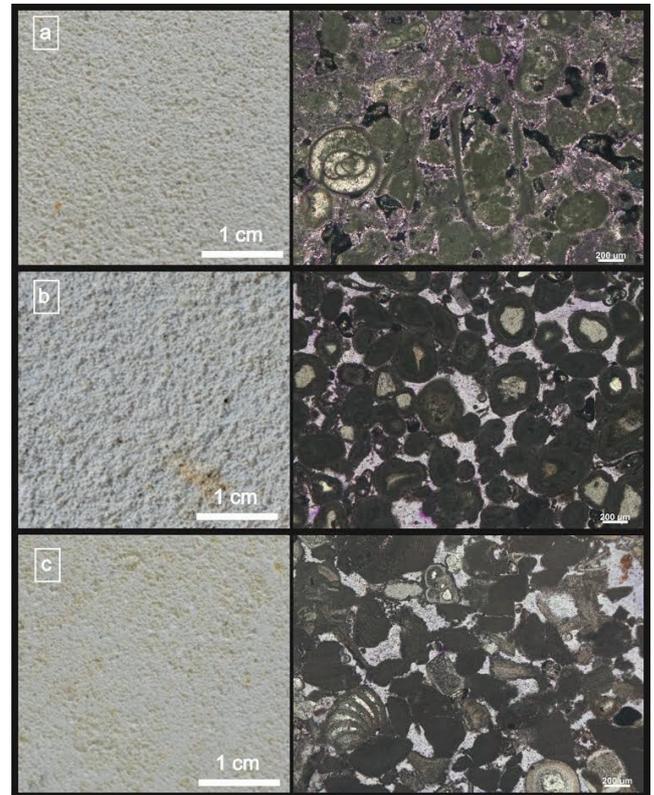
In this study we focus on the frost and high heat resistance of Miocene porous limestones of different origins and textural characteristics.

## 2 Materials and Methods

Three different Miocene limestone types from Hungary were used for the tests. Two types (Fig. 2 a, b) were extracted from Sósút quarry and one was obtained from Fertőrákos (Fig. 2 c).

The first studied limestone type from Sósút (marked by SF) is a bioclastic fine-grained limestone (Fig. 2 a). Its major textural elements are miliolid forams and small shell fragments besides micritic ooids. Its microfacies belongs to bioclastic ooid packstone. Micritic and microsparitic cement only partly occludes pores. Intraparticle porosity is predominant. The other lithotype from Sósút quarry (marked by SM) is a typical ooid-grainstone (Fig. 2 b). The micro-fabric is dominated by well-rounded or partly rounded ooids and micro-oncoids.

Pores are partly occluded by sparitic cement and partly open. The carbonate grains are well sorted with mean grain sizes of 0.3–0.4 mm. Besides calcitic grains a few carbonate coated quartz grains are also present. The third studied lithotype is a bioclastic limestone from Fertőrákos (marked by FR). It contains major amount of red algae fragment, forams and small intraclast (Fig. 2 c). The grains are moderately sorted with mean grain sizes of 0.1 to 0.8 mm. The microfacies is a bioclastic intraclastic grainstone.



**Fig. 2** Macroscopic and microscopic images of tested Miocene limestones (a: SF - fine grained limestone from Sósút; b: SM – medium grained ooidal limestone from Sósút quarry; c: FR – bioclastic limestone from Fertőrákos)

Cylindrical specimens with a diameter of 5 cm and a height of 2.5 cm were drilled and cut from stone blocks. From each lithotypes the cylindrical tests specimens were divided into 4 analytical groups; based on non-destructive test methods such as bulk density (EN 1936:2007), ultrasonic pulse velocity (EN 14579:2005) and apparent porosity measured by water saturation under normal atmospheric pressure (EN 13755:2008). This division of samples lead to groups of 6 specimens, which were used for water saturation, freeze-thaw and heating tests. One set of 6 specimens were heated up to 300 °C and another set to 600 °C and kept on the given temperature for 2 hours in electric oven. Samples were cooled down gradually at laboratory conditions (climate close to 22 °C/ RH 55). Mass and ultrasonic pulse velocity were measured before and after heating at 22 °C. 10 freeze-thaw cycles were performed according to EN 12371:2010, but specimens were saturated fully in water and frozen at –20 °C. Mass and ultrasonic pulse velocity were

recorded before and after the 10 freeze-thaw cycles. For observation of physical property changes, indirect tensile strength tests (Brazilian test method) were made according to the recommendations of ISRM (1978) [19]. The frozen samples were loaded and tested in water saturated phase; therefore these results are compared to the tensile strength of water-saturated samples. The number of test specimens and the applied test methodology (standards and guidelines) is shown in Table 1.

**Table 1** Test methods, Standards and number of samples

Method	Standard	Number of samples
Bulk density	EN 1936:2007	68
Ultrasonic pulse velocity	EN 14579:2005	68
Water saturation	EN 13755:2008	68
Freezing	EN 12371:2010	17
Heating	no Standard	17
Indirect tensile test	recommended by [3]	68

### 3 Results and Discussion

Average results and standard deviations are summarized in Table 2 for each testing group. Bulk density varies inconsiderably for the 3 types: for FR 1718–1739, for SM 1811–1821 and for SF 1591–1601 kg/m<sup>3</sup>, respectively.

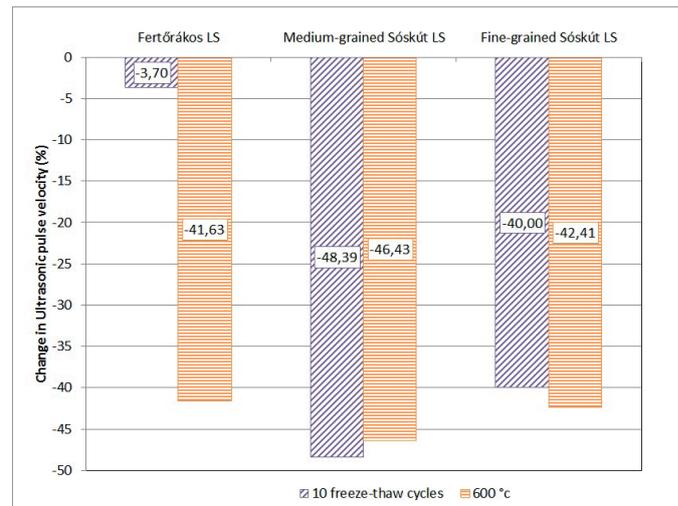
Ultrasonic pulse velocity values also show small differences, but another tendency is observed, since SF shows the highest values (2.6–2.9 km/s), FR the lowest (2.4–2.5 km/s) and SM is between the two former ones (2.5–2.7 km/s).

Apparent porosity values express the volume of the open pores in V%. SF has the highest porosity with values of 31.6–35.9 V%, which is significantly higher than the values of SM (23.0–24.4 V%) or FR (24.6–25.0 V%). From these results it can be assumed, that the parameters of Miocene porous

limestones show significant variations. These parameters are strongly controlled by depositional environment of the limestone and diagenetic processes.

Ultrasonic pulse velocity do not change after heating up to 300 °C, but decrease extensively after heating up to 600 °C without exception (FR: 41.6 %, SM: 46.4 %, 42.4 %) and after freezing except FR (FR: 3.7 %, SM: 48.4 %, SF: 40 %) (Fig. 3).

The change in mass is given in Table 1. It also shows the water absorption rate in m% - “water saturated” testing group. Data indicate that SF takes up the most amount of water (22.5 m %), while SM and FR absorb water in a nearly equivalent rate (13.1 m% and 14.5 m%).



**Fig. 3** Change in ultrasonic pulse velocity after 10 freeze-thaw cycles and heating up to 600 °C, with reference to results measured at room temperature

The porosity and dry density of the studied porous limestone are related however the data points are below the theoretic regression line calculated by Vásárhelyi [10] (Fig.4).

**Table 2** Summary of results (bulk density, ultrasonic pulse velocity, apparent porosity, change in mass, tensile strength. Limestone types and localities are abbreviated: FR- Fertőrákos quarry, SM-Sós-kút quarry medium grained, SF- Sós-kút quarry fine grained) (numerical values in brackets are standard deviations)

Testing group	Bulk density (kg/m <sup>3</sup> )	Ultrasonic pulse velocity (km/s)	Apparent porosity (V%)	After heating/freezing process		Tensile strength (MPa)
				Ultras. pulse vel. (km/s)	Change in mass (m%)	
FR - air dry	1718 (45)	2.5 (0.1)	24.6 (1.0)	2.5 (0.1)	0	2.04 (0.22)
FR - water sat.	1728 (36)	2.5 (0.2)	25.0 (1.4)	2.7 (0.3)	14.5 (1.1)	1.56 (0.27)
FR-Freeze	1739 (32)	2.5 (0.1)	24.9 (1.7)	2.6 (0.3)	-0.9 (0.4)	1.41 (0.31)
FR - 300 oC	1719 (27)	2.5 (0.1)	25.0 (1.3)	2.4 (0.1)	-0.2(0.03)	1.91 (0.11)
FR - 600 oC	1719 (27)	2.5 (0.1)	25.0 (1.3)	1.4 (0.1)	-0.6 (0.1)	1.01 (0.13)
SM - air dry	1811 (19)	2.5 (0.1)	24.4 (1.1)	2.5 (0.1)	0	1.38 (0.11)
SM - water sat.	1809 (15)	2.6 (0.3)	23.8 (1.4)	3.1 (0.7)	13.1 (0.8)	0.99 (0.20)
SM-Freeze	1821 (44)	2.7 (0.2)	23.04 (1.0)	1.6 (0.5)	1.2 (0.1)	0.21 (0.05)
SM - 300 oC	1824 (36)	2.4 (0.3)	23.22 (1.2)	2.4 (0.2)	-0.3 (0.1)	1.56 (0.07)
SM - 600 oC	1824 (36)	2.4 (0.3)	23.22 (1.2)	1.4 (0.2)	-0.6 (0.3)	0.67 (0.25)
SF - air dry	1591 (21)	2.9 (0.3)	35.6 (1.41)	2.9 (0.3)	0	1.03 (0.08)
SF - water sat.	1599 (25)	2.6 (0.3)	35.92 (1.3)	3.5 (0.4)	22.5 (1.0)	0.55 (0.06)
SF-Freeze	1602 (27)	2.9 (0.3)	35.7 (0.8)	2.1 (0.4)	0.7 (0.2)	0.14 (0.06)
SF - 300 oC	1601 (17)	2.8 (0.4)	31.6 (1.2)	2.7 (0.04)	-0.1(0.01)	1.01 (0.15)
SF - 600 oC	1601 (17)	2.8 (0.4)	31.6 (1.2)	1.7 (0.1)	-0.5 (0.1)	0.59 (0.05)

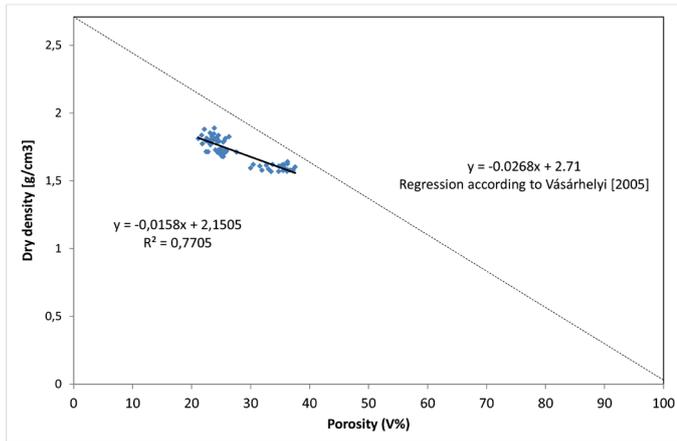


Fig. 4 Relationship between dry density and porosity of studied limestone in comparison with the theoretic regression line calculated by Vásárhelyi [10]

The results marked by “freeze” (Table 2) show the alteration in mass in m% after 10 freeze-thaw cycles. Comparing these data sets it is clear that SM and SF do not lose mass during freeze-thaw cycles. Instead an increase in mass was recorded for both lithologies (1.2 m% for SM and 0.7 m% for SF). FR loses 0.9 m% in mass and cracks appeared on its surface.

When the samples were subjected to 300 °C and 600 °C a loss in mass was recorded after heating to 300 °C and especially to 600 °C. Such a mass loss was already recorded at other limestone specimens [17, 20].

Heating different limestone specimens up to 600 °C resulted in very similar loss in weight (FR: -0.6 m%; SM: -0.6 m%; SF: -0.5 m%). Heating up to 300 °C has minor effect on weight of specimens with a material loss of 0.3m% (-0.2 m% FR; -0.3 m% SM and -0.1 m% SF).

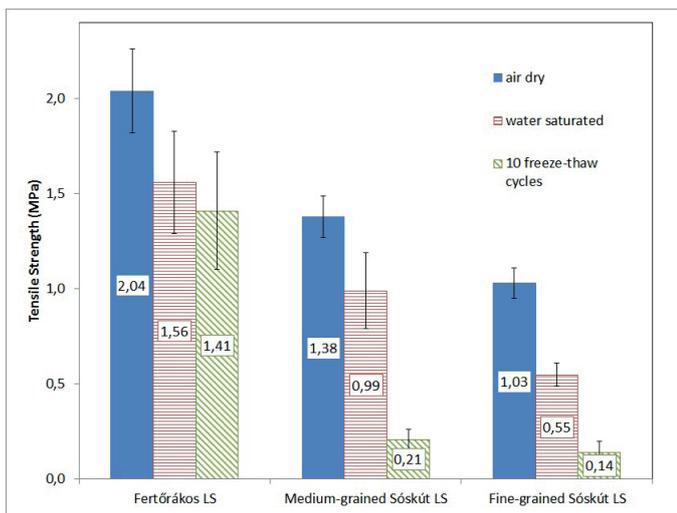


Fig. 5 Tensile strength results in air dry, water saturated condition and after 10 freeze-thaw cycles

Tensile strength of water saturated limestone specimens compared to air dry limestone specimens show a detectable decrease (Fig. 5). Freeze-thaw cycles also cause a significant decrease in tensile strength, but this decrease is not uniform. The highest loss in tensile strength was observed at Sós-kút

limestone samples. The decrease in strength is remarkable both for SM and for SF specimens. The loss is -78,8 % and -74,6 %, respectively (Fig. 6). Fertőrákos limestone does not suffer such a loss in tensile strength after 10 freeze-thaw cycles. Its strength reduction is just -9,6 % compared to the results obtained on water saturated specimens.

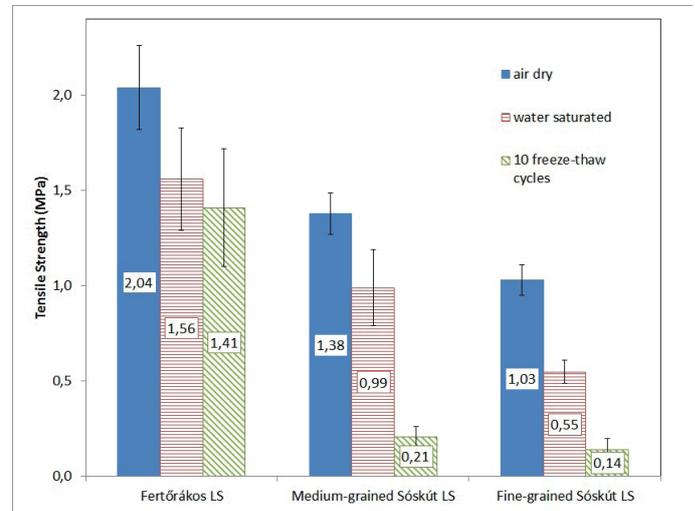


Fig. 6 Tensile strength results in air dry (20 °C), after heating up to 300 °C and 600 °C

The regression between tensile strength in dry and saturated or frozen conditions can be also calculated. It is observable that the resistance against freeze-thaw cycles is mainly controlled by deposition and diagenesis of limestone, i.e. micro-fabric. No linear regression was found in between these values (Eq. 1) (Fig. 7).

$$\sigma_{fr} = 0.10 \sigma_{dry}^{3.28} \quad (R^2 = 0.84) \quad (1)$$

After heating up to 300 °C the tensile strength do not change considerably (Fig.6). On the other hand significant decrease in tensile strength is observed when the specimens were heated up to 600 °C. Loss in strength was 50,5 %, 51,5 %, and 42,7 % for FR, SM and SF, respectively.

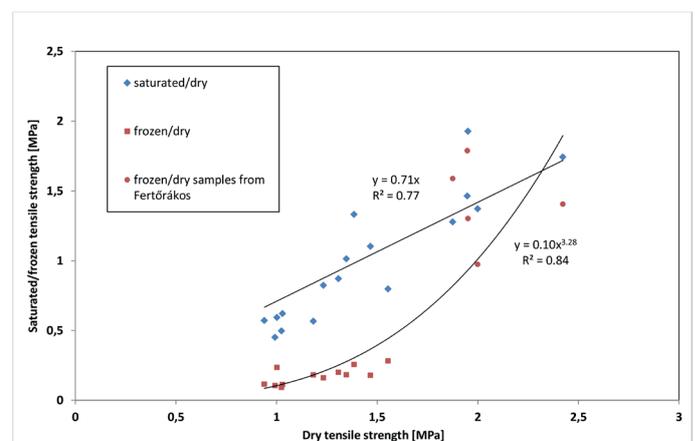


Fig. 7 Relationship between tensile strength of dry and saturated/frozen limestone specimens

When the effect of freeze-thaw is compared to the effect of heating an interesting trend is observed. Freeze-thaw reduces the strength of two limestones (SM, SF) more than heating up to 600 °C (Fig. 8). To the contrary, the heat related loss in tensile strength is more significant at Fertőrákos limestone than the freeze-thaw related strength reduction (Fig. 8). These differences suggest that micro-fabric controls the freeze-thaw durability. The control of micro-fabric in frost durability was already demonstrated by Martinez-Martinez [15].

The loss in strength related to heat (600 °C) is very similar for all the three studied limestones, which implies that the material composition (namely the presence of calcite in all studied samples) control the heat durability of limestones. It is in good agreement with the previous findings, that the transformation of calcite takes place above 400 °C [20].



Fig. 8 Change in tensile strength after 10 freeze-thaw cycles and heating up to 600 °C

#### 4 Conclusions

The mass increase of medium grained Sósút porous limestone (SM) and fine grained Sósút porous limestone (SF) after freeze-thaw cycles is related to the formation of ice crystals in the pores and related micro-cracking and opening up of pore system. These samples can absorb more water in these newly formed pores. The high porosity and weakening of bonds between the carbonate grains is also reflected in the very low tensile strength values obtained after 10 freeze-thaw cycles. Such reduction in tensile strength was not recorded at samples obtained from Fertőrákos. These differences in durability against freeze-thaw is related to micro-fabric differences, i.e. different sizes of carbonate grains, different rates of cementation and differences in porosity and pore-size. Our tests suggest that lithotypes that are characterized by poorly sorted carbonate grains and mixture of sparitic and micritic cement are more durable against freeze-thaw than the micro-fabrics with good sorted carbonate grains and uniform cement.

High temperature equally reduced the strength of all studied limestones. This suggests that micro-fabric differences are not reflected in heat resistance of limestone. Hence, the heat resistance of limestone is rather controlled by the mineralogy than the micro-fabric.

#### Acknowledgement

The financial support of National Research, Development and Innovation (NKFI) Fund (K 116532) is appreciated.

#### References

- [1] Török, Á., Rozgonyi N, Prikryl, R., Prikrylová, J. "Leithakalk: the ornamental and building stone of Central Europe, an overview". In: Prikryl, R. (ed), *Dimension stone*. Balkema, Rotterdam, pp. 89–93, 2004.
- [2] Bögöly Gy., Török Á., Görög P. "Dimension stones of the North Hungarian masonry arch bridges". *Central European Geology*, 58 (3) pp 230–245, 2015. <https://doi.org/10.1556/24.58.2015.3.3>
- [3] Al-Omari, A., Beck, K., Brunetaud, X., Török, Á., Al-Mukhtar, M. "A control factor of freeze-thaw damage of porous limestones at Castle of Chambord, France". *Engineering Geology*, 185, pp. 71–80. 2015. <https://doi.org/10.1016/j.enggeo.2014.11.018>
- [4] Beck, K., Janvier-Badosa, S., Brunetaud, X., Török, Á., Al-Mukhtar, M., "Non-destructive diagnosis by colorimetry of building stone subjected to high temperatures." *European Journal of Environmental and Civil Engineering*, 20, 6, pp. 643–655. 2016. <https://doi.org/10.1080/19648189.2015.1035804>
- [5] Török, Á., Rozgonyi, N., "Morphology and mineralogy of weathering crusts on highly porous oolitic limestones, a case study from Budapest". *Environmental Geology*, 46(3–4) pp. 333–349. 2004. <https://doi.org/10.1007/s00254-004-1036-x>
- [6] De Kock, T., Van Stappen J., Fronteau, G., Boone, M., De Boever, W., Dagrain, F., Silversmit, G., Vincze, L., Cnudde, V. "Laminar gypsum crust on lede stone: Microspatial characterization and laboratory acid weathering". *Talanta*, 162, pp. 193–202. 2017. <https://doi.org/10.1016/j.talanta.2016.10.025>
- [7] Török, Á., Licha, T., Simon, K., Siegesmund, S. "Urban and rural limestone weathering; the contribution of dust to black crust formation". *Environmental Earth Sciences*, 63, 675–693. 2011. <https://doi.org/10.1007/s12665-010-0737-6>
- [8] Alves, C., Figueiredo, C., Ilharco, L.M., Fidalgo, A., Mauricio, A., Aires-Barros, L. "Specific surface area and salt weathering of limestones: a laboratory study". *Quarterly Journal of Engineering Geology and Hydrogeology*, 46 pp. 477–484. 2013. <https://doi.org/10.1144/qjegh2012-044>
- [9] Gokceoglu, C., Turer, A., Nefeslioglu, H.A., Turer, D., Meral, C. "Safety assessment of limestone-based engineering structures to be partially flooded by dam water: A case study from northeastern Turkey". *Engineering Geology*, 209, pp. 44–55. 2016. <https://doi.org/10.1016/j.enggeo.2016.05.003>
- [10] Vásárhelyi, B. "Statistical Analysis of the Influence of Water Content on the Strength of the Miocene Limestone". *Rock Mechanics and Rock Engineering*, 38, pp. 69–76, 2005. <https://doi.org/10.1007/s00603-004-0034-3>
- [11] Vásárhelyi, B. Ván P. "Influence of the water content for the strength of the rock". *Engineering Geology*, 84, pp. 70–74. 2006. <https://doi.org/10.1016/j.enggeo.2005.11.011>
- [12] Wilhelm, K., Viles, H., Burke, O., Mayaud, J. "Surface hardness as a proxy for weathering behavior of limestone heritage: a case study on dated headstones on the Isle of Portland, UK". *Environmental Earth Sciences*, 75, paper 931, 2016. <https://doi.org/10.1007/s12665-016-5661-y>

- [13] Gizzi, F.T., Sileo, M., Biscione, M., Danese, M., de Buergo M. A. "The conservation state of the Sassi of Matera site (Southern Italy) and its correlation with the environmental conditions analysed through spatial analysis techniques". *Journal of Cultural Heritage*, 17 pp. 61–74. 2016. <https://doi.org/10.1016/j.culher.2015.05.002>
- [14] Pappalardo, G. Mineo S., Monaco C. "Geotechnical characterization of limestones employed for the reconstruction of a UNESCO world heritage Baroque monument in southeastern Sicily (Italy)". *Engineering Geology*, 212, pp. 86–97. 2016. <https://doi.org/10.1016/j.enggeo.2016.08.004>
- [15] Martínez-Martínez, J., Benavente, D., Gomez-Heras, M., Marco-Castano, L., Garcia-del-Cura, M. Á. "Non-linear decay of building stones during freeze-thaw weathering processes". *Construction and Building Materials*, 38 pp. 443–454. 2013. <https://doi.org/10.1016/j.conbuildmat.2012.07.059>
- [16] Yavuz, H., Altindag, R., Sarac, S., Ugur, I., Sengun N. "Estimating the index properties of deteriorated carbonate rocks due to freeze-thaw and thermal shock weathering". *International Journal of Rock Mechanics & Mining Sciences*, 43 pp. 767–775. 2006. <https://doi.org/10.1016/j.ijrmms.2005.12.004>
- [17] Ozguven, A., Ozcelik Y. "Investigation of some property changes of natural building stones exposed to fire and high heat". *Construction and Building Materials*, 38 pp. 813–821. 2013. <https://doi.org/10.1016/j.conbuildmat.2012.09.072>
- [18] Antal Á, Görög P, Veres Á.L., Balla P, Török Á. "Colour of stone slabs under different standard illuminations". *Periodica Poltechnica Civil Engineering*, 61(1) pp. 66–74. 2017. <https://doi.org/10.3311/PPci.9038>
- [19] Bieniawski, Z.T., Hawkes, I., "Suggested methods for determining tensile strength of rock materials - 1. suggested method for determining direct tensile strength". *International Journal of Rock Mechanics and Mining Sciences*, 15(3) pp. 99–103. 1978.
- [20] Gomez-Heras M., Alvarez de Buego M., Fort, R, Hajpál, M., Török Á., Varas M. J. "Evolution of porosity in Hungarian building stones after simulated burning". In: Fort, R, Alvarez de Buego M., Gomez-Heras M. & Vazquez-Calvo C. (Eds): *Heritage Weathering and Conservation*, Taylor & Francis/Balkema, London. Vol. I, pp. 513–519. 2006.