

Experimental study on the variation in porosity of marble as a function of temperature

Katarina MALAGA-STARZEC*, Jan E. LINDQVIST and Björn SCHOUENBORG

Summary

The current condition of many building claddings and historical monuments clearly reveals that they are not immune to weathering from daily or seasonal temperature changes. In this study, porosity changes through variation in temperature have been investigated for two marble types: one calcitic and one purely dolomitic. The samples were exposed to ascending temperatures from 40 up to 200°C. The results indicate that inter-granular decohesion starts at between 40 and 50°C. Some significant differences in temperature response for these two marble types could be distinguished. A temperature range of 40-60°C is easily reached on building surfaces in most European countries during the summer months. A better understanding of the effect that temperature has on the porosity of marble could be used to assess a suitable conditioning of marble before testing, as well as suggest appropriate impregnation and/or surface treatments of building facades and outdoor sculptures.

Introduction

The weathering of marble, clearly observed in many historical monuments, typically consists of the progressive breakdown of rock cohesion (granular decohesion) and manifests itself in the increased porosity and sugaring of the surface. This problem has recently received increased attention, since natural stone claddings in some famous buildings, such as the Amoco Building in Chicago and the Finlandia House in Helsinki started to bow and have had to be replaced (JORNET, 2000). This type of failure is commonly visible some ten to fifteen years after the completion of a building. In some cases the phenomenon has been observed after only one year. Among the many possible causes of marble decay, temperature fluctuations play an important role. There have been many studies (KESSLER, 1919; SAGE, 1988; TSCHegg, 1999; ROYER-CARFAGNI, 1999; SIEGESMUND, 2000) describing the temperature expansion of marble and of other stone types.

From these it has been demonstrated that thermal stress resulting from changes in the temperature of ambient air can be sufficient to produce micro-fractures between the mineral grains of a rock. Marble consists of calcite and/or dolomite. Calcite exhibits linear thermal expansion parallel to the *c* axis but contracts perpendicular to the *c* axis; whereas in dolomite,

both the *c* and *a* axes expand, though at different rates. These phenomena may cause the inter-crystalline bonds to fracture, resulting in a loss of strength as well as a permanent expansion. An important feature is that the fracturing is irreversible, and thereafter the porosity and volume will increase (TURNER, 1954). The quantification of porosity is not commonly used in the characterisation of marble, although its importance was long ago identified (PITTMAN, 1971). It appears that a study of porosity can provide valuable information in order to determine what properties make some marble types more susceptible to disintegration than others. In order to determine how heating to various temperatures initiates changes in the porosity, samples of calcitic marble and dolomitic marble were analysed by gas adsorption.

Experimental – testing procedure and sample preparation

Two types of marble were used in the study, one almost pure calcitic from Italy and one dolomitic from Sweden. The Italian marble specimen was almost pure calcitic (>99%) and the average grain size was 0.46mm. There was no preferred orientation of the minerals. The Swedish marble specimen was dolomitic (93%) and contained some phlogopite (4%) and tremolite (3%). The grain size distribution was bimodal (0.35 and 0.45mm respectively). The mineral grains had a clear preferred orientation. Both materials were characterised by a very low porosity.

For the investigation of the surface area, average pore size and pore size distribution, the gas adsorption (TriStar 3000 Analyser, Micromeritics) technique was used. For the sample preparation and heat conditioning a compact degassing unit was used (SmartPrep, Micromeritics). Both units were computer-controlled and all calculations were performed using Win3000 software. The surface area was calculated using the BET method, the average pore diameter by analysis of the adsorption isotherm and the pore size distribution by applying the BJH method with the Halsey equation (WEBB, 1997).

The marble samples were crushed and sieved to 2-4 mm test specimens. About 7g were used in each analysis. The samples were pre-treated at a selected temperature (40, 50, 60, 70, 80, 100 and 200°C) under a flow of pure nitrogen. During the pre-treatment, molecules previously adsorbed (e.g. water) were re-

moved from surfaces and pores. The selection of the temperatures between 40 and 80°C was aimed to imitate the conditions that could be found on natural stone claddings outdoors during summertime (PERRIER, 1996). The two highest temperatures were applied for the observation of the stone materials under extreme conditions. The duration of the heat treatment varied from one (100 and 200°C) to five days, depending on the time required for the samples to dry. Then the samples were cooled down, and the adsorption of nitrogen determined at the liquid nitrogen temperature of 77K. For each temperature of the pre-treatment, three to six samples were analysed.

Results

The effects induced by the heat treatment into the calcitic and dolomitic marble are illustrated in Figures 1 and 2. The BET-surface area (multi-point) is presented as a mean value with standard deviation.

The resulting curves for both types of marble follow the same trend, though with different amplitudes. The BET-surface area for the marbles decreases between 40 and 50°C, and thereafter starts to increase. This in-

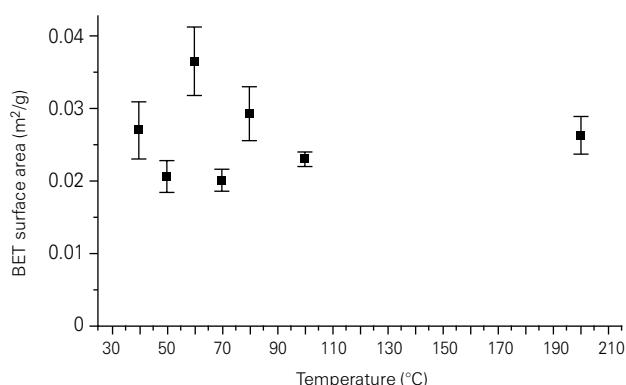


Figure 1. Variation of the BET – surface area for the calcitic marble due to temperature changes.

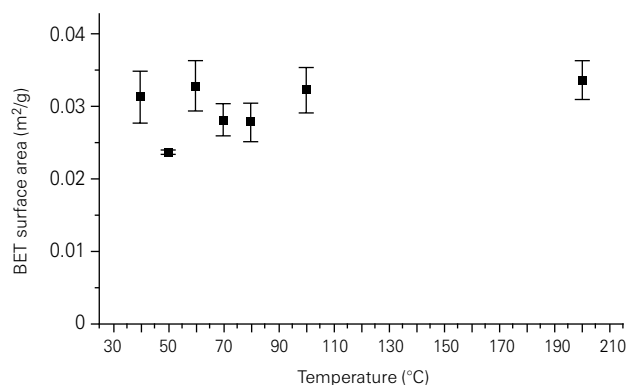


Figure 2. Variation of the BET – surface area for the dolomitic marble due to temperature changes.

crease is especially pronounced for the calcitic marble, where the value increases by almost 40% at 60°C compared to the initial one. The dolomitic marble, at the same temperature, almost regains its original BET-surface area. At about 70°C, the BET-surface area of both materials decreases. The marbles behave differently between 70 and 100°C. The calcitic marble increases its BET-surface area up to 80°C and then decreases up to 100°C, while the dolomitic marble shows a slight decrease at 80°C and an increase thereafter. From 100 to 200°C the BET-surface area increases for both marble types.

Qualitative analysis of the heat-treated samples using fluorescence microscopy shows that the porosity is concentrated around the grain boundaries. This method shows fluorescent light emanating from the pores that have been filled with fluorescent dye. Open cracks were most pronounced for the marble samples exposed to 80°C for five days (Figure 3).

The range of pores detected by the gas adsorption is from 2nm to 200nm. The pore size distribution versus area is plotted in a diagram with three pore size classes: 2–10, 10–100, and 100–200nm – the micro-porosity (pore size <2nm) is negligible for marble. The smallest pore size class, 2–10nm, is chosen to assess if any variation in the smallest pore range occurs, which would indicate initial cracking of the material. The pore size distribution curves are shown in Figures 4 and 5.

Discussion

This study demonstrated that exposure to thermal stress of the investigated marbles, excluding other factors such as humidity, resulted in changes in the values of BET-surface area and pore size.

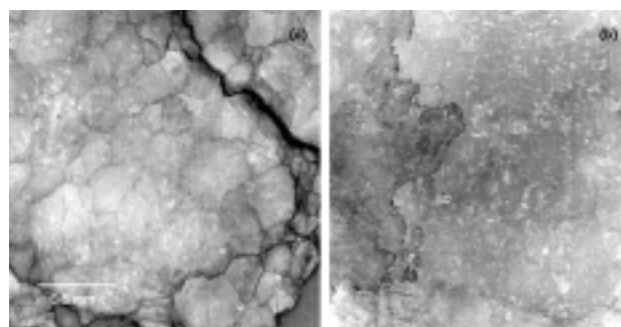


Figure 3. Photomicrographs (negative images) of polished thin sections of (a) the calcitic and (b) the dolomitic marble. The images are taken using fluorescence in reflected light. For the fluorescence microscopy, slabs with a size of 50*30 mm were vacuum impregnated at room temperature with epoxy resin containing a fluorescent dye that penetrates open cracks and pores, and can be observed in the microscopic analysis. The impregnated samples were glued onto an object glass and polished down to a 25 µm thin section.

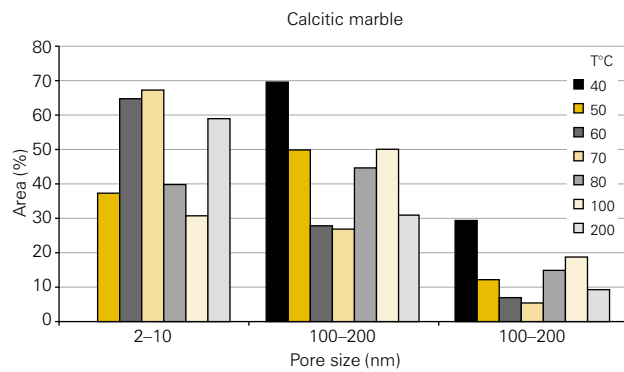


Figure 4. Pore size distribution versus area occupied by a given category of pores, established for the calcitic marble.

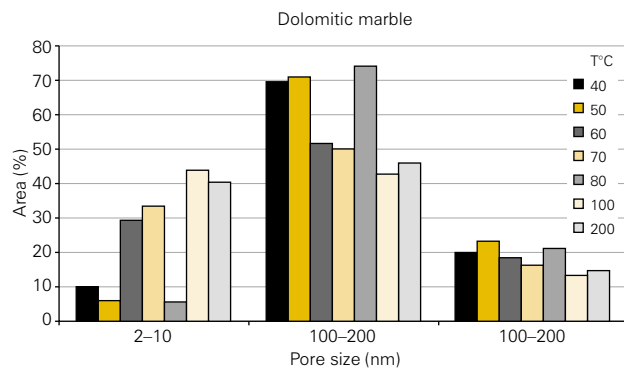


Figure 5. Pore size distribution versus area occupied by a given category of pores, established for the dolomitic marble.

The pore size distributions indicate that intergranular decohesion may already be active between 40 and 50°C where the BET-surface area decreases for both the calcitic and dolomitic marble. The decrease and increase in the BET-surface area could be explained by the thermal expansion of the mineral crystals and cracking process respectively. The fracturing is probably generated at the surface of the marble and extends over relatively small dimensions. In this investigation this phenomenon is especially noticeable for the calcitic marble. Compared to the dolomitic marble, the calcitic marble has a larger area, consisting of the smallest pores in all of the experiments. This means that the initial cracking of the dolomitic marble is delayed compared to the calcitic marble. The larger BET-surface area and mean pore size for the dolomitic marble, plus its dolomitic content, could have a mitigating effect on the generation of micro-fractures compared to the calcitic marble (MALAGA-STARZEC, 2002).

The observed changes need to be evaluated further, since they may also be influenced by other factors such as the mineralogy (clay minerals if present), fabric, or different stages in the sample preparation (e.g.

crushing, influence of liquid nitrogen on material behaviour during the analysis, or incomplete drying of the material). The pore-size distributions presented in this study are limited to the range of 2-200nm. In order to have a more general picture of the porosity variation due to temperature changes, further studies, e.g. microscopy and/or porosimetry, are therefore needed. A comparison between other types of marble frequently used for building cladding, could provide more information about significant factors influencing micro-fracturing of the stone material. Different methods of pre-conditioning the test specimens should also be investigated.

Conclusions

The temperature range of 40–70°C is easily reached on building façades in most European countries during the summer months. The results of this study suggest that the process of intergranular decohesion can begin at temperatures between 40 and 50°C for some marble types. The analysed calcitic marble is more susceptible to temperature changes than the dolomitic marble. The resultant changes of the BET-surface area and the mean pore size are quite variable depending upon several factors, such as original pore structure, the crystallographic and mineralogical characteristics of the marble types, and, as in this study, temperature variation.

A porosity change in carbonate rock samples is of considerable importance in rock mechanics and rock weathering. The differential thermal expansion/contraction associated with different mineralogical and textural properties of the materials may explain, in part, the bowing process of façade claddings. In addition, the findings provide essential information that should be consulted when conditioning all marble stones for further testing. If inter-granular decohesion already begins at temperatures as low as 40-50°C, this must be taken into account when drying test specimens for all standardised tests.

An understanding of the role of temperature on marble porosity could be used to develop a methodology for assessing suitable pre-treatments for the marble slabs and suggesting suitable surface treatments of weathered facade clads and outdoor sculptures. Research should therefore be focused on pore structural changes related to the progress of degradation, and on using pore structural measurements to assess and predict the effectiveness of selected impregnation materials in use with materials of appropriate mineralogy and texture.

This work was financially supported by the KK Foundation and the Swedish National Testing and Research Institute.

References

- JORNET A. and RUCK P., 'Bowing of Carrara marble slabs: A case study', in *Quarry – Laboratory – Monument. International Congress*, Pavia, 2000.
- KESSLER D.W., 'Physical and Chemical Tests on the Commercial Marbles of the United States', in *Technologic Papers of the Bureau of Standards*, Government Printing Office, 123, Washington, 1919.
- MALAGA-STARZEC K., LINDQVIST J.E. and SCHOUENBORG B., *Experimental study on the variation in porosity of marble as a function of temperature*, Geological Society Special Publication, No 205, 2002.
- PERRIER R., 'Mesure de la décohésion thermique des marbres par l'atténuation des vibrations en flexion', *TechniPierre*, **96**, Institut Scientifique de Service Public, France, 1996.
- PITTMAN E.D., 'Microporosity in carbonate rocks', *AAPG Bulletin*, **55**, 1873-1881, 1971.
- ROYER-CARFAGNI G.F., 'On the thermal degradation of marble', *International Journal of Rock Mechanics and Mining Sciences*, **36**, 119–126, 1999.
- SAGE J.D., 'Thermal microfracturing of marble. Engineering Geology of Ancient Work', in *Monuments and Historical Sites*, Balkema, Rotterdam, 1988.
- SIEGESMUND S., WEISS T. and TSCHEGG E.K., 'Control of marble weathering by thermal expansion and rock fabrics', in *Proceedings of the 9th International Congress on Deterioration and Conservation of Stone*, Venice, Italy, 2000.
- TSCHEGG K.E., WIDHALM C. and EPPENSTEINER W., 'Ursachen mangelnder Formbeständigkeit von Marmorplatten', *Zeitschrift der Deutschen Geologischen Gesellschaft*, **150/2**, 283–297, 1999.
- TURNER F.J., GRIGGS D.T. and HEARD H., 'Experimental deformation of calcite crystals', *Bulletin of Geological Society of America*, **65**, 883–934, 1954.
- WEBB P.A. and CLYDE O., *Analytical Methods in Fine Particle Technology*, Micromeritics Instrument Corporation, U.S.A., 1997.

Katarina Malaga-Starzec*

Department of Inorganic Chemistry,
Göteborg University
SE-412 96 Göteborg, Sweden

Swedish National Testing and Research Institute,
Building Technology, Building Materials
Brinellgatan 4,
Box 857, SE-501 15 Borås, Sweden

e-mail: katas@inoc.chalmers.se

Graduated in Geology from Göteborg University and in Environmental Science from Chalmers University in Göteborg, Sweden. PhD in Environmental Science. Main topic of research is chemical and physical deterioration of natural stone materials, with a focus on the thermal properties of the stone, porosity development and corrosion products.