THERMOPHYSICAL MEASUREMENT OF HOMOBLASTIC MARBLE IN DRY AND WATER SATURATED STAGE BY THE PULSE TRANSIENT METHOD

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Abstract

The measurements of thermophysical properties of homoblastic marble Gioia in the temperature range from –20 up to 60 °C are presented. The thermophysical parameters, namely, thermal diffusivity, thermal conductivity and specific heat, were measured by the Pulse transient technique. The data were compared for dry and water saturated stage. Detailed analysis of thermophysical data during freeze/thaw process for dry and water saturated marble in temperature range -8 to 1 °C were done, where the anomaly of water freezing process was found. Artificial ageing of the marble was studied using freeze/thaw cycles. Up to 60 cycles were performed. No significant changes in thermophysical parameters of marble Gioia were observed.

Keywords: pulse transient, marble, freeze/thaw, thermal conductivity, thermal diffusivity, specific heat

1 Introduction

Stones belong to porous materials where water in pores significantly influences material properties and plays an important role on material durability during the freeze-thaw processes [1]. The variation of thermophysical parameters concerning moisture content depends on both skeleton and pores properties, particularly on skeleton structure, pore shapes and pore size distribution, percolation threshold etc. Therefore, the thermophysical measurement becomes suitable tool for characterization of the porous materials.

A number of experimental methods were developed for investigation of the heat transport through porous structures. Generally they can be divided into two groups, namely methods that used steady state measuring regime [2] and methods using transient one [3]. Former group needs long measuring time that for porous structures can induce a redistribution of the fluid inside the pores and thus information obtained is far from measuring condition we need. Transient methods need significantly shorter measuring time and thus information obtained corresponds to condition found in real application of the pore structure.

In this paper we present the thermophysical parameters measurements of homoblastic marble Gioia, namely the thermal diffusivity, the specific heat and the thermal conductivity, in the temperature range from –20 up to 60 °C, using Pulse transient method [4]. The specimen, Gioia marble, was conditioned to obtain dry and water saturated state. Apart from standard measuring procedure, a non-isothermal measuring regime in the temperature range from -8 to 1 °C using the cooling and heating rate of 0.01 K/min was used in order to analyze freeze-thaw process. Up to 60 freeze-thaw cycles that might induce structural damage in stone skeleton were used to obtain picture on material degradation and their durability.

2 Pulse transient method

The principle of the pulse transient method [4] is shown in Fig. 1. The method can be described as follows. The temperature of the specimen is stabilized and uniform. Then a small disturbance in the form of a heat pulse is applied to the specimen. From the temperature response the thermophysical parameters can be calculated according to the model used.

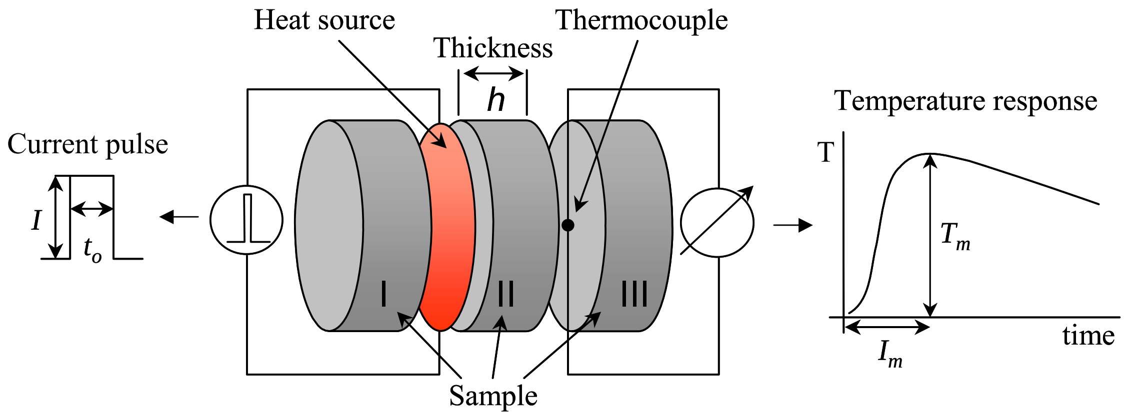


Fig 1 Experimental set up for Pulse transient method

The model of the method is characterized by the temperature function [4]

$$T(h,t) = \frac{Q}{c_p \rho \sqrt{\pi a t}} \exp\left(\frac{h^2}{4at}\right), \tag{1}$$

where $Q=RI^2t_0$ is amount of heat generated by heat source in the unit area, R is electrical resistance of the heat source, I is current supplied during time t_0, ρ is density and a, c_p are thermophysical parameters (thermal diffusivity and specific heat). The temperature function (1) is the solution of the heat equation considering appropriate boundary and initial conditions. For determination of the thermophysical properties using the one-point procedure, the maximum of the temperature response is taken as the input. The following relations [4] for calculation of the thermophysical parameters are used:

Specific heat c_p

$$c_p = Q / T_m h \rho \sqrt{2\pi e} \tag{2}$$

Thermal diffusivity a

$$a = h^2 / 2t_m \tag{3}$$

where T_m is the maximum of temperature response at the time t_m and e denotes the Euler number.

Third thermophysical parameter, thermal conductivity λ, is defined by well-known data consistency relation

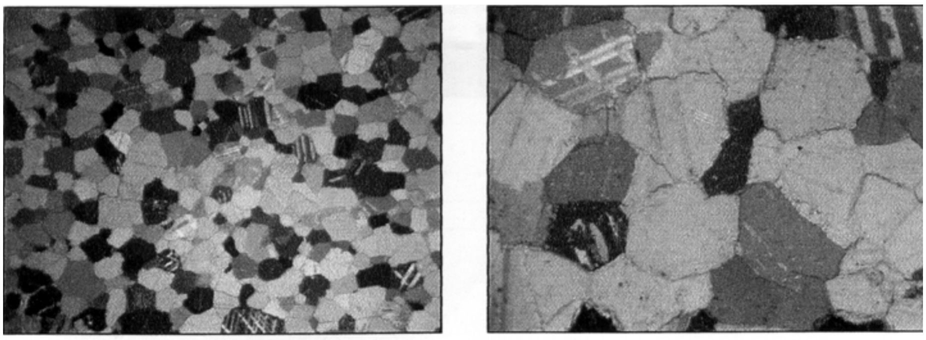
$$\lambda = a c_p \rho \tag{4}$$

The thermophysical parameters can be found also by superimposing the temperature function (1) on the temperature response by an appropriate fitting technique.

3 Experiments

3.1 Samples

Homoblastic marble Gioia belongs to calcitic marble with typical granoblastic polygonal microstructure (see Fig 2). Since this marble doesn't show any preferential orientation, it's included into isotropic porous rocks. Marble has a very low porosity as seen in basic characteristic given in Table 1. Its pore size distribution depicted in Fig 3 shows a remarkable strong nano-porosity. The samples come from Gioia quarry in Carrara, Italy.



10 x - Thin section, crossed nicols – 25 x

Fig 2 Pictures of microstructure of homoblastic marble Gioia

The samples were prepared in the form of three blocks of the cross-section 50x50 mm, where the measured active middle part of specimen set-up has thickness h = 14.6 mm. In order to provide a good thermal contact between samples the thermal paste was used. Since the sample is porous the contact sample faces were treated with epoxy layer. Dry and saturated state was established using standard procedures, where saturation was carried out with distilled water.

Table 1. Basic characteristics of homoblastic marble Gioia

Bulk density (kg m^{-3})		Water porosity (%)	
Dry	Water-saturated	Calculated	Published*
2703 ± 3	2710 ± 3	0.65 ± 0.3	0.3 ± 0.0

*given by supplier

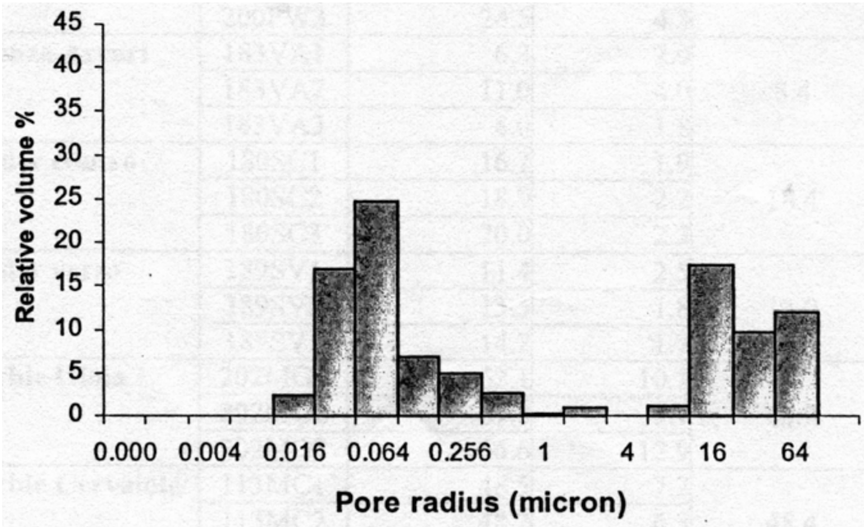
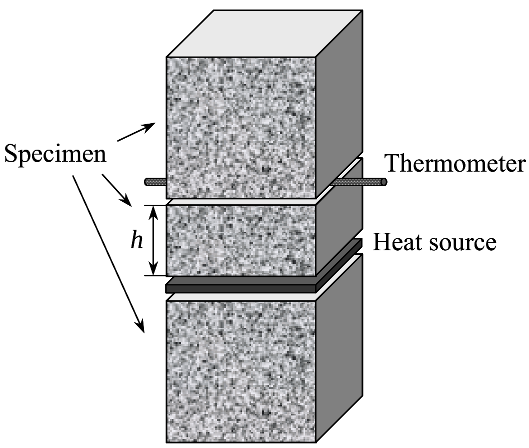


Fig 3 Pore size distribution of homoblastic marble Gioia

3.2 Experimental set-up and conditions

The instrument RTB 1.01 (Institute of Physics SAS) is used for measurements of the thermophysical properties. Basic scheme of the instrument is shown in Fig. 4. Thermostat in connection with the plate heat exchangers establishes the specimen temperature. Both, a non-isothermal measuring regime with the heating and cooling rate 0.01 K/min and an isothermal one with an isotherm within the limit of 0.02 K was used. A programmable current source KEPCO was used for generation of the heat pulse using the plane electrical resistance of 2 Ω . The plane heat source was made of a nickel foil of 20 μm etched in a form of meander and covered from both sides by Kapton foil of 25 μm. The temperature response was scanned by Keithly multimeter. A PC computer synchronizes all units. Typical parameters of the temperature response were $T_m \sim 1$ K and $t_m \sim 120$ sec.



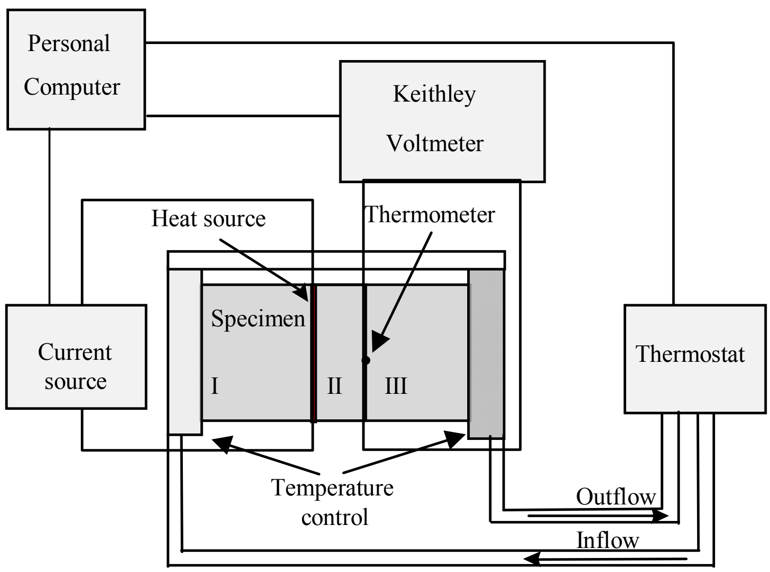


Fig 4 Specimen set-up (left) and basic scheme of instrument RTB 1.01(right)

3.3 Results

Dependence of the thermophysical properties of dry Gioia marble on temperature in the range from -20 to 60 °C is shown in Fig. 5, where the thermal diffusivity is plotted in the upper part, the specific heat in the middle and the thermal conductivity in the lower part. The large scattering of thermophysical data above 50 °C is caused by insufficient thermal insulation of measuring apparatus from surrounding. Decreasing thermal diffusivity, respectively thermal conductivity with temperature is evidently related to polycrystalline structure of Gioia marble.

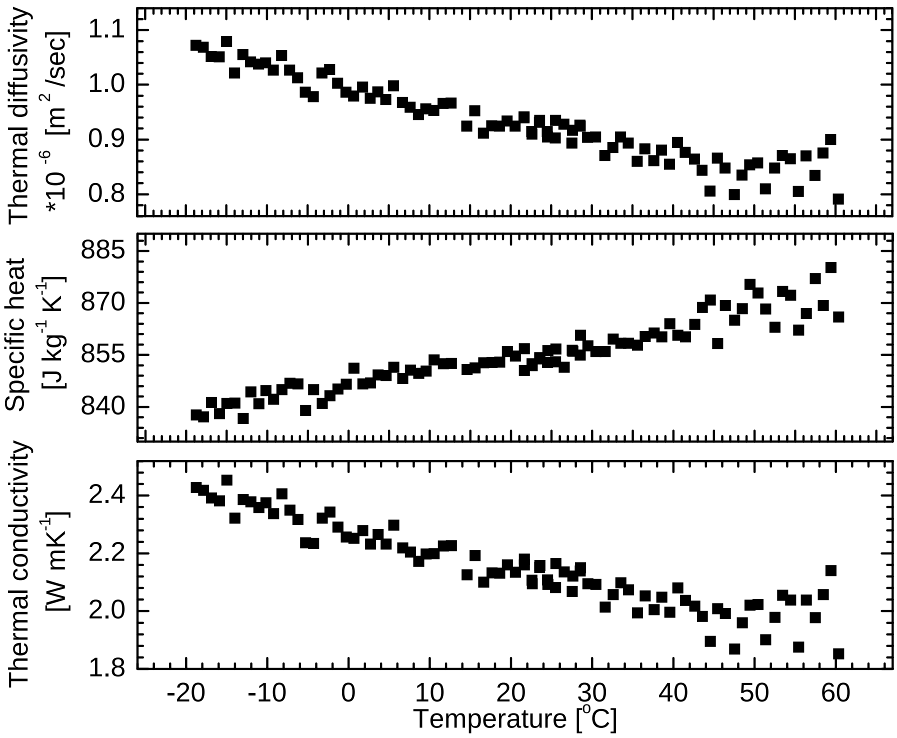


Fig 5 Thermophysical properties of dry homoblastic marble Gioia as a function of temperature

Data on the thermophysical parameters of dry and water-saturated marble in temperature range from -8 to 1 °C are shown in Fig. 6, where the thermal diffusivity, the specific heat and the thermal conductivity are plotted from up to down as a function of temperature. The measuring of thermophysical parameters during freeze/thaw process consists of step by step cooling and heating measuring regime. As one could expect, the curves of thermophysical parameters of dry marble are identical for both the cooling and the heating regime. Therefore to get better lucidity only the curves corresponding to cooling regime are depicted in Fig. 6 for dry marble.

Anomalies of the thermophysical parameters were found for water-saturated state, where the endothermic peaks connected to the phase transformation of ice induced by the heat pulses during measurement are observed just for the heating regime. Solidification (freezing) phenomenon is a complicated function of the droplet size – pore volume and its interaction with the pore surface. Thermodynamic of the pore content dictates the embryo formation and solid phase growth. Since Gioia marble has a very strong nano-porosity (seen in Fig. 3), we suppose that the creation of the solid phase (ice) in the pore volume is shifted to the lower temperatures, a few degrees Celsius below zero, because of high capillarity forces inside the pore. In such a situation the water is characterized by term an under-cooled liquid. In that way, arising solid phases of water inside the pores come immediately to “deep” frozen state, where the heat pulses supplied by measuring procedure have not sufficient energy to start the opposite thawing process and so we notice no peaks related to phase transformation of ice during cooling regime as seen in Fig. 6.

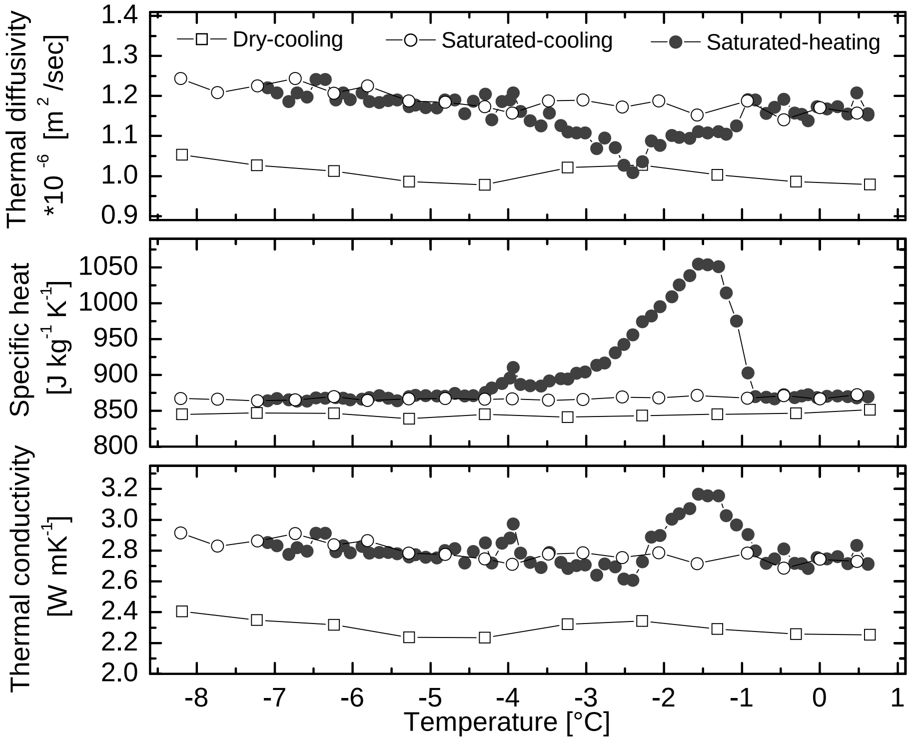


Fig 6 Thermophysical properties of dry and water-saturated homoblastic marble Gioia as a function of temperature during cooling and heating regime

Differences on thermophysical properties for dry and saturated states at 0.5 ^oC and at –6 ^oC (water in pores is frozen) are given in Table 2. While difference in specific heat for dry and water-saturated state is around 2 % which corresponds to low porosity, significantly larger differences about 20 % exist in values of so-called transport parameters, the thermal diffusivity and the thermal conductivity, for both temperatures –6 ^oC and 0.5 ^oC.

Table 2. Thermophysical properties of homoblastic marble Gioia for dry and water-saturated state

Parameter	Dried		Water-saturated	
	0.5 ^oC	-6 ^oC	0.5 ^oC	-6 ^oC
Thermal diffusivity (10^{-6} m^2 s^{-1})	0.979	1.012	1.177	1.191
Specific heat (J kg^{-1} K^{-1})	851.1	846.6	867.9	865.2
Thermal conductivity (W m^{-1} K^{-1})	2.25	2.32	2.75	2.78

Usually stone skeleton plays a significant role in the heat transport while the role of the pore content is negligible. Thermal diffusivity is a function of the sound velocity and free path of phonons [5]. Data on thermal diffusivity and related thermal conductivity indicate that elastic properties of the stone are influenced by moisture content. Here again, we suppose this is due to high capillarity forces inside the wet stone. In contrary to thermal diffusivity, data on specific heat indicate that thermodynamic of the stone is influenced by the volume of the pores and its content. Thus, their influence is very small, equivalent to stone's porosity. The thermal conductivity as a product of thermal diffusivity and specific heat (equation 4) simply follows the variation of thermal diffusivity.

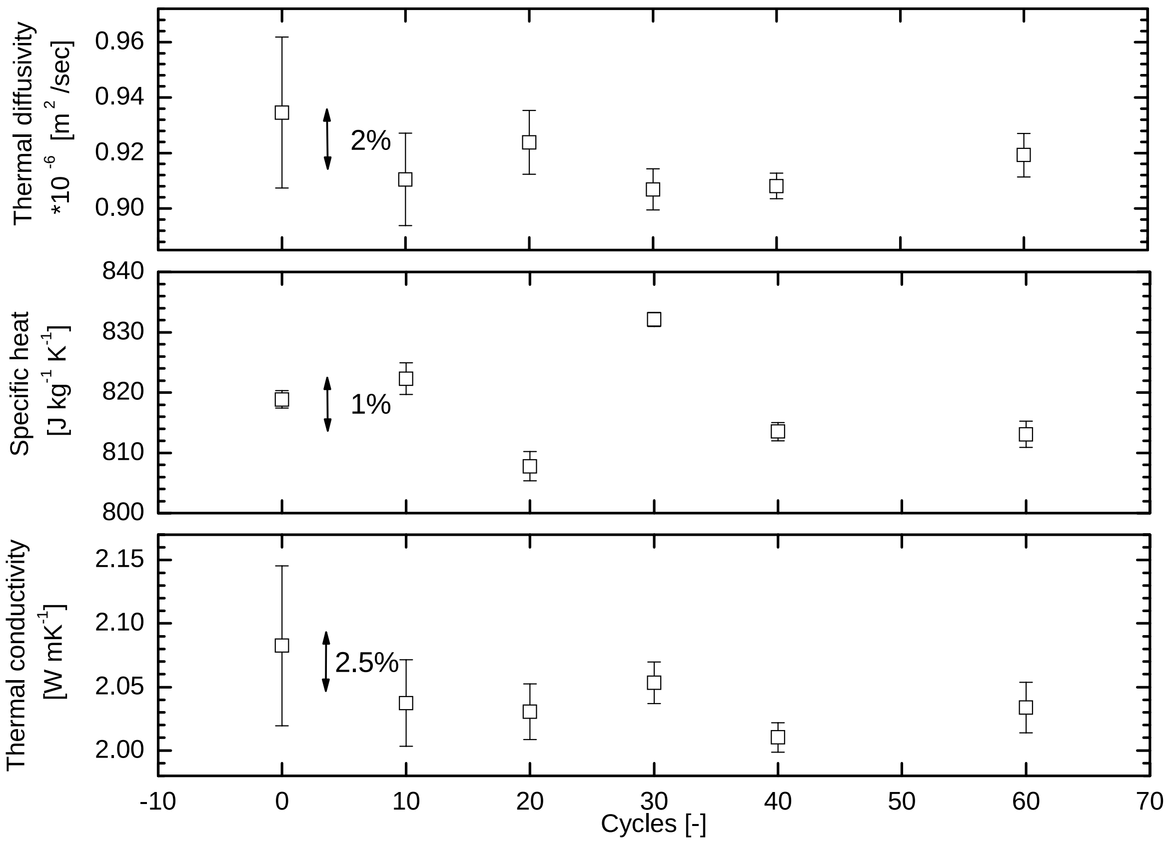


Fig 7 Artificial ageing of dry homoblastic marble Gioia (thermophysical properties in dependence on number of freeze/thaw cycles)

The volume change during water freezing induces a damage of the stone skeleton. The pore distribution is changed and heat-conducting paths are interrupted [6, 7]. Therefore cycling experiments were performed in which water-saturated Gioia marble underwent to freeze-thaw process within the temperature range – 18 ^{o}C up to 25 ^{o}C. The results are shown in Fig. 7 where again, the thermal diffusivity in the upper part, specific heat in the middle and thermal conductivity at the bottom are plotted as a function of the cycle number. All measurements were done on dry sample at room temperature. In the whole range of 60 freeze/thaw cycles no significant changes in thermophysical parameters of marble Gioia were observed, which suggests its good durability.

4 Conclusions

The presented thermophysical parameters of homoblastic marble Gioia were measured by the Pulse transient method in the temperature range from –20 up to 60 °C. The thermophysical analysis was performed for both dry and water saturated state, where the freeze/thaw process was applied in the temperature range from -8 to 1 °C.

We found out two peculiarities in thermophysical behavior of marble Gioia, the anomaly of water freezing inside the marble during freeze/thaw process and the huge increase of the thermal diffusivity of marble (comparing to its nearly zero porosity) after the marble was water saturated. In order to elucidate both observed peculiarities, we proposed theory of high capillarity forces inside the water saturated pores of marble. At first case, the higher forces inside pores keep water from freezing, which induce the state of under-cooled liquid flipping to "deep" frozen state. At second case, the high capillarity forces increase the elastic properties of marble skeleton, which are directly connected with its thermal diffusivity.

Finally, we have noticed no significant damage of homoblastic marble Gioia within 60 cycles of freeze/thaw process during artificial ageing test.

Acknowledgement

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