Fire Induced Microstructural Changes in Local Building Materials: Cases of White Marble and Limestone

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Abstract. The aim of this work is to evaluate the degradation state of natural stones after their exposure to fire. These building and decorative materials, widely used in the architectural heritage, suffer irreversible damage when exposed to high temperatures. Therefore, knowledge of their residual durability is crucial in order to determine whether the post-fire building structure should be restored, reinforced or demolished. For this purpose, limestones (calcarenites) and white marbles collected from local quarries were subjected to heating-cooling cycles in a muffle furnace at various temperatures up to 1100°C. After each exposure, the selected samples were characterized at room temperature using X-ray diffraction (XRD), micro-Raman and ATR-FTIR infrared techniques. The results obtained showed that the mineralogical nature of both calcareous and marble natural stones is a key factor in their thermal stability when exposed to high temperatures. Above 570°C, natural stones undergo calcite decarbonation at different temperature ranges. Marble, which is mineralogically monophasic, underwent decomposition at 800°C, similar to calcite in its pure state. Calcarenite was decomposed at a much lower temperature of about 700 °C. This study classifies marble as more thermally stable than calcarenite.

Introduction

Since antiquity, natural stone has been widely used as a building and decorative material in ancient edifices. It continues to play an important role in the restoration and replacement of damaged parts. However, the fire of the Great Mosque of Taroudant (Morocco), the main mosque of the Saadian dynasty, in 2013, and the fire of Notre-Dame Cathedral in Paris in 2019 have brought back the problem of preserving built heritage in the face of serious risks. It's therefore extremely important to collect experimental data on the behavior of natural stone at high temperatures in order to diagnose structures that have suffered fire damage.

When exposed to fire, natural stone undergoes a significant increase in temperature, resulting in irreversible changes in its mineralogical composition and structural properties. Several studies have examined the effects of high temperatures on the residual physical and mechanical properties of various types of stone [1-5]. The works of Zhang et al [1] and Vigroux et al focused on calcareous and siliceous stones [2]; they analyzed the effect of high temperatures on the physico-mechanical properties of seven stones with different mineralogical and physical properties. The evolution of these properties up to 1000 °C in four limestones and four marbles with different textural and structural properties was also studied by Ozguven et al. [5]. The primary colour changes that stones are likely to undergo when exposed to high temperatures have also been

identified in some studies. A non-destructive technique using colorimetric measurements to assess the extent of stone degradation, and more specifically the highest temperature reached after exposure to fire, was investigated by Beck et al. [6] and Ozguven et al. [7]. However, there are few studies on the thermal behavior of natural stones using Raman and ATR-FTIR vibrational techniques, as well as XRD. The aim of this work is to provide additional experimental data on the physico-chemical behavior of natural stones when exposed to temperatures ranging from room temperature (RT) to 1100°C. Hence, two natural stones commonly used in ancient buildings were selected: white marble and limestone/calcarenite. The investigation combined techniques that were effective and complementary in assessing the high-temperature behavior of the building stones considered: ATR-FTIR, micro-Raman and XRD.

Materials and methods

Samples

Two series of natural stones were investigated: white marble and limestone collected from different regions in Morocco (Fig. 1). The white marbles were sampled from Sidi Lamine quarries in the Khénifra region. The rock presents a white color with locally heterogeneous levels of yellow shades. Previous studies have shown that it consists mainly of calcite with traces of dolomite [8]. The limestones are sedimentary rocks extracted from a quarry near the city of Meknes, Morocco. The rock displays a yellowish-ochre hue and exhibits visible heterogeneity. Two distinct facies are discernible: one is compact and fine, while the other is porous and grainy. Preliminary analyses indicate that it is primarily composed of calcite, with an average quartz content and traces of kaolinite clay.

Only the results of a single sample, which is highly representative of the others, will be presented for each series.

(a)   (b)
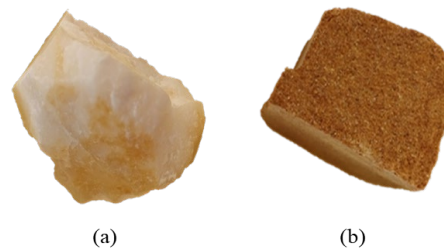
Fig. 1. The studied samples: white marble (a) and limestone (b).

Heat treatment protocol

Heating-cooling cycles were carried out using a programmable muffle furnace (Nabertherm). The thermal protocol involved a gradual increase in temperature at a constant rate of 1°C/min until the target temperature was reached, followed by a 4-hour isothermal stage to ensure uniform sample temperature. To prevent thermal shock, the cooling process was dependent on the furnace's inertia. Various temperatures were considered on the basis of TGA/DTA sample analysis: 80, 100, 200, 350, 450, 570, 800, and 1100°C. To deepen structural analyses only 570°C, 800°C, and 1100°C were chosen as they correspond to the physico-chemical transformations present in the studied natural stones. This option allows for the understanding of actual temperatures achieved during a fire [2].

Instrumentation

An Alpha II Bruker spectrometer equipped with an ATR accessory with a diamond crystal was used to collect infrared spectra in the 4000-400 cm^{-1} frequency range with a spectral resolution of 4 cm^{-1}. Powder micro-samples were pressed onto the surface of the crystal.

Raman spectra were obtained using a portable Sequentially Shifted Excitation Raman Spectrometer (SSERS) Bravo from Brucker. The spectra were collected, on compacted pellets, with excitation ranging from 700 to 1100 nm.

A Bruker D8 Advance X-ray diffractometer with a Cu Kα anode (λ = 1.5418 Å) operating at 40 kV and 30 mA was used to obtain XRD diffractograms of the powders. The measurements were carried out at room temperature over an angular range of 10-70 degrees at 2θ with a step size of 0.02 degrees.

Results and discussion

Infrared spectroscopy ATR-ATR

The ATR-FTIR analysis of limestone and white marble before heat treatment reveals the presence of calcite, identified by its typical intense bands at 1417, 874, and 711 cm^{-1} (Fig. 2). They are respectively attributable to the asymmetric $v_3(C-O)$ stretch, the $v_2(C-O)$ out-of-plane bend and the $v_4(C-O)$ in-plane bend of CO_3^{2-} carbonate group [9–11]. The limestone spectrum also exhibits a band at 1028 cm^{-1}, probably associated with the Si-O plane stretching vibration mode of clays in the form of kaolinite [12,13]. Doublet at 797-777 cm^{-1} and bands at 1165, 1082 and 693 cm^{-1} can be attributed to quartz in small quantities [10,11,14].
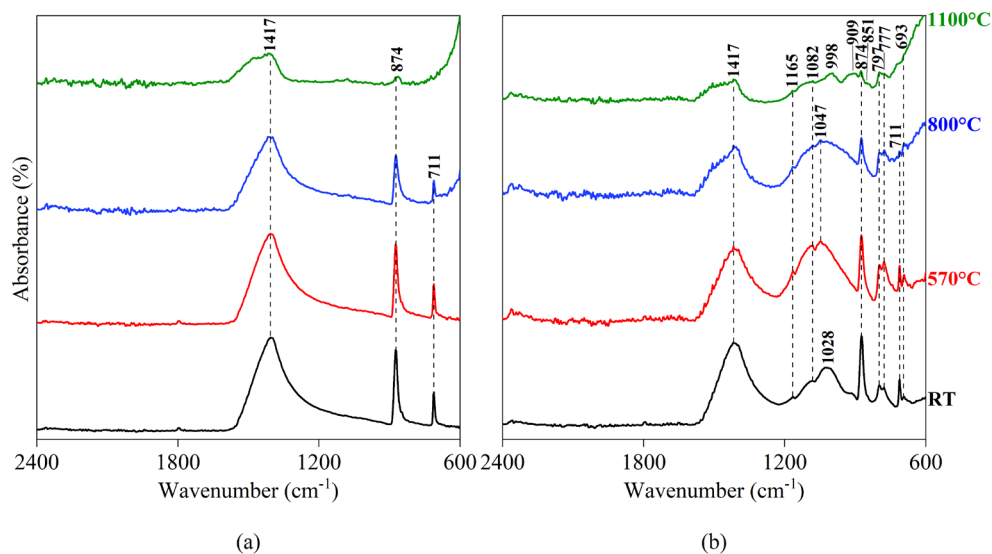

Fig. 2. ATR-FTIR spectra at room temperature (RT) of white marble (a) and limestone (b) after heat treatment at different temperatures.

The spectra collected at room temperature after heat treatment are compared with those obtained at the initial state (RT) before heating. After heat treatment of limestone at 570°C, the band associated with kaolinite (1028 cm^{-1}) shifts to 1047 cm^{-1} (Fig. 2b), indicating kaolinite $(Al_2Si_2O_5(OH)_4)$ dehydroxylation to metakaolin $(Al_2Si_2O_7)$ [13]. At 800°C, a decrease in the intensity of the calcite characteristic bands is observed. At this temperature calcite decomposes into calcium oxide, releasing carbon dioxide and forming portlandite as a result of (CaO) interaction with air moisture [2,5]. The characteristic bands of lime and portlandite, located respectively at 3460 and 3644 cm^{-1}, are outside the explored spectral range [11,15]. At 1100°C, typical calcite modes become extremely weak (v_2, v_3) or disappear (v_4) ; calcite decarbonation process is complete or almost complete. This may indicate a phase transition [16]. The emerging bands at 998, 909 and 851 cm^{-1} indicate the apparition of a new phase, called gehlenite [17,18], resulting from the reaction between metakaolin and lime according to the following reaction [11,19]:

$$Al_2Si_2O_7 + 2CaO \rightarrow Ca_2Al(AlSiO_7) + SiO_2. \tag{1}$$
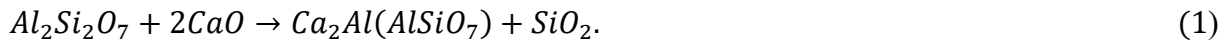
Micro-Raman spectroscopy

The micro-Raman spectra of untreated stones corroborate the results obtained by IR (Fig. 3), showing typical bands of calcite at 1086 and 712 cm^{-1}, attributed respectively to the stretching (v_1) and bending (v_4) symmetric modes of the CO_3^{2-} carbonate group [8,20]. Low intensity signals associated with quartz are also present in limestone. In particular, we distinguish the peak at 464 cm^{-1} corresponding to the symmetric stretching of $Si - O - Si$, as well as a weak line at 392 cm^{-1} associated with the lattice or network mode [8,21,22]. The kaolinite could not be identified because it occurs as a trace element in limestone.
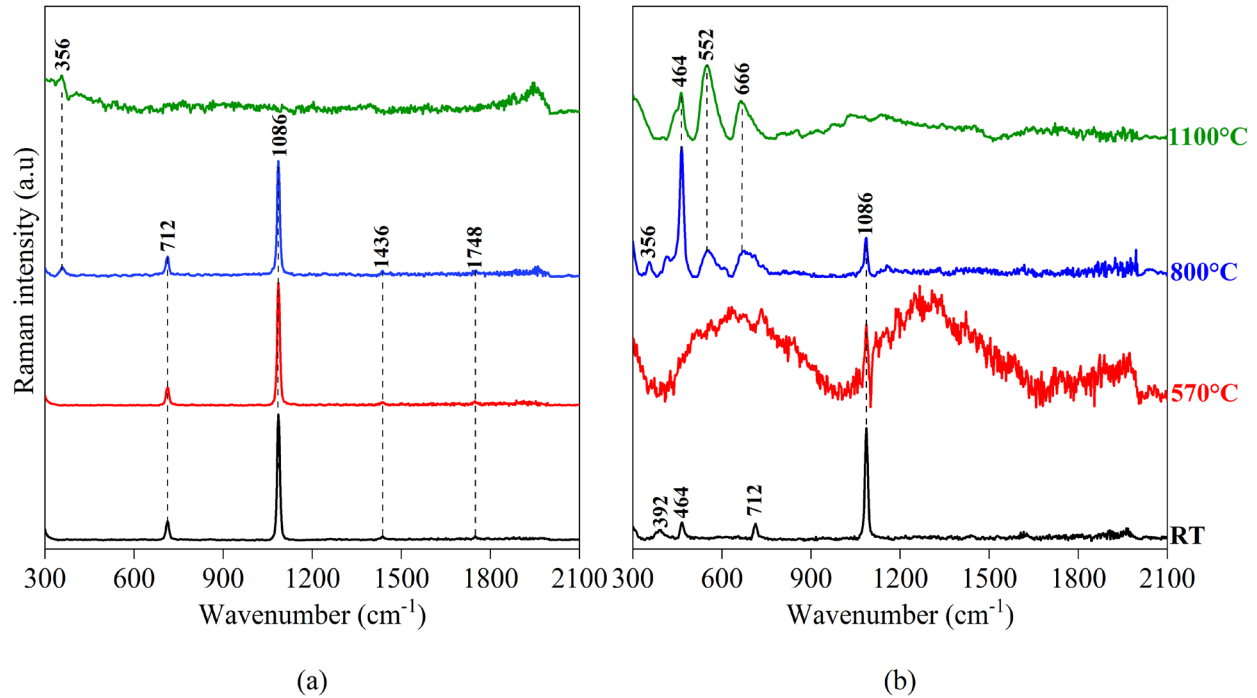

(a)   (b)

Fig. 3. Micro-Raman spectra recorded at room temperature of white marble (a) and limestone (b) after heat treatment at different temperatures.

Heat treatment at 570°C caused significant changes in the limestone sample. Only the peak attributed to calcite remained distinct at this temperature, while signals attributed to quartz were disturbed by fluorescence phenomena. With heat treatment at 800°C, the calcite peak at 712 cm^{-1} disappeared and the intensity of its main band located at 1086 cm^{-1} decreased (Fig. 3b) while new bands emerged at 666 and 356 cm^{-1}, probably related to the formation of gehlenite and portlandite [21, 23, 24]. As previously stated in the infrared section, gehlenite is formed by the reaction of metakaolin and lime. The hydration of lime is also facilitated by the humidity in the surrounding air during cooling, resulting in the formation of portlandite [2,25]. Another band is observed at 552 cm^{-1}. It can be attributed to the presence of aluminum or silicon compounds [26]. As a result, the intensity of the main silica band around 464 cm^{-1} increased, followed by a decrease as the heat treatment temperature increased to 1100ºC. This phenomenon may be due to the partial decomposition of calcite and the α-β phase transition of quartz [27]. At 1100°C, the calcite and portlandite bands disappear, while the band attributed to gehlenite becomes slightly more distinct. This suggests that the lime produced is involved in the formation of gehlenite. These results support the hypothesis of calcite decomposition already corroborated in the infrared section.

For white marble (Fig. 3a), heat treatment at 570°C and 800°C revealed a good thermal stability of this stone. After reaching a temperature of 1100°C, decarbonation of calcite occurs, resulting in the formation of portlandite identified by the band at 356 cm^{-1}.

X-ray diffraction analysis

Figure 4 shows the diffractograms of the studied stones recorded at room temperature after heat treatment at different temperatures. After treatment at 570°C, limestone diffractogram shows significant increase of the quartz characteristic line and disappearance of the low intensity peak at 12.42°2θ related to kaolinite [28]. Additionally, there is a decrease in the intensity of the peak at 29.48°2θ related to calcite (Fig. 4b) [8, 10, 11]. This is as a consequence of kaolinite dehydroxylation and phase transition of quartz [27, 29].

No significant changes were observed in the case of white marble treated at 570°C. However, after treating at 800°C, XRD analysis showed an important reduction in calcite lines and the appearance of new ones at 37.4 and 18.09° 2θ. These lines illustrate the decomposition of calcite and the formation of lime and portlandite [1,15]. The formation of portlandite occurs as soon as the lime reacts with atmospheric water vapor. After treatment at 1100°C, calcite is completely transformed into lime. In addition to peaks assigned to lime and portlandite, the limestone diffractogram also displays peaks attributable to gehlenite, due to the reaction of lime with metakaolin [19,30].
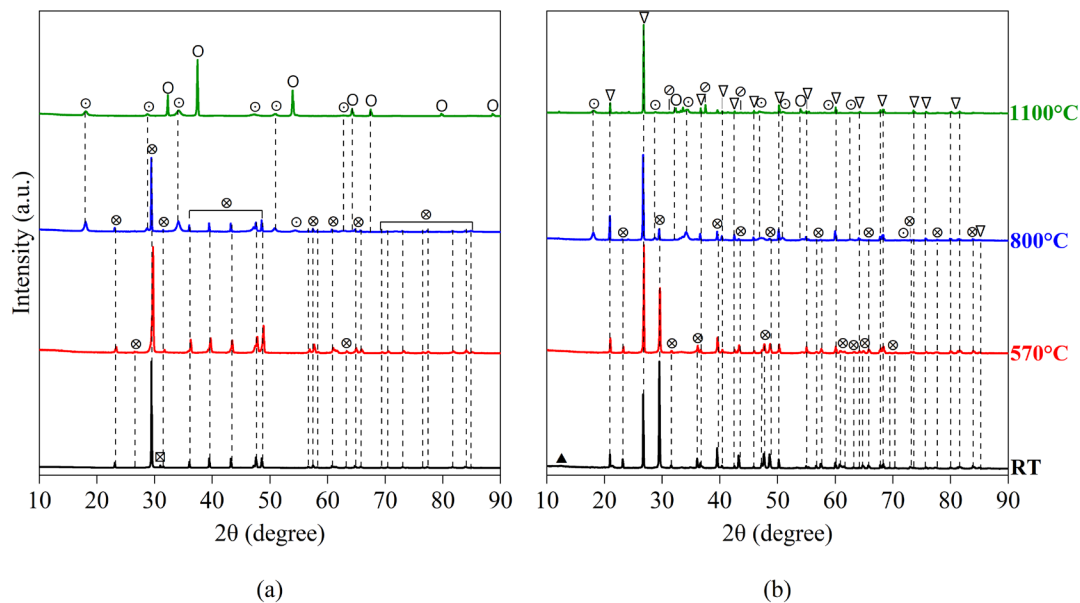
Fig. 4. Diffractograms performed at room temperature of white marble (a) and limestone (b) after heat treatment at different temperatures.

Conclusion

The investigation focused on the structural diagnosis of the effects of high-temperature exposure on building and decorative materials in architectural heritage. Specifically, the study examined the behavior of limestone and white marble when exposed to fire. The stones are sampled from quarries in Morocco.

The ATR-FTIR, Raman, and XRD structural analyses were found in perfect agreement and showed that exposure up to 570°C has very little influence on the microstructure of these materials. However, at higher temperatures, calcite, which is the main mineral in these stones, begins to decompose. In the case of marble, identified as monophasic, calcite showed a decomposition temperature around 800°C, similarly to pure calcite. Nonetheless, in the case of calcarenite, the

presence of secondary minerals proved to be a stimulating factor for the relatively early decomposition of calcite. This calcite breaks down makes the limestone less resistant to temperature compared to marble, making it more vulnerable to fire.

Acknowledgments

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