www.maajournal.com

Mediterranean Archaeology and Archaeometry
Vol. 21, No 2, (2021), pp. 191-209
Open Access. Online & Print.

DOI: 10.5281/zenodo.5057556

IMPACTS OF FIRE ON HISTORIC STONE MASONRY STRUCTURES: PHYSICOCHEMICAL ANALYSIS AND APPLICATION TO THE AL-MUSAFIRKHANA PALACE (CAIRO)

Sayed Hemeda[1,2] and Tabina Osman[3]

[1]Conservation Department, Faculty of Archaeology, Cairo University, Giza-Egypt
[2]Institute of Basic and Applied Science (BAS), Egypt-Japan University of Science and Technology (E-JUST), New Borg El-Arab city, Postal code 21934 Alexandria, Egypt
[3]Ministry of Tourism and Antiquities, Grand Egyptian Museum Authority, Cairo, Egypt

Received: 02/04/2021
Accepted: 06/06/2021
**Corresponding author: S. Hemeda (Sayed.hemeda@cu.edu.eg)*

ABSTRACT

The current paper investigates the influence of fire on historic stone masonry structures, for the purpose to assess stones structures deterioration, based on non-destructive measurements for significant changes in the physical properties and mineralogical composition of limestone. Different cubic samples of limestone used in historic buildings، were selected and subjected to increasing temperatures, from room temperature to heating at 200°C, 400°C, 600°C, 800°C in the oven for a period of 6 hours. The induced changes in the microstructure, petrophysical and mechanical properties of the limestone were examined and correlated with The petrographic analyses (polarizing microscope, XRD, SEM) and physical parameters (density, porosity, water absorption), mechanical properties (uniaxial compressive strength). Results showed that fires and high temperatures cause significant changes in the physical properties and mineralogical composition of limestone، particularly at temperatures beyond 300°C, produces considerable microcracking and causes colour changes in limestone. The developed cracks act to increase the porosity and significant reduction in compressive strength in limestone. The study included the methods of treatment through for the use of some consolidation materials (Paraloid B72) mixed with nanocomposites in the process of consolidation. Results showed demonstrated the superiority of the Paraloid B72 mixed with Nano calcium hydroxide in the consolidation and filling the spaces between the mineralogical composition for building stones. The results of this paper indicate that the deterioration of limestone depends on mineralogical composition and fabric. The consideration of mineralogical composition and rock fabric parameters, however, helps provide a more comprehensive evaluation and interpretation limestone damage.

KEYWORDS: Fire impact, Historical Stone Masonry, Nano Composites, Conservation, Calcium hydroxide, kaolinite

1. INTRODUCTION

The recent fire at MusafirKhana Palace brought attention to the severe damage that fires can cause to historic buildings, where the Cairo attended a large number of fires at the last period, an impact on the architectural heritage. Limestone are porous sedimentary rocks that have been widely been used in many historical buildings and monuments worldwide. Exposure to fire and high temperatures cause significant changes in the physical and mineralogical properties of limestone. The aim of this research is to propose a strategy to assess the fire and high temperature performance of limestone. There are several significant studies about the decomposition of the elements that form the structure, such as the effect of high temperature and fire on historical buildings. Some researchers pointed out that the susceptibility to damage in archaeological buildings concentrated mainly on the morphological changes on stone surfaces such as cracking, scaling or analyses of colour changes (Chakrabarti, 1993). the knowledge of how mechanical properties and mineralogical composition of limestone change with increasing temperature is fundamental for the conservation and restoration of fire damaged limestone monuments, the fire causes surface changes in the colour of stones and the accumulation of soot and flames at heat temperatures less than 300oC, and the effect of damage is large when the temperature is higher than 600oC at temperatures less than 300°C, surface changes occur in the colour of the stones (Chakrabarti et al., 1995; Hajpál, 2002). the physical properties decrease with increasing temperatures, and both of modulus of elasticity, Poisson's rate decrease with increasing temperatures, and Yang modulus decreases above 600oC at room temperature (Hajpál and Áörök, 2004; Brotons et al., 2013). The effect of thermal expansion on the porosity of rocks and porosity varies according to the exposure of the stones to different rates of temperature and the duration of exposure to heat, high temperatures increase the internal stresses between the grains, which It results in cracks, affecting the voids between the granules (Ozguven and Ozcelik, 2013; Ingham, 2008) .The effect of fire and high temperatures on the mechanical properties of building materials in monumental buildings, high temperature weakens the mechanical properties and then affects the durability and durability of these materials (Ugur et al., 2014; Hone bone, 1998). the properties of rocks affected by high temperatures, and performed some non-destructive tests on porosity, measuring ultra sound velocity, determining the fracture stress of the stone, and its resistance to shear tensile stresses, as it was found that the stress of fracture decreases with increasing temperatures by about 35% and the modulus of elasticity may decrease by a range of approximately 75-78% (Russo et al., 2008). The deterioration of limestone is related to its com-position and micro fabric parameters which include microstructure (geometry and morphology of grains and pores) and texture (crystallographic preferred orientation). Limestone is mainly composed of calcite crystals which exhibit distinctive thermal anisotropy. Calcite crystals expand when they are heated in the direction parallel to the c-axis, but contracts in the normal directions (Kleber et al., 2010). This anisotropy is considered to be the main factor responsible for limestone deterioration, particularly at its early stages (Ruedrich et al., 2010; Sheremeti-Kabashi, 2002; Siegesmund et al., 2000; Zeisig et al., 2002). When limestone is subject to temperature changes, thermal stresses are developed that can be sufficiently large to produce microcracks in and between its mineral grains (Battaglia et al., 1993; Robertson, 1982; Weiss, Siegesmund, et al., 2002). The widening of micro cracks due to weathering increases the porosity and pore size of limestone and changes the water transport mechanism in the stone. This renders the limestone more susceptible to damage by other deterioration mechanisms and factors, particularly water (Rüdrich, 2003; Sheremeti Kabashi, 2002). Consequently, the deterioration rate of limestone is considerably accelerated, leading eventually to serious damage or even destruction of limestone objects and structures. The measure of damage caused by fire depends on many factors, the changes at the natural stones could be influenced by the burning circumstances, is the heating one-sided or more-sided, homogenous or heterogeneous, the size of the burned stone, velocity of heating, the maximum burning temperature, stone type and its characteristics, the colour change in natural stones almost corresponds to the dehydration of iron compounds. Heat causes the development of a pink or reddish-brown colouration in brown or buff- colour, the colour changes start at a temperature of 200-300°C in most rocks. Some stones contain a small amount of organic substance, which occur that the grey colour covering the red one. Other significant kinds of decay of stones by burning are cracking, shattering, scaling, and spelling the process of scaling and spalling continued during the fire, therefore the strength of the stone is surpassed, a bursting of the hot outer part is forced, and the rock peels. Rounding off the edges can occur if there is an edge the heat can work from two sides, this form of decay is regularly seen on steps, pillars and window-heads, the susceptibility to damage in archaeological buildings depends on the components of the building material, its homogeneity and its resistance to various environmental factors. It consists of a variety of building materials and most of them are flammable, and the fire spreads very quickly and causes combustion

of organic materials and building components of the building, and works to bring about the destructive and damaging effect of the architectural elements that resist. In this study, the deterioration of limestone as a result of the fire and high temperature is examined and correlated with colour change and physico-mechanical properties measurements for a variety of historical limestone widely used in historical buildings, this should help us to understand the nature and extent of changes in limestone structure and physico-mechanical properties with progressive weathering. Archaeometric techniques for conservation, diagnostics and protection is reviewed elsewhere (Liritzis et al., 2020).

This study aims to develop new methods for assessing limestone deterioration a result of exposure to fire and high temperatures through some laboratory measurements and also, determine the variations in the properties of some natural stones which have different structural and textural properties.

2. THE ARCHITECTURAL DESCRIPTION

Al-Musafirkhana palace was designed and constructed by Mahmoud Muharram in 1779. The house consisted of two sections, the northern section one we reach from Darb al-Musamma; and the southern section one we reach from Darb al-Tablawi; the house has four facades, three entrances, and three floors (Revault and Maury, 1979), the general layout of the palace is a large open courtyard in the middle of the house, and there is the southern side Al-Takhtabush (a rectangular shape covered by a wooden ceiling with decorations). The ground floor contains three halls (Fig.1).; the first hall a large located to the left of Al- takhtabush, the Qashani hall on the eastern side of the courtyard, another hall on the northern side of the courtyard, the house contains some storerooms for storing things and food, servants' rooms, and more than the reception hall for visitors. Also, contains on a water woman and water tank, and each main hall is attached to a bathroom, the house consists of three floors (Fig.2).

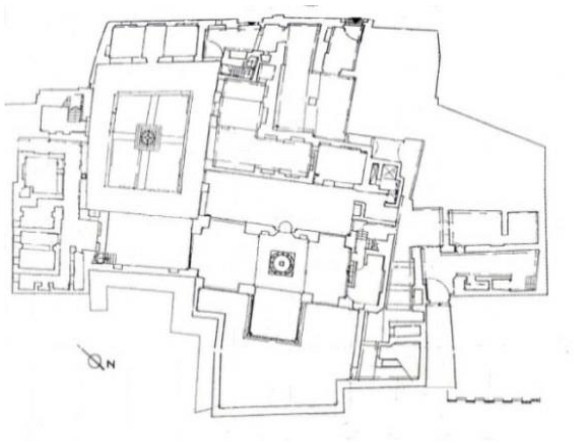


Figure 1. General layout the ground floor of Musafirkhan a Palace in the old Cairo.

Figure 2. General view for the ground floor of Musafirkhana palace after fire.

The ground floor it contains the main open courtyard, and the three main halls, the reception hall, the bathroom, some rooms, stores and the garden, the reception hall, which is a large hall for receiving merchants, consists of one hall and three iwan (Fig.3a), the open courtyard, A large courtyard in the middle of the house, arranged around most of the elements of the house. Al-takhboush it is a rectangular area extending from east to west and overlooking the courtyard and it is an important architectural element in residential buildings in Islamic times (Fig.3b), the roof is based on a round marble column, and the second floor is topped by the façade covered with a mashrabiya. Al-Qashani Hall it is the great hall for receiving merchants, the upper part is covered with Qashani and decorated with drawings, geometric shapes and various plant motifs (Kashef, 2010). The first floor it consists of Al-Assad hall and nativity hall in which the Khedive Ismail was born, the hall lead to the Al-Asaad hall and birth hall, the bathroom attached to the Al-Asaad hall. The Al-Asaad hall consists of a hall and two Iwans, bathroom is attached to it, the floor is a rectangular space and it is lower than the iwan, the nativity hall consists of a bedroom room and an iwan. The second floor it consists of a group of corridors and Haramlek Hall that overlooks the main courtyard of the Saraya in the largest mashrabiya in the world, and the hallway that leads to the Haramlek hall and the attached bathroom, the hall that leads to the Haramlek hall is a rectangular shape similar to the lower trench, and in the middle of it is a round marble column.

a b

Figure 3. various views showing the palace from the inside before the fire, a) The open courtyard before the fire; b) The Takhtabush before the fire.

The State of Preservation Al- MusafirKhana was burnt to the ground in November 1998, where the fire caused damage a great loss to the architectural components of the building (Fig.4). The measure of damage caused by fire depends on many factors, the changes at the natural stones could be influenced by the burning circumstances, is the heating one-sided or more-sided, homogenous or heterogeneous, the size of the burned stone, velocity of heating, the maximum burning temperature, stone type and its characteristics, the colour change in natural stones almost corresponds to the dehydration of iron compounds. Heat causes the development of a pink or reddish-brown colouration in brown or buff- coluor, the colour changes start at a temperature of 200 -300°C in most rocks (Fig.4a).

a b c

Figure 4. A general view of the palace from the inside showing the damage and the impact of the fire; a) Photograph showing degradation of limestone blocks and Colour change; b)Photograph showing cracks and Colour change of limestone from a fire-damaged block ; c) Photograph showing roasted and burned ceilings wooden.

Some stones contain a small amount of organic substance, which occur that the grey colour covering the red one. Other significant kinds of decay of stones by burning are cracking, shattering, scaling, and spalling (Fig.4b),the process of scaling and spalling continued during the fire, therefore the strength of the stone is surpassed, a bursting of the hot outer part is forced, and the rock peels. Rounding off the edges can occur if there is an edge the heat can work from two sides. This form of decay is regularly seen on steps, pillars and window-heads, the susceptibility to damage in archaeological buildings depends on the components of the building material, its homogeneity and its resistance to various environmental factors. It consists of a variety of building materials and most of them are flammable, and the fire spreads very quickly and causes combustion of organic materials and building components of the building, and works to bring about the destructive and damaging effect of the architectural elements that resist (Fig.4c).

3. MATERIALS AND METHODS

Archaeological and historical buildings stones can be influenced by high temperatures or due to fire.As a result of the effect of fire, a number of damaged and decompositions occur in the elements forming them. The stone materials investigated in this study consist

of five sets from the limestone blocks, collected from the from the Al-Musafirkhana palace in old Cairo. The groups were divided so that each group consisted of three cubic samples. To study the influence of fire on historical buildings stones, dry limestone samples were heated in an oven at five different temperatures namely (22 C°, 200 C°, 400 C°, 600 C°, and 800 C°). for 6 hours, warming up took 1 hour, and after controlled heating the samples cooled down slowly in the oven, the test conditions do not fully reflect the processes that take place during natural fire. Nevertheless, this method allows filling in the existing gap in knowledge of the thermal behaviour of limestone's, the samples were tested before (at 22°C) and after the heat experiments at each temperature. Heating at high temperatures proved to be an effective method of thermal weathering for calcific stones (Franzoni et al., 2013). The induced alterations in microstructure and physical and mechanical properties of the heated marble samples were investigated and compared to those of the unheated samples. The measurement of the physical and mechanical properties before artificial thermal weathering requires drying the samples by heating at 60 C° to constant mass.

3.1. Petrographic and Mineralogical Examination

3.1.1. Polarizing microscope examination

The mineralogical composition and petrographic characteristics of the limestone samples were studied. This was performed using X-ray diffraction measurements and polarizing light microscope. The changes induced in the microstructure of the samples after heating were investigated on thin sections under Leica polarizing light microscope. The examination with a polarized microscope depends on preparing thin sections of the sample with a thickness of 0.03 mm, and the section is affixed to a transparent glass slide with Canada balsam and the surface is flat, the colour is observed through the overlap between the sample components. The aims of the examination with a polarized microscope is to study the optical properties, identify the shapes of crystals and the components of rocks, and verify the processes of transformation of minerals (Russo and Sciarretta, 2012). Identify mineral impurities such as iron compounds and clay minerals, the connection of mineral components with each other, the physical or chemical change that occurred to them, and determine the products of damage. Photomicrographs under Cross Polarized Nichols (XPL) were taken by a Leica (ICC 50 HD) camera attached to the microscope.

3.1.2. X-Ray Diffraction Analysis.

Mineralogical characterizations of the samples were carried out with X-ray diffraction by means of a Philips X-Ray Diffraction equipment model PW/1710 Philips with Cu Ka radiation operating at 40 Kv and 20 mA. Spectra were taken in the range 5°–60° 2θ and step times of 1 s/step. Were used the reflection peaks between 2θ = 2o and 60o, corresponding spacing (d, A) and relative intensities (I/Io) were obtained. The diffraction charts and relative intensities are obtained and compared with ICDD files. The samples were prepared and exposure to different temperatures, comparing the results with reference samples before the fire.

3.1.3. Scanning Electron Microscope

Scanning Electron Microscopy (SEM) SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyzes), with accelerating voltage 40-100 K.V., magnification14x up to 100000 and resolutions for Gun.1n). The scanning electron microscopy depends on the passage of a beam of electrons through the electronic probe under a voltage ranging from 40-100 kV on the surface of the sample. The scattered electrons are captured through an electronic detector and sent to a display screen after several processes. Scanning electron microscope aims to investigations fine fissures. The morphological shape, the secondary components intertwining between the layers of rocks, the determination of the degradation and damage, the secondary changes resulting from the conversion of some minerals to another, and the changes in the mineral components of the rocks and clay minerals, as well as evaluating the consolidation materials and their success in completing the polymerization process, their ability to penetrate and fill the pores, the form of bonding and the depth and penetration of the consolidation material .This procedure was carried out at the Building Materials Research Center - Scanning Electron Microscope Unit in Dokki – Egypt.

3.1.4. Colour change

CIELLAB colour change is a global measure of brightness; the colorimetric measurements were carried out at different stages of exposure fire to evaluate the alteration of color before and after fire. We used three-dimensional colorimetric system L*a*b* (also known under the name of CIELAB) (Bratitsi et al., 2018). The CIELAB color parameters (L*, a*, b*) was used to quantify the changes in color; where the value (L*) indicates bright white, the value (a*) measures red and green, and the value (b*) measures yellow and blue, these scales are designed to give colour measurements (Ibrahim et al., 2019). In the form of

identical optical units, it expresses the total colour difference (E) the difference in colour (Δ L*, Δ a*, Δ b*).The measurement of colour change aims to determine the percentage of change in colour from the normal range and an evaluation of these samples before treatment or aging if industrial obsolescence of the treated samples .According to international standards .The difference in the lightness (Δ L*), the chromaticity coordinates (Δ a* and Δ b*) for the samples before and after artificial aging were calculated using following equations :(Δ l*= l*t - l*0) (Δ a*= a*t - a*0) (Δb*= b*t - b*0), Where:"0" represents the values before exposure to fire "t" denotes those samples to after fire ,the value of (Δ E) does not exceed five degrees in the field of stone restoration, where the total colour change of the surface of the samples was measured after exposure to fire at temperatures of 200°C, 400°C, 600°C, 800°C, and compared to the standard sample before the fire, and determine the percent of the colour change of samples after fire. The colour change begins at a temperature of 200 -30 °C in most rocks, the phenomenon of colour change in rocks depends on the combustion conditions and the mineral components. Organic materials begin to convert to coal at 500°C.

3.2. PETROPHYSICAL AND MECHANICAL PROPERTIES

3.2.1. Physical properties

The physical properties (Bulk density (ρ), apparent porosity (n), and water absorption (Wa), of these samples were determined by calculating the volume of each sample, measuring the dry weight and the wet weight of each sample., the physical properties were calculated as follows.

Density is one of the important physical properties for determining the properties of rocks, and defined as is the weight of a unit volume of a specific volume of dry solid mineral material at 105 °C (constant weight) to the weight of the same volume of water, or density is the unit of mass of a substance over a unit of mass of volumes, g/cm^3. Whereas, the bulk density of samples was calculated by dividing the dry weight of samples to the bulk volume (Manoudis et al., 2009). Density was determined as shown in equation = m /V g/cm, where: ($_\rho$) is the density in g/cm^3 ($_m$) is the mass in gm. And ($_V$) volume in cm^3. Porosity is one of the basic physical properties of rocks. Porosity influences the internal surface area per unit material volume and this in turn. Defined as the ratio between the volumes of voids to the total volume of the sample (Robertson, 1982).

Porosity of rock and stone helps to determine the strength and durability (AGI Glossary 1980), but also permits estimates of the content of moisture and flow through the masonry, and the porosity may increase with the presence of fine cracks and primary or closed breaks (AGI Glossary 1980). Porosity was determined as shown in equation. n = (A- B) / (V × 100), where: n is the porosity in %, A is the mass of the dried specimen, B is the mass of the soaked specimen, and V the total volume of the sample.

Water Absorption the weight of water absorbed by the rock after 24 hours of immersion in water divided by its oven-dried weight expressed as a percentage of its oven-dried weight. It was calculated by dividing the absorbed water weight (after a bath of 24 h, in vacuum) by the dry weight of specimens or is the ability of the stone to absorb water, which is an important property because it is related to porosity, as shown in equation for water absorption W(%): W = (A-B) /A × 100. Where: A the dry weight, B the wet weight in gm.

3.2.2. Mechanical properties

Uniaxial compressive strength is the maximum load per unit area that the stone can bear without crushing. A higher uniaxial compressive strength indicates that the stone can with stand loads tending to reduce size, to determine the uniaxial compressive strength ($_{UCS}$) was performed on at least 5 cubic specimens of 5 cm side length using digitec machine equipped with universal testing machine ($_{UTM\ II}$) software. The load was applied on the specimens perpendicular to the foliation plane with a loading rate of 750 N/s until failure. The uniaxial compressive strength was calculated as the maximum load divided by the area of the loaded surface. Specimens are tested in ASTM 170. They should be cubes at least 2'' to 3'' on each side. Each face must be perfectly flat and they must be parallel or perpendicular with each other. Faces must be smooth with no tool marks and there should be no nicks at the corners (Hemeda, 2019, 2020), (ASTM, 1985). The uniaxial compressive strength affected by several factors, the mineral composition, grain size, water content, porosity and permeability, fractures, loading rate. Where the sample is placed between the plates of the loading machine and then vertical stress is applied to it provided that the collapse of the sample is within (5-10) minutes and that the pressure produced at the moment of the collapse of the sample is called the non-confined uniaxial compressive strength, which is calculated as in the following equation. σc = (P/A). Where: σc = uniaxial compressive strength (MPa), P = strength ($_{MN}$), A = cross-sectional area m^2. (Hemeda, 2021).

4. RESULTS AND DISCUSSIONS

In the study, colour change and whiteness, physical and mechanical properties change, are taken into account to investigate the effect of high temperature

in a fire on natural stones. The physical and mechanical properties of the studied limestone samples before and after fire are presented in Table 1. The accessible porosity of the limestone samples increased progressively by 4.92%, 9.45%, 22.70%, after heating at 200 C°, 400 C°, 600 C°, respectively. This increase of porosity is attributed to the thermally induced cracks between calcite grains. Similarly, the capillary water absorption of the limestone samples increased progressively with increasing high temperature due to the increase in the proportion of capillary pores and the improved connectivity of pores caused by heating (Ahmad, 2020). The effect of temperature on the physical properties of limestone seems to be intensified by heating at temperatures higher than 200˚C; the microscopic investigation of the heated samples confirms this result. Remarkable changes represented by development and expansion of intergranular and intragranular cracks, in the microstructure of the limestone samples heated beyond 200 °C have occurred. Below this heating temperature, the induced microstructural changes are relatively small and less significant (Fig. 5).

X-Ray diffractometric data of the limestone samples before to the fire. Show that calcite is the main mineralogical phase in both the studied materials (fresh sample). With few percent of secondary minerals. Such as quartz and the microcline ($KAiSi_3O_8$), but samples after fire at 200°C. Show that calcite is the main component of limestone (Fig. 5). ,this explains that the limestone were not affected by the fire at this temperature, but samples at 400°C, show calcite with few percent of quartz, microcline, and iron oxides (hematite) (Fig.6), the samples after the fire turned from cream white color to the color dark red or grayish-red. Other samples have turned pinkish-red, and this explains that the samples contain iron oxides, and the red color that appeared after the fire depends on the percent of the iron oxides in the samples, or the samples maybe contain of a few the clay minerals that have turned after fire transform color red. But samples at a temperature at 600°C, showed the results of the analysis the presence of calcite, a few of quartz with the disappearance of some secondary minerals, and organic residues. Moreover, the samples at 600°C turned from creamy white color to gray (Fig.7), this explains that the samples during the fire escalated from them Carbon dioxide is the product of the oxidation process of calcium carbonate, which led to the formation of gray, especially since the fire oven is sealed, or the samples may contain some organic residues that have turned gray by the fire (Fig. 8). As for the samples at a temperature of 800°C (Fig. 9), the calcite mineral showed 100%, the samples were transformed from creamy white colour to dark white, with the appearance of microcracks on the surface of the samples (Fig. 10). Gradually ,the samples were transformed into powder from lime in the room temperature , this indicates that the samples absorbed the water vapour the room atmosphere, which led to a high thermal shock, as a result of which the samples turned fine powder, and the results were confirmed again with the preservation of the samples inside the dryer, as the samples inside the dryer were not affected except for some parts of the samples that were exposed to the normal atmosphere, Its fragment and gradual collapse.

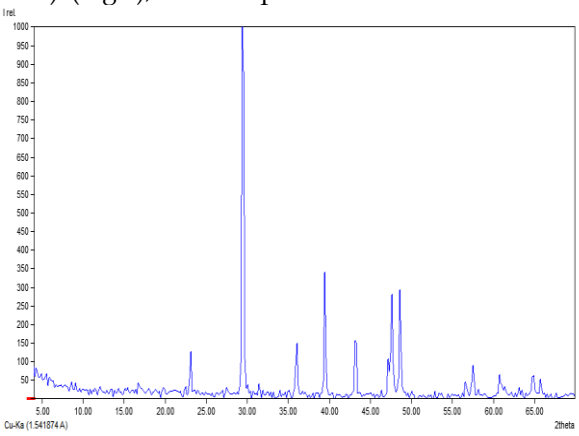


Figure 5. Representative XRD pattern of limestone specimen before exposed the fire. (Fresh sample) Major Constituent; Calcite, Dolomite, quartz. .Minor Constituent; feldspar, Goethite, Clay mineral.

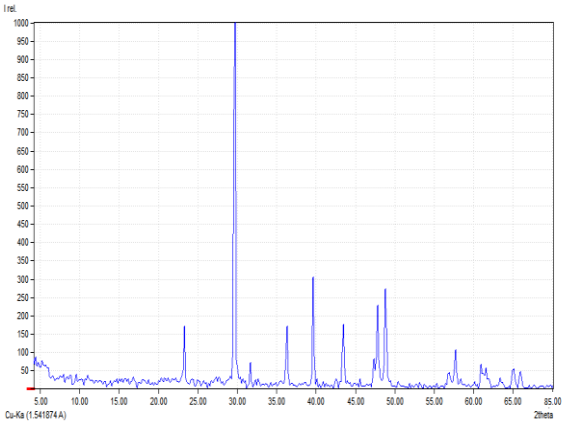


Figure 6. Representative XRD pattern of limestone specimen after exposed the fire, at 200°C Major Constituent; Calcite, quartz, hematite .Minor Constituent; feldspar, Goethite.

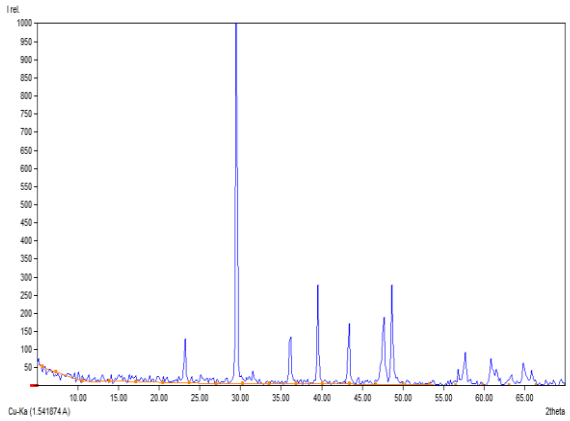


Fig.7. Representative XRD pattern of limestone specimen after exposed the fire, at 400°C. Major Constituent; Calcite, quartz, hematite .Minor Constituent; feldspar, Goethite.

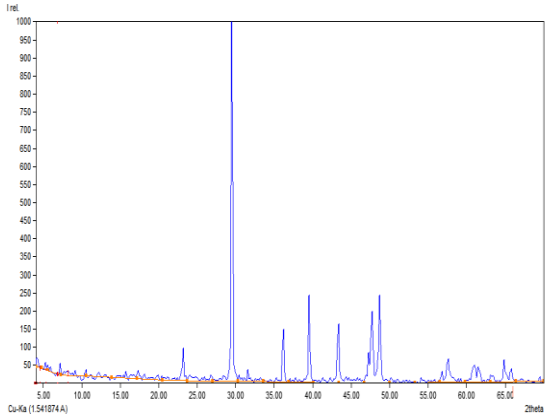


Fig.8. Representative XRD pattern of limestone specimen after exposed the fire, at 600°C. Major Constituent; Calcite, quartz, hematite .Minor Constituent; feldspar, Goethite.

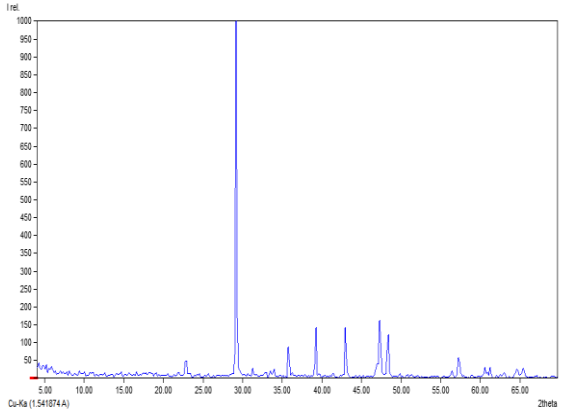


Fig.9. Representative XRD pattern of limestone specimen after exposed the fire, at 800°C. Major Constituent; Calcite, quartz, hematite .Minor Constituent; feldspar, Goethite.

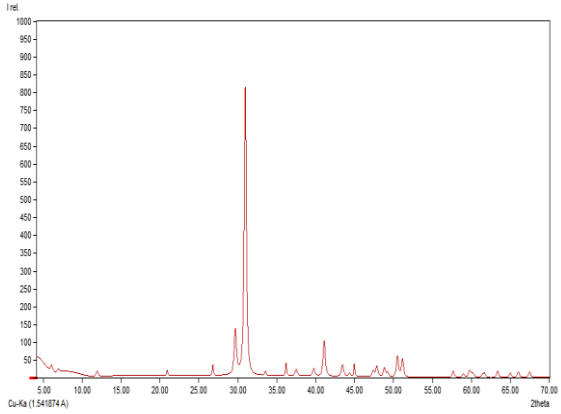


Fig.10. Representative XRD pattern of limestone specimen after exposed the fire in site. Major Constituent; Calcite, quartz, hematite .Minor Constituent; feldspar, Goethite.

4.1. COLOR CHANGE

The colorimetric measurements were carried out at different stages of aging to evaluate the alteration of color before and after fire exposed (Ibrahim et al., 2019).We used three -dimensional colorimetric system L*a*b* (CIELAB), (Kubovsky & Kačik, 2014). Was used (L*, a*, b*) to quantify the changes in color. The difference in the lightness (Δ L*), the chromaticity coordinates (Δ a* and Δ b*) for the samples limestone's before and after fire. The study shows that there is a color change in the natural stones when they are exposed to different temperatures. The views of the samples exposed to different temperatures are given in Color change is observed while the temperature rises. However, after 800°C, samples were dominated by the white color. The reason is that a white coat occurs on the surface at above 850°C, while a small quantity of white coat also appears at 800C°. Following the exposure to high temperatures through the methodology outlined above a discolouration of the limestone was noted. The original sample is character by a natural creamy white colour. Changes in mineral composition of limestone after heating were accompanied by changes in colour. No changes in the samples heated at 200C° (Fig. 11), but significant changes in colour of limestone were visible macroscopically in samples heated above 350°C° and higher temperatures. Using polarized microscopic examination, was possible to record the colour changes which cannot be discern by human eye. A reddish- brown discolouration was noted once the stone was exposed at 400C°. A light grey colour was observed following exposure hours at 600°C. The colour of the stone became white after exposure at 800C°; however, some alteration products as a result of the calcite deterioration could not be identified under microscope.

Following the exposure to high temperatures through the methodology outlined above a discolouration of the limestone was noted. The original sample is character by a natural yellow colour. Changes in mineral composition of limestone after heating were accompanied by changes in colour. On samples heated at 200°C changes were negligible. Significant changes in colour of both limestones were visible macroscopically in samples heated above 300°C and higher temperatures. Using polarized microscopic examination, was possible to record the colour changes which cannot be discern by human eye. A reddish-brown discolouration was noted once the stone was exposed at 400C°. A light grey colour was observed following exposure hours at 600°C. The colour of the stone became white after exposure at 800oC (Fig. 11).; however, some alteration products as a result of the calcite deterioration could not be identified under microscope. X-ray diffractometry analysis was made to distinguish such materials. Portlander [Ca $(OH)_2$] and quartz (SiO_2) minerals were detected in addition to calcite ($CaCO_3$). It appears that alteration of the mineralogical structure of the marble takes place at elevated temperatures. Chemical analyses were made to understand the extent of any chemical changes due to heat effect. Results are presented in Table 1. One should note that there are no considerable chemical changes and significant variations in loss of ignition.

The natural colour of limestone is related to the mineral composition and contains hydrated iron oxide, the material changed colour to pink or reddish brown at 250 – 300°C, and to more reddish at 400 °C. The stone becomes a grey-white powder at 800°C, the calcination of calcium carbonate begins at 600°C and proceeds rapidly beyond 800 C° (Chakrabarti, 1996), and the strength is reported to reduce once calcination occurs. main objective of physical and mechanical tests were to estimate the average temperature on the fire-exposed side of the blocks during the fire and examine dependence of other engineering parameters on temperature changes, bulk physical properties changes in addition to their differences in mineral composition and fabric, the studied limestone differ mainly in their values of density, porosity and water absorption, the values of apparent and real densities do not show extreme changes after heating, with the steepest change shown in samples heated at 600°C when a significant decrease of density and increase of open and total porosity were recorded in Table 1, the density of the samples and their uniaxial compressive strength were observed to decrease with gradually increasing temperature exposure over the 6 hour period, with significant reduction in the uniaxial compressive strength for samples exposed at a temperature of 800°C, the density of samples decreased by 20% for the same exposure, the sample turning from its natural grey colour to white, the generation of the cracks is related to shrinkage of clay minerals due to the loss of structural waters. This suggests that the texture of limestone influences the behavior of minerals at elevated temperatures. The cement type and amount of cementing minerals of the limestone play the primary role in determining the thermal behavior of such limestone. Other clay minerals as cement were recorded at different temperatures, kaolinite was detected up to 450°C, but above this temperature the mineral structure collapsed in most limestone, chlorite gives greenish colour to the sandstone but at above 450°C it transforms, the carbonates such as calcite and dolomite are stable in limestone up to 600 C°, the transformation of carbonates to Ca and Mg oxides does not lead to colour changes. Meanwhile, the textural change can be very abrupt when high amounts of carbonate present in the newly formed portlandite (it is generated only above 750°C), can absorb air moisture, causing volume expansion; this can lead to the collapse of limestone structure. Type and amount of mineral components of the limestone play the primary role in determining the thermal behavior of such limestone. Other clay minerals as were recorded at different temperatures, as kaolinite was detected up to 450°C, but above this temperature the mineral structure collapsed in most limestone, chlorite gives greenish colour but transforms at above 450°C, the carbonates such as calcite and dolomite are stable in limestone up to 600°C, the transformation of carbonates to Ca and Mg oxides does not lead to colour changes. Meanwhile, the textural change can be very abrupt when high amounts of carbonate present in the newly formed portlandite (it is generated only above 750°C), can absorb air moisture, causing volume expansion; this can lead to the collapse of limestone structure.

Table 1. Shows the color change values of the samples limestones before and after fire.

samples	Colour Change			(⊗E)2 - (⊗E)1			⊗E2)2 - (⊗E1			Sum	⊗E2)2 - (⊗E1√
	L*	a*	b*	L*	a*	b*	L*	a*	b*		
Natural stone	80.5	2.5	13.6	-	-	-	-	-	-		
200 C°	79.4	3.1	14.7	1.1	- 0.6	- 1.1	1.21	0.36	1.21	2.78	1.67 <5
400 C°	68.6	5.4	14.4	11.9	- 2.9	- 0.8	141.4	8.41	0.64	150.45	12.27 >5
600 C°	63.5	2.4	7.2	17.0	0.1	6.4	289.0	0.01	40.96	329.97	18.17 >5
800 C°	66.7	1.00	11.5	13.8	1.5	2.1	190.4	2.25	4.41	197.06	14.04 >5

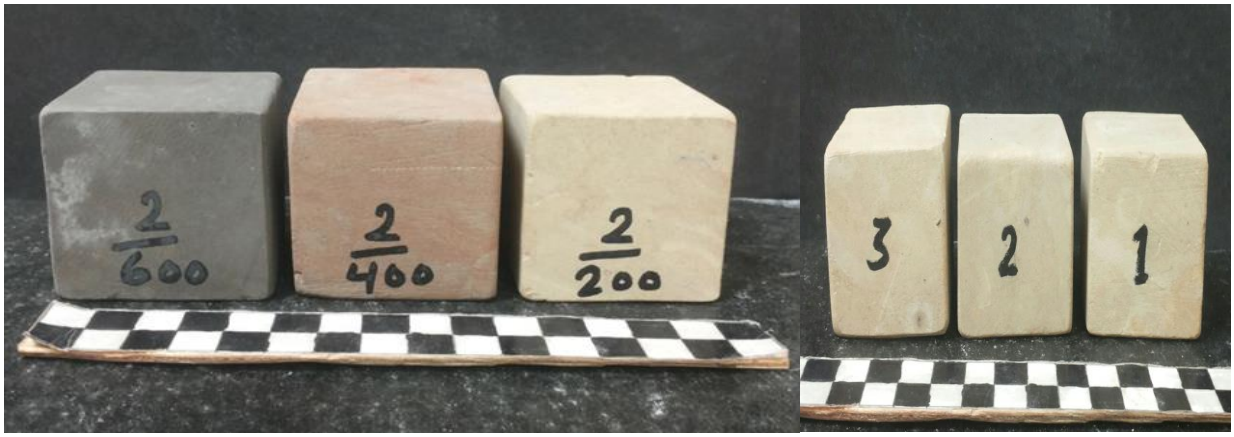


Figure.11. photos showing the colour change of stone samples before and after the fire.

Examination results by scanning electron microscope after exposure to fire. results It is evident in the mineral formation at a temperature of 200C° (Fig.12.a)., but in some sections the spread of fine cracks between the grains, the formation of some gaps, and the beginning of the disintegration of the bond between the crystals and some of them as a result of the effect of heating, but at a temperature of 400°C, clear changes appeared in the heterogeneity between the grains, and the loss of the bond between the crystals and some of them, the voids formed resulting from the expansion processes of minerals and the spread of micro cracks, the collapse of the constructive composition and the separation of crystals, but at a temperature of 600°C, the separation of crystals and the collapse of the crystal structure, inhomogeneity, the emergence of vacuums and large gaps as a result of the vanishing of some minerals and their transformation or the formation of other minerals, due to the influence of high temperature, and the transformation of some crystals To form an indistinct longitudinal fiber, but at a temperature of 800°C, some sections showed heterogeneity, and Separation of the crystals, the dissolution of the bonding material between the granules, the spread of fine cracks, and the deep gaps caused by the transformation of the minerals. As for the results of examining samples with a scanning electron microscope after exposure to fire. The results of the examination of the natural stone samples before the fire showed that the main component of limestone is calcite, where the grains and crystals of the mineral appeared in a medium-to-fine shape and compact overlapping, with the interconnection of the grains, but some gaps appeared and the erosion of the edges of the crystals of calcite mineral, as the results showed. Examination of the stone samples after the fire and at a temperature of 200°C that there was no clear change in the mineral composition, but some sections showed the spread of fine cracks between the grains and the formation of some gaps and the beginning of the dissolution of the bonding between the crystals and some of them as a result of the effect of heating, but some sections of the stone samples after the fire at a temperature 400C° (Fig.12.c), clear changes in the heterogeneity between the grains, and the loss of the cartilage material, which led to the disintegration and breakdown of the bonding between the crystals and some of them, the occurrence of gaps and voids resulting from the expansion processes of minerals and the spread of micro cracks, the collapse of the constructive structure and the separation of crystals, and the stone samples showed after the fire and at a temperature of 600°C (Fig.12.e). The separation of crystals, the collapse of the crystal structure, inhomogeneity, the appearance of voids and large gaps as a result of the erosion of some minerals and their transformation or the formation of m Other minerals, due to the effect of high heat, and the transformation of some crystals into the form of longitudinal fibers that are not clearly defined, pictures As for the stone samples that were exposed to fire at a temperature of 800°C (Fig.12.g), some sections showed heterogeneity, separation between crystals, and fading Intergranular bonding material, micro cracks spreading, and deep cavities resulting from metamorphism (Fig.12.i).

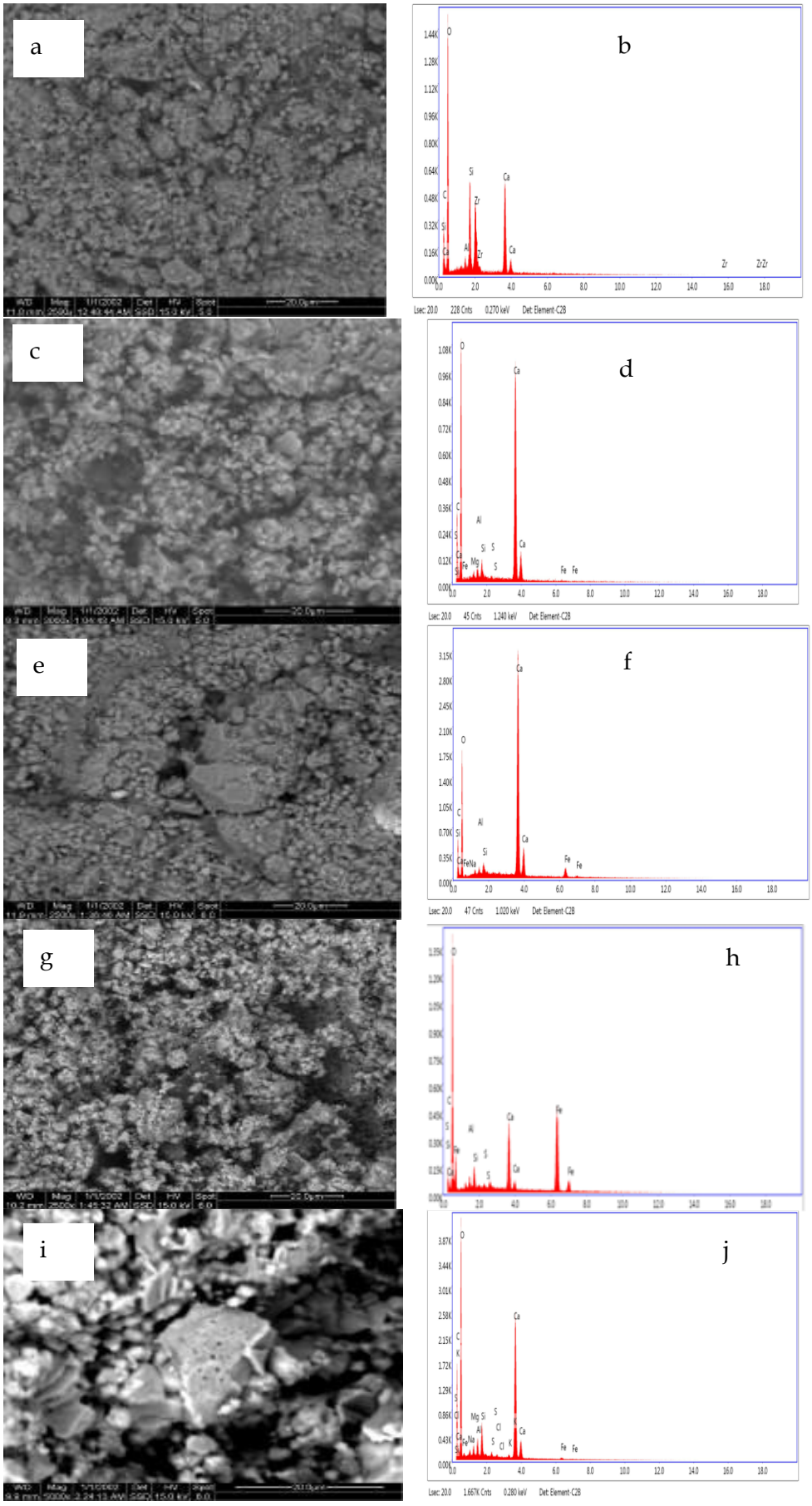
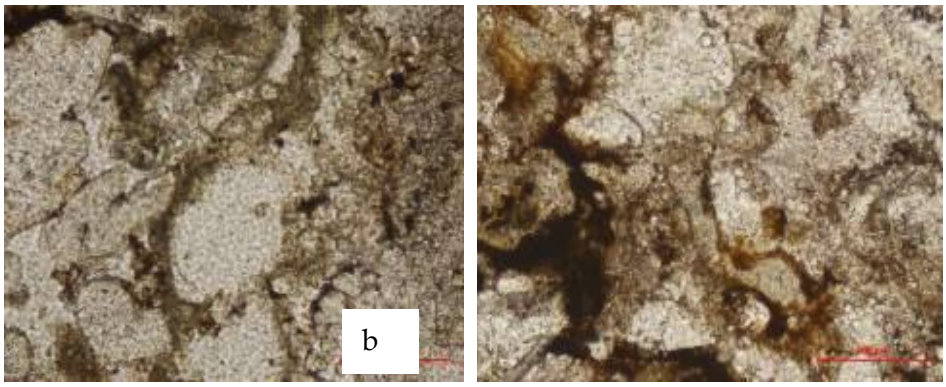
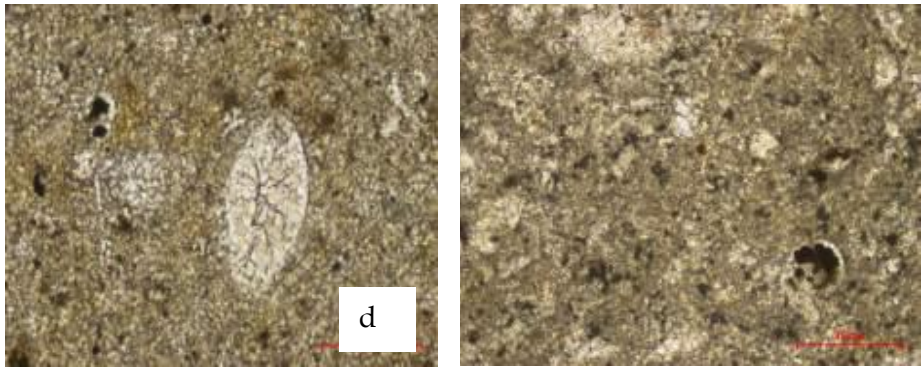


Figure 12. SEM micrographs images with EDX showing textural and mineralogical characteristics of samples before and after the fire; a) at room temperature showing fine – grains calcite with few secondary minerals such as quartz and dolomite; b) at room temperature contain calcite, Sulphur, Aluminium and Silicon; c) at 200°C, the thermal expansion of the minerals caused a void between the grains and increased of the porosity; d) at 200°C, contain calcite, Iron oxides, Sulphur, Aluminium and Silicon; e) at 400°C, the thermal expansion of the minerals caused a void between the grains and increased of the porosity; f) at 400°C, contain calcite, Iron oxides, , sulphur, Aluminium and Silicon; g) at 600°C, the high temperature caused Collapse of some of the minerals composition; h) at 600°C, contain calcite, Iron oxides, sulphur, Aluminium and magnesium; i) at 800°C, the high temperature caused Collapse of some of the minerals composition; j) at 800°C, contain calcite, Iron oxides, sulphur, Aluminium and magnesium.

4.2. *Effect of temperature on properties of stones*

The original mineralogical structure of the limestone prior to fire hazard was determined on thin sections recovered at surfaces that were not directly exposed to flames in the fire. Such portions of the samples were considered to be slightly affected by the heat, and may form a basis for comparison purposes. A polarized microscope and a point counting equipment were utilized in the study. The texture of the limestone blocks consisting of mainly fine calcite minerals (Fig.13.a). Cleavage surfaces of calcite minerals were easily visible with a quite clear appearance. Disturbances such as color changes and loss in transparent texture were not observed in the crystals and in their rims. The first group of petrographic thin-section analyses Consisted of fire exposed materials. Some samples of fire -exposed at 600°C. They were in semi-opaque condition with a light gray color as observed under polarized microscope. Samples that were slightly exposed to heat or not affected during the fire at all, on the other hand, did not exhibit any significant alterations (Fig.13.b). Additional five samples constituted the second group. These samples of limestone blocks and heated up to 800°C in increments of 200°C in order to investigate microscopic and mineralogical alterations as well as changes in the porosity (Fig.13.c).. Color of the samples turned out to light gray between 450 and 600°C. Thereafter color of the samples became white. Samples were all cracked and deteriorated once at 600°C, threshold temperature was exceeded. They completely lost their structure and texture at 800°C, producing dust with an average diameter of 3–4 cm. Pictures of some samples that were remained intact and enabled thin section slicing after heating are given in (Fig.13.e,f) to illustrate above-mentioned temperature related changes. Color change with gradual temperature increase was also evident in heated samples (Fig.13.g,h). Separations along cleavage surfaces, inter-crystals, disintegration and loss of transparency reflected as gray color formations were observed beyond 600°C during microscopic investigations. At 800°C, however, some alteration products as a result of the calcite deterioration could not be identified under microscope (Fig.13.i,j).





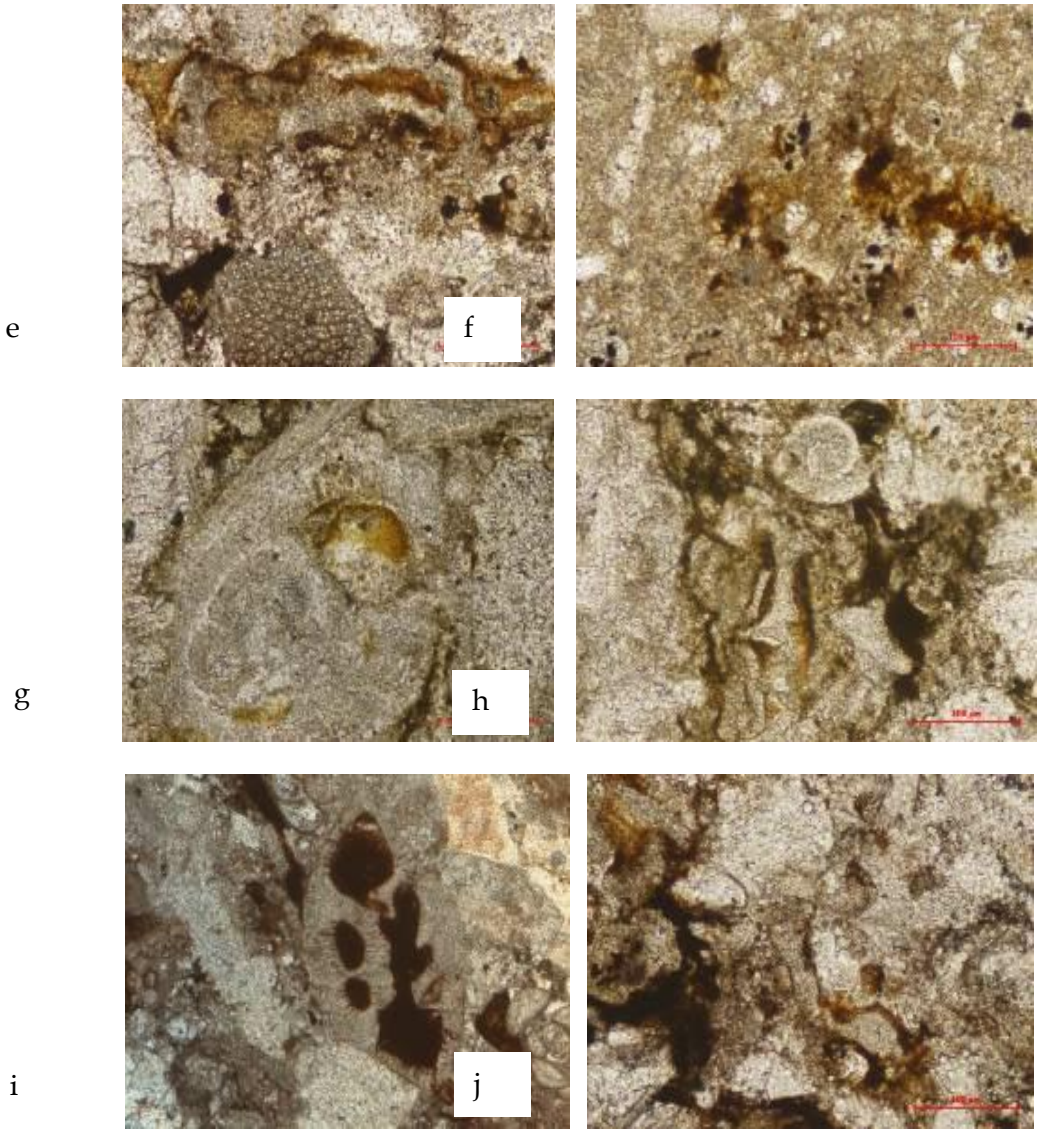


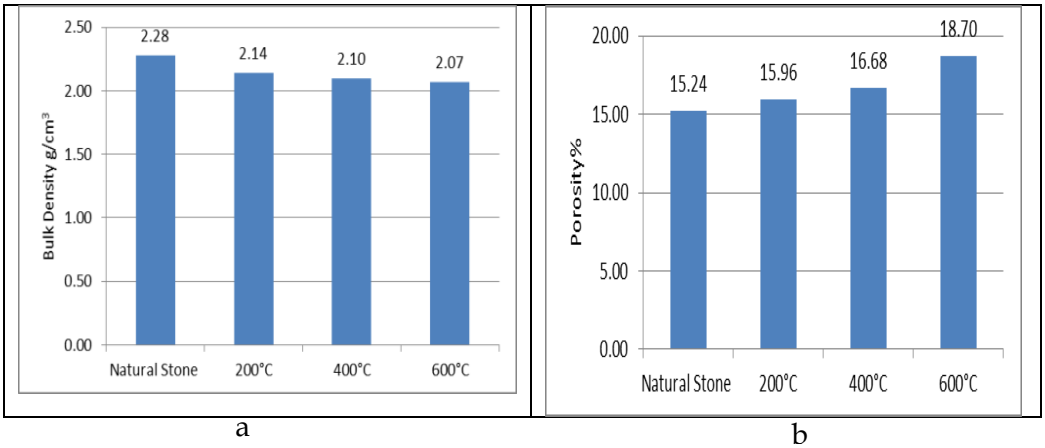
Figure 13. Thin section micrographs images showing mineralogical characteristics of samples before and after the fire; a) Fresh sample contain micrite limestone, bioclast calcite and abundantly fossils are present (Oda); b) Fresh sample contain micrite limestone, bioclast calcite and abundantly fossils are present (Oda Gastropod; c) at 200°C, contain micrite limestone, Bioclast calcite and abundantly fossils are present (Oda Gastropod); d) at 200°C, contain micrite limestone, Bioclast calcite and abundantly fossils are present (Oda Gastropod); e) at 400°C,contain Micrite limestone. Moderately crystalline calcite and large amount the dark red colour hematite mineral.f) at 400°C, contain Micrite limestone. Moderately crystalline calcite and large amount the dark red colour hematite mineral; g) at 600°C, contain sparitic limestone, crystalline calcite and small amount of opaque minerals, fossils with amounts of Gastropod, a large a mounts of the hematite; h) at 600°C, contain sparitic limestone, crystalline calcite and small amount of opaque minerals, fossils with amounts of Gastropod, a large a mounts of the hematite; i) at 800°C, contain sparitic limestone, crystalline calcite and small amount of opaque minerals, fossils with amounts of Gastropod, a large a mounts of the hematite; j) at 800°C, contain sparitic limestone, crystalline calcite and small amount of opaque minerals, fossils with amounts of Gastropod, a large a mounts of the hematite.

The grain densities of intact rocks given in Table 2. Were assumed to be showing no significant changes after heating since the rocks were basically made up of calcium carbonate and the heating temperatures were much lower than the carbonate dissociation temperature 800°C. Bulk densities measured after completion of heating periods showed are decrease up to 10.24% of initial value for all samples except for whose velocity decrease to 9.5% of the initial value. Most of this decrease occurred at 600°C, heating temperature, following very small decrease up to 300°C. The bulk density of all samples markedly increased with Increasing temperature. This was due to thermal cracking such as spreading and increasing of internal fissures and voids, usually along grain boundaries and separation of cleavage planes inside the grains.

The effect of the fire on the physical properties of the limestone is investigated by determining the variations of porosity and water absorption by weight before and after the fire-exposed limestone (Yavuz et al., 2010). Porosity tests were performed on samples taken from the limestone blocks. Several tests on samples representing the fire-exposed side yielded an average porosity value of fire 16.64%. On the other hand, five limestone samples from the undamaged side were gradually heated in the oven. Heating process has progressed in such a manner that samples were heated by increasing temperature of the oven from 20°C to the target value at varying rates so that heating temperature was reached in 45 min for all temperature levels. Samples were then kept in the oven for 6 h after the temperature increased to the target value. Uniaxial compressive strength of the limestone samples exhibited strong dependence on temperature elevations (Hall & Hamilton, 2016). This was well reflected by the samples. It can be seen in that uniaxial compressive strength of five samples tested at varying temperatures including the room temperature (20°C) decreased with gradually increased temperature with some exceptions (Fig.14.a). Tests at 400 and 600°C deviated strongly from the general trend. This behaviour can be attributed to temporary strength gain due to the reduction in moisture content of the samples prior to crack initiation. The uniaxial compressive strength corresponding to the fire temperature, however, can be read in Fig. 10 as fire 30MPa. Samples from the fire-exposed surfaces, on the other hand, were tested in two groups. One of the groups consisted of five samples that were preheated up to 300°C. (Fig. 14.b). Samples heated beyond this temperature were not suitable for uniaxial compressive strength testing due to excessive disintegration. It is noteworthy that uniaxial compressive strength corresponding to the room temperature in this group is very close to the one obtained at the average fire temperature in the group of samples from the intact block surface (Fig. 14.c). The overall response of the samples to temperature increase in these two groups is similar. It appears that strength of the samples are close to each other when the 400–600°C residual off set temperature in the fire exposed block samples is taken into consideration. It is noteworthy that uniaxial compressive strength at 200°C is corresponding to the room temperature in this samples is very close to the one obtained at the average fire temperature in the samples before fire. As for the uniaxial compressive strength of the samples heated at a temperature of 400C° , 600C°, it showed a rise in the compressive strength, which may be due to the burning and solidification of clay minerals. Closer inspection of these samples showed that samples failed along a residual crack, which might have been developed during the fire or have been already there before the fire hazard as shown with (Fig. 14.d).

Table 2. Variation of the properties for samples stone before and after fire.

properties / Temperature	Bulk Density g/cm3	Decrease %	Porosity %	Increase %	Water Absorption %	Increase %	UCS Mpa	Increase %
Natural stone	2.28	-	15.24	-	6.67	-	24.80	-
200 OC	2.14	6.14	15.96	4.92	6.86	2.85	24.10	3.60
400 OC	2.10	7.90	16.68	9.45	7.74	13.19	29.20	16.80
600 OC	2.07	9.21	18.70	22.70	8.93	33.88	30.50	22.00
800 OC	--	-	-	-	-	-	-	-



a b

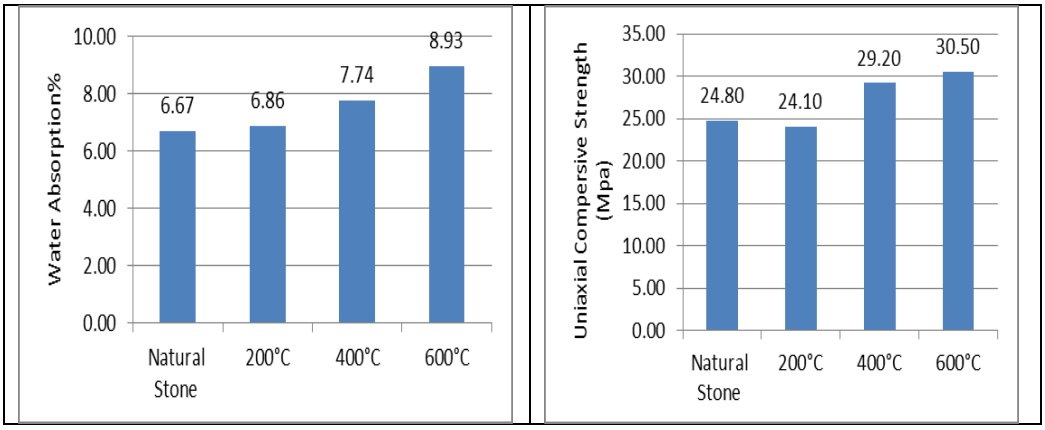


Figure 14. Average values of the physical and mechanical for samples stone before and after fire; a) Average values of bulk density; b) Average values of porosity; c) Average values of water absorption; d) Average values of compressive strength.

4.3. Treatment and Conservation processes

The treatment and conservation of archaeological buildings is an important process, given the durability and continuity of these buildings, the restoration process is of a special nature and depends on the full experience of the nature and characteristics of the different styles of ancient buildings, the first stages of treatment and conservation begin with various cleaning methods, which aim to remove dust and foreign bodies that have accumulated on the external surfaces of buildings.

a b

Fig.15. General View showing the State of Preservation and the degradation of building stones; a) photo showing the current state of the hall before restoration; b) photo showing the mechanical cleaning process using simple tools

Mechanical cleaning depends on removing dust, dirt, and foreign objects stuck on the outside of the buildings, using some tools and a simple manual number of brushes (Brian and Srphen, 1987), chisels and various scalpels. The nature of suspended materials and their connection to the surface control the variety and multiplicity of tools, as well as the different cleaning process. Chemical cleaning use wet chemical cleaning to remove inks, varnishes and various fatty materials in which no chemical cleaning is used, where the high polarity of water helps to dissolve and dissolve the links between particles of dirt. Water used with some chemical solutions that increase work efficiency. Moreover, remove dust and dirt with the help of the brush, and water is used under pressure as a fine mist either by spraying or in water vapour (Fig.15).

Consolidation process aims to strengthen and cohesion of the internal structure of building materials and to bind the weak and separate parts that have been exposed to various damage factors, the strengthening process is one of the most important maintenance works due to its inability to restore it and possible unwanted effects (Laurenzi & Tabasso, 2004) .The consolidation material must be compatible with the nature and components of the building materials, and achieve the required cohesion, and be porous, the

success of the hardening material depends on penetrating the pores of the stone and connecting the separate grains which gives the stones and other building materials a high resistance against the influence of the surrounding environment factors. Paraloid B-72 is an acrylic co-polymer of ethyl methacrylate and methyl acrylate (70/30), It is soluble in acetone, ethanol, toluene and xylene. The Paraloid B-72 is characterized by good adhesion strength as well as oxidation and light resistance, transparency and mechanical resistance (Pinto and Rodrigues, 2008). Acrylate resins are generally characterized by heir low solvent evaporation rates, and can be safely used as excellent adhesives with archaeological the stones. Paraloid B72 is also characterized by viscosity and adhesion strength suitable for the adhesion the artefacts (see e.g. for ceramics, Mohamed Moustafa Ibrahim et al., 2021).

Nanomaterial are homogeneous liquid that relies on the chemical composition of the use of very small nano droplets to reach a new technique for archaeological conservation Nanoparticles are used to improve mechanical properties of the adhesive mixtures. The improvements in strength, thickness, mechanical performance and overlap length obtained by using the nano materials in the process on joining. The use of nano-adhesives gives a good quality to the mechanical properties. The paraloid B.72 (5% concentration) one of the best material, which was mixed with nano calcium hydroxide, nano kaolinite, and nano carbonate calcium, applied to samples of limestone (Ibrahim et al., 2019).. It is clear from the results that the calcium hydroxide nano material led to a complete and good bonding between the grains constituting the limestone material, penetration and diffusion in the voids and the formation of a network of polymer and nanomaterials particles between the weak and healthy grains, and this is due to the great role played by the nanomaterials used in improving the mechanical properties For the polymer "Paralloid B.72", but the results indicate the failure of nano-kaolinite and calcium carbonate in the treatments, which may be due to the insufficient distribution within the grains, and then the formation of a dense film of polymer and nano-material particles on the surface of the samples, which impeded the access of the treatment material to the inside of the samples , and then the failure of the material to connect the internal grains and form bonds between the grains and some of them (Fig.16.a), there are some factors that affect the pressure resistance of them, as the increase in the size of the cracks leads to a decrease in the pressure resistance, as well as an increase in the salt concentration in the pores of the stones and the spaces between the grains, and the weathering factors It plays a mediating role in the weak resistance of stones. Through the results of the experimental study, this proved the success and excellence of the mixture of paraloid solution with nano calcium hydroxide in consolidation the limestone blocks affected by fire.

a b c

Figure 16. General View showing the restoration and consolidation process after fire ; a) Photo showing consolidation using nano calcium hydroxide; b) Photo showing the current state of the arch after restoration; c) photo showing the current state the entrance after restoration

5. CONCLUSIONS

The archaeological stone buildings are exposed to fire and some damage occurs to them, at the effect of heat changes take place in the inner structure and mineral composition, which influences the petro physical parameters, the heat resistance depends on the type of cementing mineral the amount of the cement (grain/cement ratio)the grain size (fine, medium, coarse)the grain to grain or matrix to grain contacts the compact stones show more dramatic change in porosity at elevated temperature the porous and

cement rich stone is more adaptable, these can adopt the addition strength caused by thermal expansion the silica cemented, ferruginous or clayey stones are less sensitive than the carbonate ones (disintegration at higher temperature). whether it is damage to the outer surface of the building stones or damage to the internal structure of the stones, and depending on the damage to the temperature of the fire and the mineral composition of the building stones, at a temperature lower than 300°C with a change in the colour of the building stones if they are they contain iron oxides that take a red colour, with the occurrence of some fine cracks, but at higher temperatures some transformations of the minerals that make up the building stones occur with the beginning of the dissolution and collapsing of the bond between the grains and the spread of cracks, and at temperatures higher than 600°C, the stage of calcification of the limestone begins and a transformation into lime at a degree 800°Cas limestone collapsed at this temperature and turning from its natural grey colour to white. Fires and exposure to high temperatures cause, the change in the internal composition and mineral composition of natural stones, which leads to changes in the petro physical properties, as well as an increase in size, exposure of natural stones to different rates of heat leads to different expansion of some of the minerals that make up rocks and stones and the formation of fine cracks, the effect of high temperature leads to an increase in the rate of porosity, and a decrease in the pressure resistance, the resistance of natural stones to fire depends on their mineral components, the quantity and quality of the binder material, the size of the grains, where the fine-grained stones are more heat-resistant than the coarse grains, as well as the clay content of the stones, where the stones with the clay content are more heat resistant than the limestone. When fire damaged limestone blocks are exposed to subsequent weathering a further decrease in strength is obtained and this could lead, in practical situations to the collapse of building. For example, the use of water in fire fighting of historic stone structures may lead to more damage because of the sudden and localized changes in temperature when the cold water hits the overheated stone. It is clear from the results that the calcium hydroxide nano material led to a complete and good bonding between the grains constituting the limestone material, penetration and diffusion in the voids and the formation of a network of polymer and nanomaterials particles between the weak and healthy grains, and this is due to the great role played by the nanomaterials used in improving the mechanical properties for the polymer "Paralloid B72", but the results indicate the failure of nano-kaolinite and calcium carbonate in the treatments, which may be due to the insufficient distribution within the grains, and then the formation of a dense film of polymer and nano-material particles on the surface of the samples. These particles impeded the access of the treatment material to the inside of the samples, and then the failure of the material to connect the internal grains and form bonds between the grains and some of them. There are some factors that affect the pressure resistance of them, as the increase in the size of the cracks leads to a decrease in the pressure resistance, as well as, an increase in the salt concentration in the pores of the stones and the spaces between the grains, and the weathering factors playing a mediating role in the weak resistance of stones.

REFERENCES

Ozguven, A and Ozcelik, Y. (2013) Investigation of some Property Changes of Natural Building Stone Exposed to Fire and High Heat, *Construction and Building Materials*, 38, pp. 813-821.

AGI Glossary (1980), Glossary of Geology, R.L., Betes and J. A., Jackson, Eds., 2nd Edition. Falls Church, Virginia, America Geological Institute, 751, p.260.

Ahmad, A.E. (2020) Investigation of marble deterioration and development of a classification system for condition assessment using non-destructive ultrasonic technique. *Mediterranean Archaeology and Archaeometry* Vol. 20, No 3, pp. 75-89

ASTM (1985). Standard Test Methods for Specific Gravity of Soil. D 854.

B. Chakrabarti, (1993) an assessment of effects of fire damage to stone in buildings & procedures for restoration and conservation of stone in some historic stone buildings, BRE Note, N 15/93, Garston.

B. Chakrabarti, T. Yates and A. Lewry, (1995) Effect of fire damage on natural stonework in buildings, Construction and Building Materials, 10, 7, 539-544.

B. Chakrabarti., (1996), Effect of Fire Damage on Natural Stone Working Building: Building Research Establishments, Vol. 10, No. 7, PP. 539-544.

Battaglia, S., Franzini, M., & Mango, F. (1993). High-sensitivity apparatus for measuring linear thermal expansion: Preliminary results on the response of marbles to thermal cycles. Il Nuovo Cimento, 16(4), 453–461. https://doi.org/10.1007/BF02507653

Bratitsi, M., Liritzis, I., Vafiadou, A., Xanthopoulou, V., Palamara, E., Iliopoulos, Y. (2018) critical assessment of chromatic index in archaeological ceramics by munsell and rgb: novel contribution to characterization and provenance studies Mediterranean Archaeology and Archaeometry, Vol. 18, No 2, pp. 175-211

Brian J., and Srphen, C., Physical Geology, U.S.A, 1987, P. 688.

Brotons, V. et al., (2013), Study of Creep Behaviour of a Calcarenite, San Julian's Stone (Alicante) Materials Deconstruction.

Chernyaer, E.B., Methods and Technique of Performing Restoration of Wall Painting of the XVIIth Century in the Church of St., Demetrius of Salonika, Greece, 1996.

Fabien, A., (2010) Mechanical Properties and Structure Behavior of Masonry at Elevated Temperatures, PhD Thesis, the University of Manchester.

Franzoni, E., Sassoni, E., Scherer, G. W., & Naidu, S. (2013). Artificial weathering of stone by heating. Journal of Cultural Heritage, 14(3 SUPPL), e85–e93. https://doi.org/10.1016/j.culher.2012.11.026

Hall, C., & Hamilton, A. (2016). Porosities of building limestones: using the solid density to assess data quality. Materials and Structures/Materiaux et Constructions, 49(10), 3969–3979. https://doi.org/10.1617/s11527-015-0767-3

Hemeda. S., (2019), Geotechnical and geophysical investigation techniques in Ben Ezra Synagogue in old Cairo area, Egypt, Herit Sci. 7, 23.

Hemeda, S., Sonbol, A. (2020), Sustainability problems of the Giza pyramids. Herit Sci 8, 8 (2020). https://doi.org/10.1186/s40494-020-0356-9

Hemeda, S. (2021), Numerical Analysis of Geotechnical Problems of Historic Masonry Structures. Geotech Geol Eng 39, 2461–2469 (2021). https://doi.org/10.1007/s10706-020-01638-2

Hemeda, S.(2021), Geo-environmental monitoring and 3D finite elements stability analysis for site investigation of underground monuments. Horemheb tomb (KV57), Luxor, Egypt. Herit Sci 9, 17 (2021). https://doi.org/10.1186/s40494-021-00487-3

Hone bone D. B., (1998), Weathering and Decay of Masonry, In Conservation of Buildings, Decorative Stone, Vol. 2, London

I. Ugur et al., (2014), Analysis of the Alterations in Porosity Features of some Natural Stones due to Thermal Effect, Ultrasonic, Vol. 54, Issue 5, PP. 1332-1336.

Jeremy P. Ingham (2008), Application of Petrographic Examination Techniques to the assessment of Fire-damaged Concrete and Masonry Structures: Materials Characterization, Vol. 60, No. 7, P. 700-709.

Kleber, W., Bautsch, H.-J., Bohm, J., & Klimm, D. (2010). Einführung in die Kristallographie. De Gruyter. https://doi.org/10.1515/9783486598858

Laurenzi, Tabasso, M., Products and Methods for the Conservation of Stone, Problems and Trends, 10th, Inter, Congress on the Deterioration and Conservation of Stone, Sweden, 2004, PP. 269-282.

Liritzis, I, Zacharias, N, Iliopoulos, I, Palamara, E, Xanthopoulou, V, Sideris, A, Vafiadou, A, Papageorgiou, I (2018b) Characterization and provenance of ceramic artifacts and local clays from late Mycenaean kastrouli (Greece) by means of p-xrf screening and statistical analysis. Journal of Cultural Heritage. Journal of Cultural Heritage 46, 61–81.

Liritzis, I, Laskaris, N, Vafiadou A, Karapanagiotis I, Volonakis, P, Papageorgopoulou, C, Bratitsi, M (2020) Archaeometry: An Overview. SCIENTIFIC CULTURE, Vol. 6, No. 1, pp. 49-98, DOI: 10.5281/zenodo.3625220

M. Hajpál and Á. Török, (2004) Mineralogical and colour changes of quartz sandstones by heat, Environmental Geology, 46, 311-322.

M. Hajpál, (2002) Changes in sandstones of historical monuments exposed to fire or high temperature, Fire Technology 38, 4, 373-382.

M. M. Ibrahim, S. O. Mohamed, Y. K. Hefni, A. I. Ahmed (2019) Nanomaterials for Consolidation and Protection of Egyptian Faience form Matteria, Egypt, J. Nano. Res. 56 39-48.

M. M. Ibrahim, W. S. Mohamed, H. M. Mohamed (2019) Comparative and Experimental Studies for Evaluation of Paraloid B-72 in Traditional and Nano Forms for Joining of Pottery Samples Journal of Nano Research ISSN: 1661-9897, Vol. 61, pp 61-71

Mohamed Moustafa Ibrahim, Wael Sabry Mohamed and Hamdy Mohamed Mohamed (2021) Experimental study for evaluation of PARALOID® B72 and its nanocomposite with nano TIO2 and nano ZNO for consolidation of pottery samples. SCIENTIFIC CULTURE, Vol. 7, No. 2, (2021), pp. 101-111 DOI:10.5281/zenodo.4570180.

Mohamed, k., (2010) Musafirkhana palace: the last architectural treasure, The Journal of Architecture, 15(6):795-826, Volume 15 Number 6.

P.N. Manoudis, A., Tsakalof. I. Karapanagiotis, I. Zuburtikudis: Fabrication of Super-Hydrophobic Surfaces for Enhanced Stone Protection, 2009, P. 5.

Palmer, L. A., and Parsons, D. A.: A Study of the Properties of Mortar and Bricks and their Relation to Bond London, 1995, P. 12.

Pinto, F & Rodrigues, D., Stone Consolidation: The Role of Treatment Procedures, Journal of Cultural Heritage, No. 9, El Sevier, 2008, PP. 38-53.

Revault, J. and Maury, B., Palais et Maison du Caire III (Cairo, Institut Français d'Archéologie Orientale du Caire, 1979).

Robertson, E. C. (1982). Physical Properties of Building Stone. In Conservation of Historic Stone Buildings and Monuments (pp. 62–86). National Academies Press. https://doi.org/10.17226/514

Ruedrich, J., Rieffel, Y., Pirskawetz, S., Alpermann, H., Joksch, U., Gengnagel, C., Weise, F., Plagge, R., Jianhua Zhao, & Siegesmund, S. (2010). Development and assessment of protective winter covers for marble statuaries of the Schlossbrücke, Berlin (Germany). Environ Earth Sci. https://doi.org/10.1007/s12665-010-0765-2

S. Russo, F. Sciarretta, (2012) Experimental and Theoretical Investigation on Masonry after High Tem-peratures Exposure, Exp. Mach, 52, PP. 341-359.

S. Russo, G. Goscato, F. Sciarretta, (2008), Behavior of a Historical Masonry Structure Subjected to Fire, MAS Int. 2,(1), PP. 1-14.

Sassoni, E., & Franzoni, E. (2014). Influence of porosity on artificial deterioration of marble and limestone by heating. Applied Physics A: Materials Science and Processing, 115(3), 809–816. https://doi.org/10.1007/s00339-013-7863-4

Sheremeti-Kabashi, F. (2002). Untersuchungen der Gefügeanisotropie von Carrara-Marmor und deren Ein-fluss auf die Verwitterung (Issue April). Ludwig-Maximilians-Universität München.

Siegesmund, S., & Dürrast, H. (2011). Physical and mechanical properties of rocks. In Siegfried Siegesmund & R. Snethlage (Eds.), Stone in Architecture: Properties, Durability (4th ed., pp. 97–225). Springer. https://doi.org/DOI 10.1007/978-3-642-14475-2_3

Siegesmund, S., Ullemeyer, K., Weiss, T., & Tschegg, E. K. (2000). Physical weathering of marbles caused by anisotropic thermal expansion. Int J Earth Sci, 89(1), 170–182. https://doi.org/10.1007/s005310050324

Siegesmund, S., Weiss, T., & Tschegg, E. K. (2000). Control of marble weathering by thermal expansion and rock fabrics. Proceedings of the 9th International Congress on Deterioration and Conservation of Stone, 205– 213. https://doi.org/10.1016/b978-044450517-0/50102-1

Terrace, G., Porous, Building Material, Material Science for Architectural Conservation, ICCROM, Rome, 2005, P. 87.

Ugur, I., Sengun, N., Demirdag, S., & Altindag, R. (2014). Analysis of the alterations in porosity features of some natural stones due to thermal effect. Ultrasonics, 54(5), 1332–1336. https://doi.org/10.1016/j.ultras.2014.01.013

Weiss, T., Siegesmund, S., & Fuller Jr., E. R. (2002). Thermal stresses and microcracking in calcite and dolomite marbles via finite element modelling. In S. Siegesmund, T. Weiss, & A. Vollbrecht (Eds.), Natural Stone, Weathering Phenomena, Conservation Strategies and Case Studies (pp. 89–102). The Geolog-ical Society of London.

Yavuz, H., Demirdag, S., & Caran, S. (2010). Thermal effect on the physical properties of carbonate rocks. International Journal of Rock Mechanics and Mining Sciences, 47(1), 94–103. https://doi.org/10.1016/j.ijrmms.2009.09.014

Zeisig, A., Siegesmund, S., & Weiss, T. (2002). Thermal expansion and its control on the durability of marbles. In Siegfried Siegesmund, T. Weiss, & A. Vollbreecht (Eds.), Natural Stone, Weathering Phenomena, Conservation Strategies and Case Studies (The Geolog, Vol. 205, pp. 65–80). https://doi.org/10.1144/GSL.SP.2002.205.01.06