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Proceeding Paper

Effect of Freeze–Thaw Cycles on the Flexural Strength of Greek Natural Stones †

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Abstract: The purpose of this study is to explore the potential influence of cyclic freezing–thawing on the flexural strength of Greek natural stones that are extensively utilized for construction or decoration purposes. Such testing approaches are an indispensable part of the stone selection criteria due to their ability to assess the stone's durability. It is especially crucial in locations where exposure to freeze–thaw cycles is common. For this study, samples from various types of stones, including limestones, calcite and dolomite marble, cipollino marble, schists, and mylonites, were examined to assess their flexural strength under concentrated loads and their associated values after freeze–thaw cycles in compliance with European standards (EN). The results show that stones of the same type have comparable flexural strength behaviour. Only in a few cases were significant increases or decreases in strength observed. Specific stones demonstrated a substantial reduction in their flexural strength when exposed to freeze–thaw cycling despite their initially calculated high values without having undergone the frost durability test.

Keywords: freezing–thawing; flexural strength; ornamental stones; statistical analysis

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1. Introduction

Greek natural stones have been widely employed in numerous construction projects for thousands of years due to their enduring durability and their striking visual appeal. Nevertheless, natural stones inevitably undergo various degradation processes as a result of both natural and artificial destructive factors throughout their lifespan. One of the most significant natural decay factors is weathering caused by freezing and thawing. This degradation is due to climatic temperature changes, and it negatively affects the mechanical properties of the stone, limiting its durability. Freeze–thaw resistance is a crucial aspect of stone durability that holds great significance for stone export, particularly in regions with severe exposure conditions.

The effect of freeze–thaw cycles on the deterioration degree of natural stones has been proven to relate to the moisture content [1,2], which is usually transported in the stone's pores via the diffusion of vapor from the air and the capillary transport of the liquid phase. The porosity, pore structure, and pore size distribution might be significant factors affecting the durability and degradation of the stone, determining the interaction between material and moisture, the degree of saturation, and the potential freezing of water inside the pores. When water freezes in a porous material, the material may be damaged. Chen et al. [1] and Hori and Morihiro [3] have explained the mechanism for the freeze–thaw damage of rocks when they were frozen at low temperatures and then thawed. Prick et al. [4] and Bellanger et al. [5] have underlined the importance of the porous network's characteristics, such as the distribution of pore size. Freeze–thaw cycles severely affect the mechanical properties of stones, such as strength and compressibility [6,7]. Hale and Shakoor [8] reported that porosity values in the range between 2 and 7 vol% caused a significant reduction in the compressive strength of sandstones during multiple freeze–thaw cycles. Ruedrich et al. [9] performed long-term investigations on the physical weathering of building stones induced by freeze–thaw action. Khanlari and Abdilor [10] studied the influence of freeze–thaw cycles on the physical and mechanical properties of sandstones and observed that by increasing the number of freeze–thaw cycles, the P-wave velocity and uniaxial compressive strength decreased, whereas the porosity values showed an increasing trend. Momeni et al. [11] investigated the degradation in the engineering properties of Alvand granitoid rocks under freeze–thaw cycles using a series of physico-mechanical tests. Noor-E-Khuda et al. [12] studied the effect of accelerated weathering using freeze–thaw cycles on thin granite panels used in veneer claddings, and their results showed noticeable evidence of the physical degradation of the examined specimens. Pápay and Török [13] focused on the frost and heat resistance of Miocene porous limestones of different origins and textural characteristics and assumed that the parameters of these limestones were strongly controlled by the depositional environment of limestone and diagenetic processes. A detailed literature review covers the main topics in stone deterioration due to the freeze–thaw effect. However, special attention is focused on the physical weathering of a stone or the stone's compressive strength, and the results are given for a small number of stones. Thus, this indicates that further research is required to investigate the impact of freezing–thawing on the flexural strength of stones, which is a crucial aspect of the stone selection process aimed at assessing the stone's durability. This is particularly significant in areas where freeze–thaw cycles are prevalent.

On this basis, the present study aims to contribute to the investigation of the effect of frost deterioration on the strength behaviour of stones by examining several types of Greek natural stones that are widely used for construction and decorative purposes. For all materials under evaluation, the flexural strength under concentrated loads after exposure to freeze–thaw cycles has been determined. Additional flexural strength tests were conducted without performing frost resistance cycle testing to compare the corresponding results. The frost resistance of specimens was assessed via controlled freezing and air-thawing in water cycles within a temperature range between +17 °C and −12 °C. The freeze–thaw tests were carried out for 48 cycles, and the flexural strength of one-hundred and twenty-two samples from limestones, marbles, schists, and mylonites quarried from different Greek regions was determined in compliance with applicable European (EN) standards. These tests were conducted at LITHOS, the accredited Ornamental Stones Quality Control Laboratory of the Hellenic Survey of Geology and Mineral Exploration (HSGME).

2. Materials and Methods

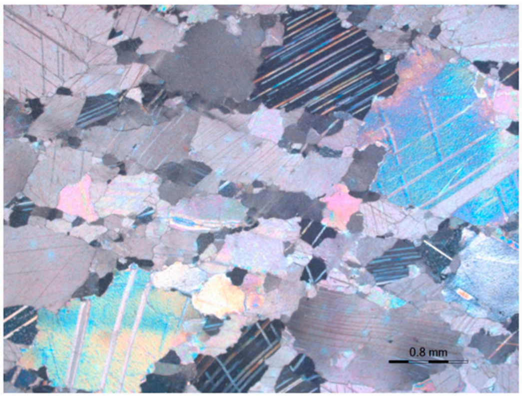
Greek ornamental stones are among the most famous stones, and Greece is a major producer and exporter of these materials at a global level. Thus, it is crucial to ensure the quality of the final products and reduce the risk of using stone of poor durability on projects, especially in locations that experience different climate conditions. For this reason, various mineralogical types of limestone (i.e., biomicrite, bioclastic, sparitic, microsparite, dolomite, etc.), marble (calcite, dolomite, and cipollino), and calcareous schists and mylonites according to EN 12407 [14] for petrographic assessments are considered to obtain a complete investigation of the potential effect of frost deterioration on their flexural strength. A total of one-hundred and twenty-two stones (thirty-nine limestones, seventy-one marbles, twelve schists, and mylonites), which are samples sent mainly by quarry owners to determine the samples' physical–mechanical properties and petrographic characteristics, were tested in the laboratory. A minimum set of twenty (ten for initial flex testing and ten more for freeze–thaw cycling and flex testing after) specimens of each stone was appropriately prepared in the form of rectangular prisms 180 × 90 × 30 mm within ±1 mm, in accordance with EN 12372 [15]. All specimens were dried at 70 ± 5 °C to constant mass and then stored at 20 ± 5 °C until fully tempered. A uniformly increased load at a rate of 0.25 MPa/s determined flexural strengths after specimen failure. The reported flexural strength value was determined as the arithmetic average of ten tested samples from the same material. For each material, ten specimens were exposed to 48 freeze–thaw cycles according to EN 12371 [16] and strength-tested afterward. Before frost resistance testing, specimens were initially moisture-saturated via immersion in tap water for at least 48 h and then placed in the freeze–thaw chamber according to EN 12371 [16]. Each cycle consists of a 6 h freezing period in the air from +17 °C to −12 °C, followed by 6 h of thawing from −12 °C to +17 °C, during which the specimens were immersed in water. After the completion of this test, all specimens were prepared for the determination of flexural strength, as described above. In addition, standard-sized thin sections measuring 27 × 47 mm and 30 µm in nominal thickness were prepared for petrographic examinations. To determine whether an observed strength loss (or gain) is genuine, the data per stone type were critically assessed via mathematical–statistical t-distribution analysis [17].

3. Results

The flexural strength values obtained after 48 freeze–thaw cycles were compared to those of materials not subjected to freeze–thaw cycles. Based on statistical analyses, standard deviations varied significantly in all types of stone. Limestones exhibit larger changes relative to the other materials tested, displaying a reduction in strength of approximately 74%. Of this amount, 50% exhibit a decrease in strength ranging from −25% to −67%, with correspondingly high standard deviations ranging from 2.0 to 8.8. According to the statistical analysis for the tested limestones, the number of degrees of freedom is defined by the relation $\nu = n - 1 = 39 - 1 = 38$, where n denotes the observations (thirty-nine average values of flexural strength). Confidence intervals of ±1.5, ±1.8, and ±2.4 and ±1.4, ±1.7, and ±2.3 were computed at confidence levels of 90%, 95%, and 99%, respectively, concerning the initial mean flexural strength value of 15.3 MPa (with a standard deviation of 5.4) and the mean value after exposure to 48 cycles of freezing–thawing 12.6 MPa (with a standard deviation of 5.2). For example, out of all intervals computed at the 95% level, 95% should contain the parameter's true value, which is 15.3 ± 1.8 (MPa) and 12.6 ± 1.7 (MPa), respectively, for the two studied cases. This means that the flexural strength of these limestones is affected by freeze–thaw cycle testing at the above confidence levels. The confidence interval is defined by the distribution of the location of the sample mean relative to the true mean divided by the sample's standard deviation after multiplication by the standardized term $n^{-0.5}$. According to petrographic analyses, limestones consist of 90–100% calcite with minor or trace amounts of quartz, aragonite, dolomite, albite, feldspars, or chlorite.

The results of thirty-two calcite marbles indicate almost a 9% decrease in their mean strength value (from 16.2 MPa to 14.7 MPa). The corresponding computed confidence intervals at confidence levels of 90%, 95%, and 99% are ±1.3, ±1.6, and ±2.2, respectively, for the initial mean strength value, while these values are ±1.4, ±1.7, and ±2.3 for the mean value of the flexural strength after frost resistance testing. Calcite marbles consist of 85–100% calcite with minor dolomite, mica, quartz, muscovite, or epidote. Figure 1 illustrates a thin section micrograph of a calcite marble comprising calcite and minor dolomite, showing granoblastic and equigranular texture, and compact to irregular fabric. The white coloration results from its mineralogical composition (calcite) and the characteristic red-coloured ribbons that result from the impregnation of Fe-oxides/hydroxides along its tectonic fractures.

Twenty-three dolomite marbles were tested as well. Half presented generally low initial flexural strength values ranging between 2.3 MPa and 6.3 MPa. According to the petrographic examination, they have fine-grained texture, with hypidiomorphic dolomite crystals, calcite veins, and agglomerates, or calcite veins along tectonic fractures. Initial flexural strength values that were close to 15.0 MPa were determined for three of these stones that presented medium to fine-grained texture, hypidiomorphic to allotriomorphic dolomite crystals, and scattered calcite crystals. Only one of the dolomite marbles tested had a relatively high initial strength (18.5 MPa), while the average for the limestones tested was 8.8 MPa. The mean post-test value was 8.2 MPa, showing no effect of frost resistance on flexural strength.



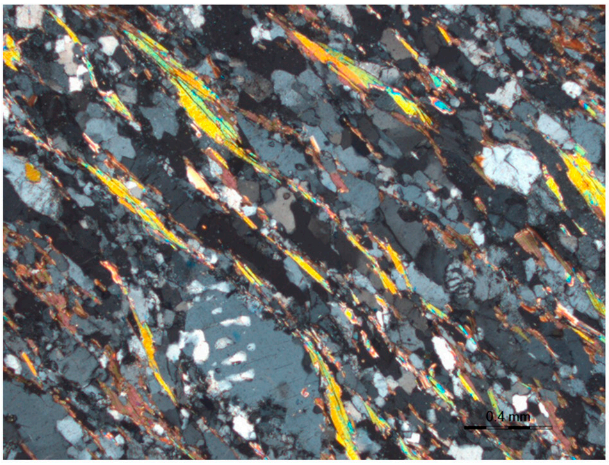
Calcite marble

Mineral composition	%
Calcite	95
Dolomite	5

Figure 1. Thin section micrograph of a calcite marble.

Greek cipollino marbles generally had higher flexural strength values compared to those obtained for calcitic and dolomitic marbles. A mean value of 22.1 MPa was determined for the sixteen stones (one hundred and sixty specimens), while a slight decrease of −4% was calculated for the corresponding flexural strength after freeze–thaw cycling (21.2 MPa). Ten of the sixteen materials tested lose strength (up to −20%) and the other six gain strength by +5% or +10%. Calcite is the main mineral component of cipollino marble, accounting for 70–92%, with quartz, muscovite, chlorite and albite also identified.

The calculated initial mean flexural strength of twelve schists and mylonites quarried from four different Greek regions was 29.2 MPa and the corresponding post-test value was 27.3 MPa. Petrographic examination of the stone with the highest initial strength (45.1 MPa) revealed fine-grained mylonite, hypidiomorphic, oriented and elongated crystals, undulated extinction of quartz phenocrysts, and mica-fish of muscovite. It is composed of 36% quartz, 32% feldspars-albite, 30% muscovite-mica and minor kaolinite, chlorite and opaque minerals. The initial strength determined for six of these stone types had values greater than 30.0 MPa, while only two of them had values less than 20.0 MPa. Six of these lose flexural strength (from −11% to −25%), three show a decrease between −5% to −2%, while two gain strength up to +9%. A thin section micrograph of a schist is shown in Figure 2.



Schist

Mineral composition	%
Feldspars	41
Quartz	40
Biotite	14
Muscovite	4
Chlorite	1

Figure 2. Thin-section micrograph of a schist.

In general, marbles, schists, and mylonites proved to be resistant to freeze–thaw cycles without any signs of deterioration, possibly indicating the important role of their composition. These results are plotted in Figure 3.

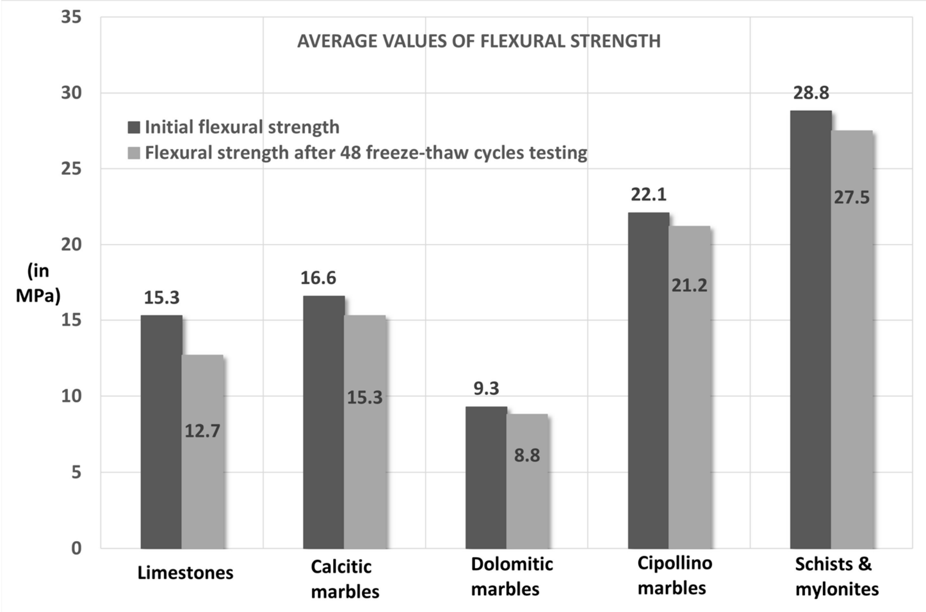


Figure 3. Average values of flexural strength.

4. Discussion

In this paper, an attempt was made to identify materials with flexural strengths that were affected by freeze–thaw cycles. For this purpose, a large number comprising five types of natural stone were tested. To determine whether or not the difference between the mean flexural strength without and with the application of freeze–thaw cycles is significant, statistical analysis is used.

Although all the specimens were optically unaffected by the freezing and thawing process, the comparison showed a significant decrease of about −34% to −67% in the corresponding average strength values of ten of the thirty-nine limestones. This reduction was most pronounced in biomicrite, biopelmicrite, or fossil-bearing and bioclastic limestones. Since the mineral composition of all limestones was almost the same, the amount of bioclasts, skeletal grains or particles, or fossil traces that made up the affected limestones played a crucial role. Twelve of the limestones tested showed a reduction in strength between −10% and −30%, while only eight showed a reduction of almost −3% (up to −9%). It should also be noted that one of the limestones tested showed an unexpectedly remarkable increase (51%) in the corresponding strength values after being exposed to 48 freeze–thaw cycles, and this was possibly influenced by the presence of organic traces or other intrinsic properties, such as microstructure, texture, or internal stresses, parameters that are outside the scope of this paper. Correspondingly, six of the limestones' strength increased by +1% up to +8%.

Overall, the post-flexural strength of three calcite marbles decreased significantly from −44% to −30%, eleven decreased from −26% to −10%, and eight decreased from −9% to −4%, although one actually increased in strength. The initial flexural strength of the tested dolomite marbles in most cases was very low. The behaviour relative to freeze–thaw exposure was correspondingly the same, with very low post-test values.

The freeze–thaw test seems to mainly have a negative effect on three of the sixteen cipollino marbles, which lost between −13% and −20% of their flexural strength. The other materials tested showed a slight decrease in flexural strength ranging from −2% to −10% and a corresponding slight increase from +5% to +10%, which means that there was no significant change in the calculated average values after freezing and thawing. The same results were obtained from the twelve schists and mylonites tested, and their average initial strength value was 29.2 MPa and the corresponding post-test value was 27.3 MPa (a slight decrease of −6.5%).

An attempt to correlate the results between the calculated mean flexural strength and the corresponding values obtained after the freeze–thaw test, except for the values of the limestones, showed a linear relationship with a very good correlation (with a coefficient of determination $R^2 = 0.934$), as shown in Figure 4. Limestones could not be included in the overall results because no correlation equation could be found due to their random behaviour after exposure to the freeze–thaw test.

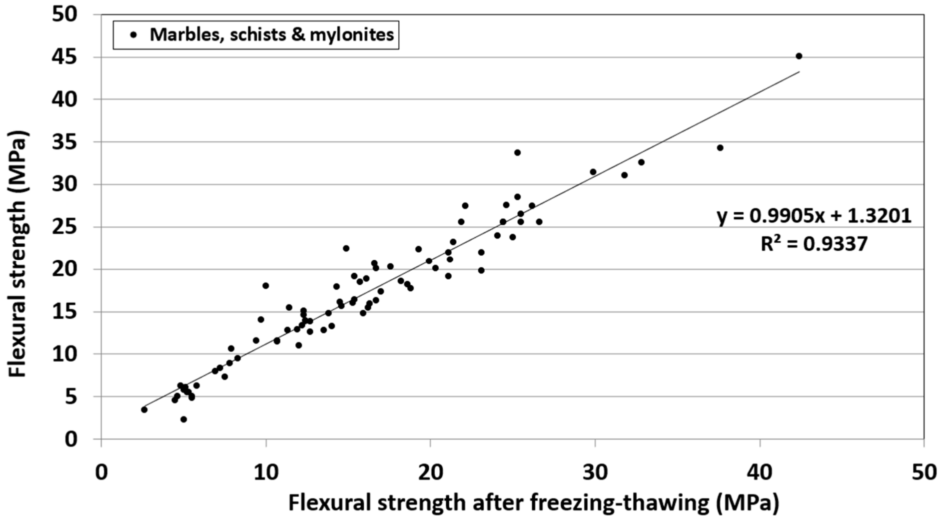


Figure 4. Linear relationship between the corresponding mean flexural strength values.

5. Conclusions

The main objective of the present work was to investigate the potential influence of freeze–thaw cycles on the flexural strength of Greek natural stones, which are widely used as building materials in various construction projects. The selected materials to be tested represent a large part of the total production in terms of quarrying in Greece. In addition, Greece is now one of the world's leading natural stone producers in terms of production and export volumes. The durability of the stone is therefore of great importance, especially for locations with harsh climatic conditions. All specimens from thirty-nine limestones, seventy-one marbles, twelve schists, and mylonites were prepared for testing according to European standards. The comparison between the corresponding average values of flexural strength under concentrated loads and those obtained after carrying out the freeze–thaw cycle test showed that limestones were generally the most affected materials (in general, a reduction of almost 18%), especially those containing organic fragments such as bio-clasts, skeletal or bearing trace fossils, etc. Calcite marbles, particularly cipollino marbles, schists, and mylonites, which are generally more durable stones than the other materials tested, did not seem to be significantly affected by the freeze–thaw cycle tests (generally up to 9%). It should also be noted that the flexural strength values calculated for dolomite marbles were generally very low, and there was a reduction in their strength by an order of 7% after being subjected to the freeze–thaw test. The conclusions for all types of tested stones were supported by statistical analysis, showing the frost deterioration effect on the limestones. Further research into the reasons for the differences between the corresponding flexural strength values is suggested by the theoretical interpretation obtained from the above statistical analysis. In addition, a linear relationship with a very good correlation was found between the corresponding test results, except for those of the limestones, due to their random behaviour after exposure to freeze–thaw cycles. The mechanism for the loss or even increase in the flexural strength of specific isolated cases could possibly be explained by their heterogeneity; the content of dolomite, which is the main mineral component; the presence of veins and joints; and the degree of welding. However, further explanations of this mechanism could be given after a detailed study of the stones' microstructure, a specific issue that was beyond the scope of this research study. The main purpose of this paper was to look at the general patterns of how frost damage may affect the flexural strength of stones and the types of stones that are affected. A detailed characterisation study of the limestones tested above will be carried out, and the results will be presented in a future research paper.

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References

1. Chen, T.C.; Yeung, M.R.; Mori, N. Effect of water saturation on deterioration of welded tuff due to freeze–thaw action. *Cold Reg. Sci. Technol.* **2004**, *38*, 127–136. [CrossRef]
2. Matsuoka, N. Mechanisms of rock breakdown by frost action: An experimental approach. *Cold Reg. Sci. Technol.* **1990**, *17*, 253–270. [CrossRef]
3. Hori, M.; Morihiro, H. Micromechanical analysis on deterioration due to freezing and thawing in porous brittle materials. *Int. J. Eng. Sci.* **1998**, *36*, 511–522. [CrossRef]
4. Prick, A. Critical degree of saturation as a threshold moisture level in frost weathering of limestones. *Permafr. Periglac. Process.* **1997**, *8*, 91–99. [CrossRef]
5. Bellanger, M.; Homand, F.; Remy, J.M. Water behaviour in limestones as a function of pores structure: Application to frost resistance of some Lorraine limestones. *Eng. Geol.* **1993**, *36*, 99–108. [CrossRef]
6. Beier, N.A.; Sego, D.C. Cyclic freeze–thaw to enhance the stability of coal tailings. *Cold Reg. Sci. Technol.* **2009**, *55*, 278–285. [CrossRef]
7. Proskin, S.; Sego, D.; Alostaz, M. Freeze–thaw and consolidation tests on Suncor mature fine tailings (MFT). *Cold Reg. Sci. Technol.* **2010**, *63*, 110–120. [CrossRef]
8. Hale, P.A.; Shakoor, A. A laboratory investigation of the effects of cyclic heating and cooling, wetting and drying, and freezing and thawing on the compressive strength of selected sandstones. *Environ. Eng. Geosci.* **2003**, *9*, 117–130. [CrossRef]
9. Ruedrich, J.; Kirchner, D.; Siegesmund, S. Physical weathering of building stones induced by freeze–thaw action: A laboratory long-term study. *Environ. Earth Sci.* **2011**, *63*, 1573–1586. [CrossRef]
10. Khanlari, G.H.; Abdilor, Y. The influence of wet–dry, freeze–thaw and heat–cool cycles on physical and mechanical properties of upper red sandstones, central part of Iran. *Bull. Eng. Geol. Environ.* **2014**, *74*, 1287–1300. [CrossRef]
11. Momeni, A.; Abdilor, Y.; Khanlari, G.R.; Heidari, M.; Sepahi, A.A. The effect of freeze–thaw cycles on physical and mechanical properties of granitoid hard rocks. *Bull. Eng. Geol. Environ.* **2016**, *75*, 1649–1656. [CrossRef]
12. Noor-E-Khuda, S.; Albermani, F.; Veidt, M. Flexural strength of weathered granites: Influence of freeze and thaw cycles. *Constr. Build. Mater.* **2017**, *156*, 891–901. [CrossRef]
13. Pápay, Z.; Török, Á. Effect of thermal and freeze-thaw stress on the mechanical properties of porous limestone. *Period. Polytech. Civ. Eng.* **2018**, *62*, 423–428. [CrossRef]
14. *EN 12407:2019*; Natural Stone Test Methods–Petrographic Examination. Comite Europeen de Normalisation: Bruxelles, Belgium, 2019. Available online: https://standards.iteh.ai/catalog/standards/cen/b45895d3-a75a-4059-8f8e-4f8307ac7f61/en-12407-2019 (accessed on 30 September 2019).
15. *EN 12372:2006*; Natural Stone Test Methods—Determination of Flexural Strength under Concentrated Load. Comite Europeen de Normalisation: Bruxelles, Belgium, 2006. Available online: https://standards.iteh.ai/catalog/standards/cen/304e13c4-a1ea-4a80-af45-ce1a644b5316/en-12372-2006 (accessed on 6 December 2006).

16. *EN 12371:2010*; Natural Stone Test Methods—Determination of Frost Resistance, EN Standards. Comite Europeen de Normalisation: Bruxelles, Belgium, 2010. Available online: https://standards.iteh.ai/catalog/standards/cen/25486f74-e1f4-4daf-b53e-8f14f9e0ce8f/en-12371-2010 (accessed on 24 March 2010).
17. Student. The probable error of a mean. *Biometrika* **1908**, *6*, 1–25. [CrossRef]