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Estimating thermal damage in a limestone exposed to elevated temperatures using P-wave velocity tests

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Abstract

Ultrasonic velocity is a property that provides information about the internal structure of rocks and is related to the content of pores and microcracks. Rocks exposed to fire show an increase in their porosity, expansion of existing microcracks and generation of new ones as a consequence of the temperature.

This study analyzes the variation of porosity and P-wave velocity in samples of a limestone exposed to temperatures of 200, 400, 600 and 800 ºC and cooled on two different methods, slowly and quickly. Open and total porosity are determined to obtain the variation of the microporosity, whereas mercury intrusion porosimetry tests are used to analyze the pore size distribution. Ultrasonic pulse transmission tests were carried out to determine the variation of P-wave velocity as temperature increases.

Samples exposed to 200 ºC show values of porosity similar to those of non-heated specimens. Porosity starts to increase noticeably from 400 ºC. Samples exposed to 800 ºC quadrupled the initial porosity (non-heated samples). However, there are not significant differences related to the cooling method. Mercury intrusion porosimetry tests show a remarkable increase in intraparticular pores in the range of ultramicropores.

As for the porosity, P-wave velocity shows no significant changes on samples exposed to 200 ºC compared to the non-heated samples. Between 400 and 600 ºC the most drastic decrease is observed and from 600 ºC the decline is less pronounced. At 800 ºC, P-wave velocity decreases up to 50% in comparison with the non-heated limestone. A thermal damage factor is calculated using the P-wave velocity results, based on two previous published equations. The value of this coefficients factor allows the thermal damage to be classified from "*undamaged*" to "*secondary damage*". These categories can be compared with the observed changes in porosity and the visual inspection of the tested samples.

Keywords

High-temperature, limestone, P-wave velocity, mercury intrusion porosimetry, thermal damage factor.

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1 Introduction

Porosity is a key property of rocks exposed to high temperatures, as it is significantly affected by temperature. Regarding changes in limestone porosity, it is possible to distinguish three different behaviors: (i) porosity shows a slight increase, almost imperceptible, on limestone exposed up to 200/300ºC; (ii) from 300 to 600°C, the increase in porosity is more pronounced as the exposure temperature rises; and (iii) above 600°C, porosity shows drastic changes, increasing rapidly to high temperatures (Martínez-Ibáñez et al., 2021; Martinho et al., 2017; Zhang & Lv, 2020). The change in porosity of limestones under the influence of temperature is the combined result of physical effects and chemical effects (mineral dehydration, mineral phase transformation…), and thermal cracking caused by uneven thermal expansion (Meng et al., 2020). The rate of variation in porosity can be influenced by the original porosity of the rock since low-porosity rocks show a more drastic change in porosity at high temperatures (Ozguven & Ozcelik, 2014; Yavuz et al., 2010). Regarding the cooling effect, porosity may increase significantly more in samples that are slowly cooled compared to those that are quickly cooled. This is attributed to the degradation of a larger amount of the constituent minerals during a prolonged cooling process (Brotóns et al., 2013). These results can be verified through the determination of microporosity using mercury intrusion porosimetry (MIP), which provides a more precise understanding of the structural changes that temperature induces in rocks. MIP results confirm that the evolution of porosity follows the three phases described above. At low temperatures, the volume and size of pores increase slowly (Martínez-Ibáñez et al., 2021). At medium temperatures, porosity increases at a quicker rate (Zhang et al., 2017), and at high temperatures, porosity increases significantly, especially in micro- and ultramicropores. At high temperatures, some limestones experience a shift in their pore distribution from unimodal to bimodal, with a notable increase in macropores that represents microcracks (Andriani & Gioacchino, 2014).

The velocity at which ultrasonic waves propagate through rocks is influenced by porosity. Changes in the velocity of longitudinal wave (hereinafter P-wave) allow for the evaluation of damage caused by temperature, such as the formation of new pores and microcracks. The effect is different depending on temperature and it is possible to distinguish three different damage levels, similar to those observed for porosity. P-wave velocity shows little changes on rocks exposed up to 300°C, although some cases show a slight increase in wave velocity around 100°C (Yavuz et al., 2010; Zhang et al., 2015). Between 300 and 600°C, P-wave velocity decreases more sharply (Yang et al., 2019). Specifically, in this temperature range, the transformation of quartz grains, the decomposition of clay minerals, and the expulsion of constitution water generate cracks due to thermal contraction, leading to an increase of the number and volume of pores. At high temperatures, above 600°C two different trends are observed: sometimes takes place a more pronounced decrease than in the previous range (Sun et al., 2017) or a less pronounced decrease (Wu et al., 2013). At this temperature range, the influence of thermal stress becomes greater, and microcracks start to appear within the crystals, connecting to macrocracks, which leads to an increase in pore size. Meanwhile, calcite begins to decompose and transform into lime, and the calcite structure collapses completely when the temperature reaches 900°C, causing the samples to fracture and present numerous cracks. Additionally, quartz grains transform from β-quartz to β-tridymite at 870°C, increasing the volume of quartz grains by 16%. Therefore, the P-wave velocity decreases in some cases and remains constant or decreases less sharply in others (Yang et al., 2019).

In order to evaluate the thermal damage, different coefficients or damage factor (DF from now) have been defined based on the evolution of different rock properties with temperature exposition. Zhao et al. (2009) defined the DF based on the theory of elasticity and the variation that the modulus of elasticity undergoes as the exposure temperature increases. This DF has been expressed as a function of the P-wave velocity, according to equation (1) where the subscript T indicates the value for a given temperature and the subscript 0 corresponds to the non-heated rock.

$$D_T = 1 - \left(\frac{V_{P,T}}{V_{P,0}}\right)^2 \tag{1}$$

Zhang et al. (2015) redefined this DF using equation (2) where K_T is the DF, V_T is the P-wave velocity, the subscript T indicates the value for a given temperature, and V_{max} is the value of P-wave velocity to the non-heated sample.

$$K_T = 1 - \left(\frac{V_{P,T} - V_{P,max}}{V_{P,max}}\right)^2 \tag{2}$$

The authors established a thermal damage scale in five categories, ranging from "*No damage*" to "*Completely damaged*", based on the value of the DF and correlated with visual observations of the samples.

As a result of temperature exposure, limestones exhibit an increasing in the size and volume of pores and microcracks, leading to significant variation in porosity. Furthermore, there is no doubt about the relationship between the increase in porosity and the decrease in ultrasonic wave velocity. This fact suggests that thermal damage in limestone can be assessed using a non-destructive test, such as the ultrasonic wave velocity test, which is the focus of this research.

2 Materials and methods

The rock tested in this research is a bioclastic limestone known as Pedra de Borriol (PB hereinafter), commonly used in the construction of cultural heritage structures in eastern Spain. It is a Cretaceous rock mainly composed of calcite (75-85 %) and dolomite (15-20 %) with traces of quartz, illite, goethite and hematite (Garrido et al., 2022). Blocks with dimensions of 300×140×100 mm were obtained from a quarry located in Borriol (Castellón, eastern Spain). Cylindrical and prismatic samples were extracted from these blocks. They were divided into groups of ten cylindrical and twenty prismatic specimens and subjected to a specific target temperature: 200, 400, 600, and 800 ºC. An additional group of five was dried at 100 ºC, with the resulting measurements serving as reference values (non-heated samples). The heating process was carried out with a rate of 5 ºC/min until reaching the target temperature, it was maintained for 1 hour. Next, half of the specimens were cooled in the air until reaching room temperature (slow cooling), whereas the other half were cooled by water immersion (quick cooling) and then dried in a conventional oven. The tests were carried out, at room temperature, 24 hours after heating treatment. The cylindrical samples were used to determine the P-wave velocity tests according to ISRM suggested methods (Aydin, 2015). The prismatic specimens were used to determine the porosity according to ISRM suggested methods (Franklin, 1979). MIP tests was carried out by the Technical Research Services of the University of Alicante using a POREMASTER-60 GT equipment from QUANTACHROME INSTRUMENTS. The pore range between 10^{-6} and 1 mm was analysed. One sample was tested for each target temperature and cooling method, in addition to a non-heated sample.

3 Results and discussion

3.1 Total and open porosity

The tests conducted on non-heated PB samples show a mean porosity value of is 2,34 ± 0,57 %, indicating that this limestone can be considered a low-porosity rock. Below 400 °C, the porosity shows slightly changes. After that, it shows a strong increase as temperature increases. At 600 °C and 800 ºC the porosity is nearly two times and four times the initial value (under 100 °C), respectively (Fig. 1a). There is not significant influence of the cooling method. The quickly cooled specimens show the same percentage of porosity, or slightly bigger, than those slowly cooled, except for the samples exposed to 200 ºC. The percentage of open porosity increases as the exposure temperature increases with a logarithmic trend. In the non-heated sample, open porosity represents a 44% of the total porosity and reaches 86 and 91% in samples exposed to 800 ºC, cooled slowly and quickly, respectively. In all cases, the samples subjected to quick cooling present a higher percentage of interconnected porosity.

The porosity of rocks exposed to temperatures up to 200 ºC hardly varies as reported by Tian et al. (2014), Meng et al. (2020) and Zhang and Lv (2020), although this limit extends up to 300 ºC according to the rocks tested by Yavuz et al. (2010), Brotóns et al. (2013) and Martínez-Ibáñez et al. (2021) and even up to 400 ºC in research works carried out by Ozguven and Ozcelik (2014). This behavior is observed in the case of the PB limestone. When the exposure temperature gets over 400 ºC, porosity increases more drastically, as was published by Meng et al. (2020), Zhang et al. (2017) and Zhang and Lv (2020) (Fig 1b). In the case of PB, from 400 ºC onwards, porosity increases even at a faster rate, although the most significant change corresponds to temperatures exceeding 600 ºC, when the decay of carbonates causes the opening of fissures and the generation of new pores.

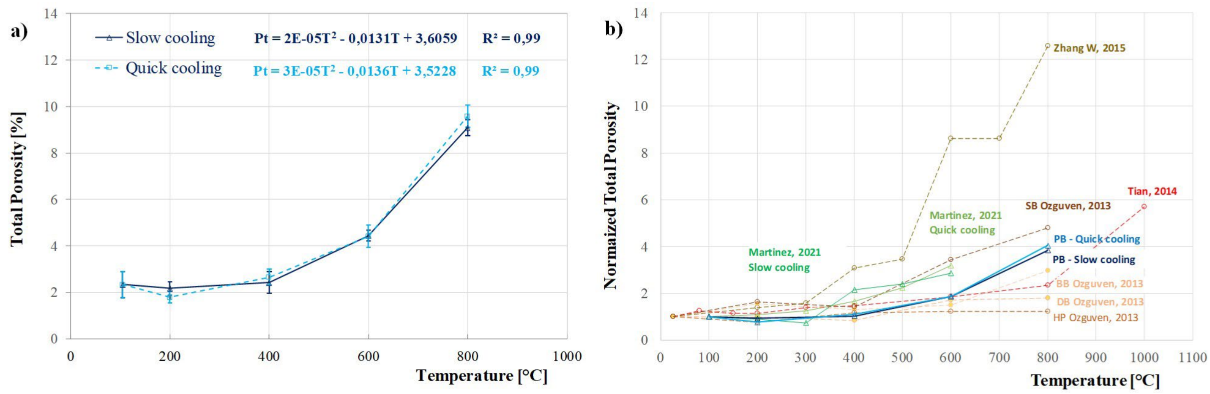

Fig. 1 Variation of total porosity ion a) PB samples and b) in others limestone exposed to different temperatures.

Regarding the cooling method, if the results are compared with those obtained for another carbonated rock from the Iberian Peninsula, the Prada limestone (Martínez-Ibáñez et al., 2021), the variation of this property with temperature is very similar to that observed in the PB, despite the lower value of the initial porosity of the Prada limestone. Brotóns (2013) exposed to high temperatures high-porosity calcarenite samples (porosity mean values of 22,1% in non-heated samples) and later cooled them in two different ways. The 90% of the total porosity in this calcarenite is open porosity. In slowly cooled samples, open porosity shows a low increase up to 300 °C, less than 2%, and from this temperature onwards a linear increase up to 14% was recorded at 600 °C. In the lower temperature range, rapidly cooled samples show a greater increase in porosity (7%) showing little variation between 300 and 600 ºC. The author attributes this effect to the fact that in slowly cooled samples, a greater amount of the constituent minerals is degraded during a longer cooling process. Consequently, calcarenite porosity increases considerably more in slowly cooled samples than in quickly cooled samples, unlike the results observed in Prada limestone and PB, where minimal differences were found between the cooling methods. Calcarenite interconnected porosity does not change, maybe because open porosity constitutes almost 90% of the total porosity, even on non-heated samples. However, in the PB limestone, open porosity constitutes 44% of the total porosity in the non-heated samples and increases twice at 800 ºC. These results suggest that, more than the initial value of the total porosity of the rock, the changes in this property with temperature are influenced by the interconnection between pores and fissures.

3.2 MIP Tests

The previous section shows the evolution of porosity, in terms of open and total porosity. Since it is evident that the heat treatment generates new pores and microcracks, their size evolution should be analyzed by means of MIP tests. The pore size has been analyzed using curves of the derivative of the volume with the logarithm of the pore diameter (Fig. 2). It is observed that as the exposure temperature increases, the volume of all pore sizes also increases. Based on the pore classification used by Sun et al. (2016), most of the observed pores are in the range of ultramicropores (average diameter less than 1 µm) and micropores (average diameter between 1 and 10 µm), although the volume of all pore sizes increases as the temperature increases. A small volume of other pore sizes is observed in the diameter range between micropores and mesopores, which do not increase as temperature increase. A pore set with a diameter of 4 nm is observed in the samples exposed to 200 ºC, similar to that found in the non-heated sample. Samples exposed to 400 ºC, lack the presence of this 4 nm pore family. For higher temperatures, the pore-size distribution becomes multimodal with a wide range of represented diameters, between 60 nm and 10 µm. Nevertheless, the diameter range is slightly smaller in the quickly cooled samples. Up to 800 ºC, the pore volume increases as the exposure temperature increases and two peaks stand out at 4 nm and 200 nm, which are more pronounced in the slowly cooled samples.

Limestones tested by Andriani and Germinario (2014) show a unimodal distribution of porosity consisting of micropores observed at room temperature. After exposure to 700 ºC, a bimodal distribution consisting of micropores (46.0%) and macropores (46.4%) is observed, in contrast to the PB where the distribution becomes multimodal starting at 400 ºC. Additionally, the volume of mercury extruded is lower at higher temperatures, as observed in the PB limestone.

Gómez-Heras et al. (2013) used this test to study the porosity of non-heated samples of two different sandstones, as well as samples of these two rocks from buildings affected by fires. The total porosity of both sandstone increases with temperature, as does the average pore size. The pore distribution changes from a unimodal pattern to a multimodal pattern as has been registered in PB.

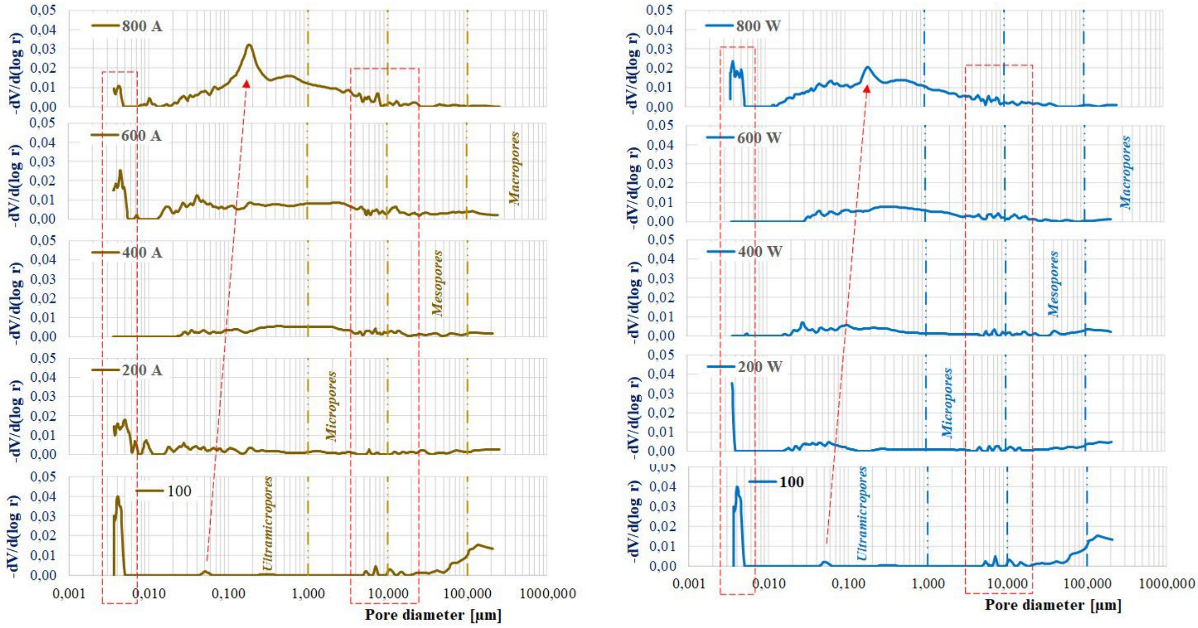

Fig. 2 Curves of the derivative of the volume vs. pore diameter of slowly (left) and quickly (right) cooled PB samples.

The interparticle porosity accounts for 25%, and the intraparticles porosity accounts for 75% of the total porosity of the non-heated samples. These values fall within the range of those obtained in the previous section, as shown in Table 1. The interparticle porosity is lower than the intraparticle one for any tested temperature. Both type of porosity is smaller on samples quickly cooled with the exception of those exposed to 200 ºC and slowly cooled. Total porosity increases twice on samples exposed to 600 ºC and four times on samples exposed to 800 ºC, as shown by conventional porosity tests.

Table 1 Results of interparticle, intraparticle and total porosity from MIP tests. SC: Slow cooling; QC: Quick cooling

Temperature [ºC]	Interparticle porosity [%]		Intraparticle porosity [%]		Total porosity [%]	
	SC	QC	SC	QC	SC	QC
100	0.45		1.35		1.80	
200	0.49	0.80	2.19	1.16	2.68	1.96
400	0.72	0.68	2.25	1.70	2.97	2.38
600	1.50	0.56	5.29	2.98	6.79	3.54
800	0.55	0.62	7.29	6.95	7.84	7.57

Interparticle porosity does not show significant changes with heating excepting those samples exposed to 600 ºC and slowly cooled. Intraparticle porosity increases as temperature increase, the greatest increase starting at 400 ºC. Consequently, the increase in total porosity of this rock as effect of the heat treatment is mainly governed by the evolution of intraparticle porosity. As regards pore tortuosity, defined by the difference between the volume of mercury intrusion and extrusion, 600 ºC is a threshold temperature. In slowly cooled samples, no changes are observed from this temperature onwards, the extruded volume remains between 30 and 40%, indicating significant pore tortuosity. However, in samples subjected to quick cooling, the extruded volume is between 60 and 70% at low temperatures and, from 600 ºC onwards, it decreases as the temperature increases, showing a minimum of 20% at 800 ºC. This indicates that quick cooling increases the tortuosity of the pores when the samples are exposed to temperatures above 600 ºC. This effect may be due to a disaggregation of the rock matrix induced by water immersion which modifies the porous network in greater extent as temperature increases.

3.3 P-wave velocity

PB non-heated samples show the mean value of P-wave velocity is 5404 ± 48 m/s. The general trend indicates P-waves velocity decreases as temperature increases as expected. At 200 ºC, the P-wave velocity decreases by 8.5 and 14.4%, on slowly and quickly cooled samples, respectively, compared to the values measured on the non-heated samples. At 400 y 600 ºC, the velocity decreases drastically. At 600 ºC were estimated up to 34.3 and 40.4% on samples slowly and quickly cooled, respectively. From 600 to 800 ºC, it is recorded a slightly decrease of 9.6 and 6.1% on samples slowly and quickly cooled, respectively. As it can be seen, the results obtained in the samples quickly cooled are slightly lower than those obtained for slowly cooled ones, except in the samples exposed to 800 ºC (Fig. 3a). There are not remarkable differences for both cooling methods to the variation of P-wave velocity.

Therefore, the results reveal three temperature ranges with varying effects on P-wave velocity, which aligns with the findings previous published. At low temperatures, a slight decrease in P-wave velocity is observed. Free water turns into steam that escapes from open pores, which increases pore volume. At the same time, heating causes particles to expand, which decreases the volume of some pores. The combined action of both phenomena, pore volume sometimes decreases and sometimes increases. The results obtained on PB samples coincide with these previously published by Yavuz et al. (2010), Zhang et al. (2015), Zhang, Y. et al. (2017a), Yang et al. (2019) and Martínez-Ibáñez et al. (2021). At intermediate temperatures, the dramatically decrease of P-wave velocity is influenced by different factors. First, thermal stress causes the expansion of particles and the original pores are compressed and even disappear. Second, when there is not enough space for the expansion of the particles, the bonds between some particles are broken and new cracks are generated around the particles. The arrangement of the particles is relatively disordered and the volume of pores increases, which slows down the propagation of the waves. In addition, the transformation of quartz grains, the decomposition of clay minerals and the expelled constitution water generate thermal contraction cracks and the number of pores increases. This can be observed in PB samples up to 600 ºC, as is the case of limestones tested by Zhang et al. (2015) and Zhang et al. (2017).

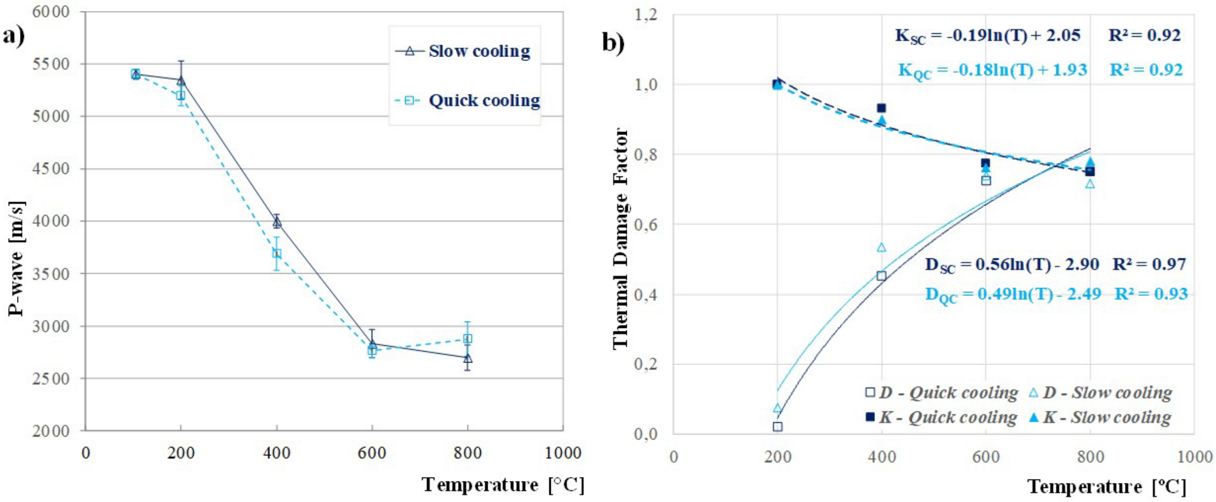

Fig. 3 a) P-wave velocity and b) thermal damage factor variation as temperature increases on PB samples.

At high temperatures, the wave velocity decreases. This can be observed in PB samples from 600 °C onwards. At this temperatures, the predominant process on limestones is the decomposition of carbonates. In PB samples, the pore volume increases, although it has been verified that intraparticle porosity increases without a significant increase in the interparticle porosity. This effect especially happens at 800 ºC, which implies a poor connection between pores. It does not happen in the limestone tested by Yang et al. (2019), which show a new significant drop in P-wave velocity. The strong decrease at temperatures around 800 ºC is attributed to the thermal stresses as a result to the transformation of quartz from β-quartz to β-tridymite at 870 °C (Sun et al. 2017), which increases the volume of the grains and leads to significant cracking of the rock. Respect the cooling method, quickly cooled samples show a slightly greater decrease in P-wave velocity than slowly cooled ones, suggesting that quick cooling increases cracking and/or opening of existing fissures in PB limestone.

3.4 Thermal damage factor

In this study the thermal damage factor (hereinafter DF) have been analyzed using the DF of Zhao et al. (2009) that varies from 0 (less damaged) to 1 (more damaged) and also using the DF of Zhang et al. 2015) that varies from 1 (less damaged) to 0 (more damaged), both based on P-wave velocity. Table 2 shows the thermal damage factor obtained on PB samples with both, equations (1) and (2) (section 1).

Table 2 Thermal damage factor values of PB samples exposed to different temperatures.

Temperature [ºC]	D_T (eq. 1)		K_T (eq. 2)	
	Slow cooling	Quick cooling	Slow cooling	Quick cooling
200	0.02	0.08	1.00	1.00
400	0.45	0.53	0.93	0.90
600	0.73	0,74	0.77	0.76
800	0.75	0.72	0.75	0.78

Values of both coefficients exhibit the same trend that P-wave velocity: samples exposed to 200 ºC scarcely are damaged, those exposed to 400 and 600 ºC show an important damage and there are not remarkable differences on samples exposed to 600 and 800ºC, both are significant damaged. There are not noteworthy differences on results depending of cooling method. Besides, the variation can be approximated by means of logarithmic correlations with a high coefficient of determination (Fig. 3b). PB is mainly composed of calcite, dolomite, quartz and iron. These minerals undergo few changes at low temperatures, this is the reason no significant variation in the thermal damage factor is observed at 200ºC. Above this temperature, more relevant mineralogical changes happen, such as the change from Goethite to Hematite, the decomposition of dolomite first, and later the decomposition of calcite at higher temperatures. These mineralogical changes are responsible for a more pronounced variation in the thermal damage coefficient up to 600ºC. Since this temperature, the decomposition of calcite has not yet finished and the volume of cracks produced increases, but the ultrasound waves do not lose more velocity then the damage factor don not show significant changes.

According to the thermal damage scale defined by Zhang et al. (2015), samples exposed to 200 ºC can be classified as rock "*undamaged*", those exposed to 400 ºC as "*micro damage*" and those exposed to 600 and 800 ºC as "*secondary damage*". The level of damage based on K_T values, does not represent the changes recorded in porosity and the visual inspection of the PB samples exposed to the thermal treatment. In addition, the K_T damage factor varies in a smaller range of values than D_T does. Therefore, D_T is more appropriate to describe the thermal damage on PB limestone.

As a final summary of the results of this research, the Figure 4 is shown.

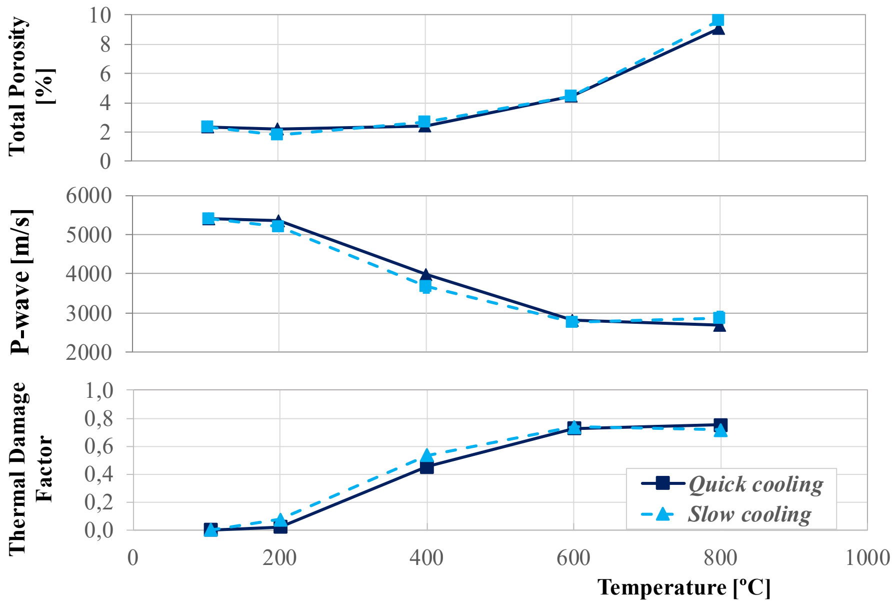

Fig. 4 Summary of the main results of this study.

4 Conclusions

This research analyzes the effect of the exposure to different temperatures on porosity and P-wave velocity of a limestone commonly used in construction. The main conclusions of the current study are:

1. Regarding the variation of the open and total porosity, 400 ºC is a threshold temperature to the PB limestone. Below this temperature, the porosity hardly changes and over it increases strongly.
2. The MIP tests show little changes of the interparticle porosity as temperature increases in comparison with the intraparticle porosity that shows an increase similar to those registered on open and total porosity. The more remarkable increase of porosity take place in the ultramicropores range, although thermal exposure accentuates the multimodal character of the porosity.
3. The P-wave velocity shows three different rates of variation as temperature increase: scarcely changes at 200 ºC (respect to the non-heated samples), drop drastically at 400 and 600 ºC and there are no remarkable differences between the results obtained at 600 and 800 ºC.

4. As porosity increases, P-wave velocity decreases. Although, there is a threshold value of porosity from the P-wave velocity does not change even if porosity remains increasing. On PB samples this value might be 2 times the initial porosity (non-heated samples) reached at 600 ºC, since the P-wave velocity hardly decreases for higher porosity.
5. The damage factor calculated by means of the equation of Zhao at al. (2009) is more appropriate to describe the thermal damage on PB limestone.

In any case, the results suggest that P-wave velocity can be a suitable test to estimate the thermal damage on limestones exposed to high temperatures.

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