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Fire resistance of roofing slates: Mechanical, mineralogical and aesthetic changes alongside temperature increase

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ABSTRACT

Fire is a major destructive agent for dimension stone. Practically all historic buildings have suffered one or more fires over the course of their lifespan. There are numerous studies on the effect of fire on stone. Generally speaking, these effects can be divided into aesthetic and structural. Aesthetic effects involve a color shift to reddish hues, due to the oxidation processes triggered by temperature increase. Moreover, structural effects involve the formation of cracks and delaminations that may cause the rock to disintegrate. However, even though roofing slates are a group of metamorphic rocks that are widely represented in the historical architectural heritage of many European countries, none of the scientific studies alluded to above have taken them into account. The present study examines 6 lithotypes, covering the metamorphic range of rocks used as roofing slates. The roofing slates were subjected to a heating test reaching 900 °C, and then analyzed using X-ray diffraction and fluorescence, Thermogravimetric and Differential Thermal analyses, and were also tested for bending strength and water absorption following the European standard for roofing slates, EN 12326. All samples studied exhibited a reduction in their bending strength, together with an increase in water absorption. Likewise, the oxidation processes triggered by the high temperatures induced a general oxidation of the iron, lending all of the samples a reddish hue. On the other hand, the roofing slate samples proved to be non-combustible and did not release any toxic or hazardous fumes.

1. Introduction

Fire is one of the most significant threats to monumental and architectural stone heritage. There is practically no historical church, cathedral or palace which has not suffered one or more fires throughout its history. Fire events alter the constructive properties and aesthetics of dimension stones. Fire damage can be considered a catastrophic event, which can bring severe destruction for ornamental rocks in a short period of time. The temperature of a domestic fire depends largely on the flammable materials involved, but can easily sustain temperatures of 750 °C for several hours or even days. The weathering triggered by a domestic fire can be grouped into two main groups: aesthetic changes, shown by a turn to reddish hues due to a general oxidation of the Fe^{2+}, and structural changes, with a general decline in mechanical resistance [1]. Aesthetic variations stem from changes to the mineral phases. The Fe^{2+} ion is oxidized to Fe^{3+}, causing, on the one hand, the color to become more reddish, while, on the other, diminishing gloss. These aesthetic effects have been observed in different types of lithologies, such as marbles, limestones, granites and sandstones [i.e. 2,3–7]. This thermal oxidation begins at between 250 and 300 °C, depending on the nature of the rock [8]. Rocks with a predominance of phyllosilicates and clay minerals are affected by dehydroxylation processes, which facilitate the ionic release of Fe^{2+}, which are subsequently oxidized to Fe^{3+}. Glauconite and muscovite take on a brownish tone, while chlorite becomes yellowish. Regarding structural change, temperature variation implies a volumetric modification. Rock-forming minerals usually have different thermal responses, entailing differential stresses on the rock matrix. During a fire, there is a sudden increase in temperature up to several hundred degrees Celsius [9]. The contractions and stresses generated in the rock compromise its integrity, and may easily lead to its disintegration. However, mineralogical and structural changes in ornamental stones begin at even lower temperatures, reached by natural processes.

Roofing slates form a group of low-grade metamorphic rocks used in construction for covering purposes, and have been used at least since the Roman Empire [10]. This group comprises rocks (metalutite, slate *sensu*

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Table 1
Lithology, origin and XRF characterization (as a %) of the samples.

Sample	Lithology	Origin	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
BRA	Metalutite	Minas Gerais Brazil	64.5	15.2	6.7	0.17	2.7	0.6	1.6	3.3	0.9	0.17	3.8
ITL	Carbonate slate	Liguria Italy	34.5	9.2	3.5	0.12	2.7	24.1	0.7	1.7	0.4	0.09	23.1
ECA	Slate	La Baña Spain	53.5	21.7	9.3	0.09	3.2	0.3	1.2	3.5	1.1	0.23	5.0
BUR	Slate (volcanic origin)	Lake District UK	58.4	13.8	5.5	0.07	3.6	5.1	1.6	2.9	0.7	0.13	7.3
VXE	Phyllite	Lugo Spain	56.5	18.5	8.0	0.14	3.5	1.6	2.2	3.2	0.8	0.17	4.7
ALT	Mica-schist	Alta Norway	84.9	6.1	2.6	0.04	0.3	1.1	0.7	2.5	0.6	0.03	0.9

stricto (*s.s.*), phyllite and mica-schist) which, under appropriate mining conditions, can be split into thin, large and flat shingles. From a commercial standpoint, a roofing slate has to comply with other constructive conditions, compiled in the different standards for roofing slate [11]: resistance to weathering, proper mechanical behavior, and waterproofing. Regarding resistance to weathering, roofing slates are rather inert with respect to external agents, since they are composed of minerals that remain stable under atmospheric conditions. However, sometimes it is possible to find small amounts of weatherable minerals, namely iron sulfides and carbonates. Iron sulfides can oxidize, forming red iron oxide stains, while carbonates may transform into gypsum. Mechanical behavior refers to the resistance of shingles to bending caused by the load of other shingles, branches or snow. In order to achieve maximum bending strength, shingles must be cut with their length parallel to their lineation, L_0 [11]. It is therefore decisive to identify this lineation during the manufacturing process, sawing the slate blocks along it. However, sometimes is not possible to distinguish L_0, in which cases saw operators must cut the blocks relying on their own experience. Depending on the intensity of L_0, its trace can sometimes be seen on the shingle surface. Mechanical behavior is also related to the type of rock. Slate *s.s.* and phyllite present higher values than low-grade slate and mica-schist [11], since the development of the slaty cleavage is optimum. Water absorption (0.2 to 0.8 %) is virtually nonexistent in these rocks, due to their fine grain and the low development of their pore system [12]. Because of this low water absorption, roofing slates are not generally affected by freeze–thaw cycles.

Some authors have investigated the mineralogical changes of slates during thermal processes, not considering them as construction materials but as rocks. Sánchez-Soto, Ruiz-Conde [13] found, using Differential Thermal Analysis (DTA) and Thermogravimetric analysis (TG), two critical temperatures, 640 °C and 725 °C, associated with the dehydroxylation of structural OH groups. At these temperatures, there is a significant loss of mass (7.15 %). Chlorite, one of the main minerals in slate, begins to disappear at 600 °C, and by 800 °C there are no remains of this mineral group (Cambronero, Ruiz-Román [14]).

As for the rest of dimension stones, roofing slates are also affected by fire exposure. Due to heightened concern over domestic fires, together with the high fire resistance of materials manufactured with asbestos, in the 1950s–60s artificial asbestos slate shingles entered the market. However, the performance of this product proved to be lower than the performance of true slate shingles [15]. Moreover, the legislation regarding the health risks associated with asbestos saw these products removed from the market by the end of the 20th century. Roofing slates have a set of special characteristics that make them very different from the rest of ornamental rocks regarding fire response. Slate is dense (2.7–2.8 gr/cm^3), with very low porosity and water absorption, and when used for roofing, it can be considered as a bi-dimensional material as regards fire, meaning that there is no thermal gradient inside the rock. The entire slate body is heated/cooled simultaneously, preventing the creation of this thermal gradient that is one of the main triggers of crack development in ashlars, or tri-dimensional rocks. According to the EN 12326 norm for roofing slates [16], this material is considered class A1, which means "Not contributing to fire". In this sense, the North American National Slate Association (NSA) ordered a standardized test on the reaction to fire on a roofing slate cover, finding that "no portion of the roof covering material was blown or fell off the test deck in the form of flaming/glowing brands" [17]. Common knowledge is that slate non-flammable. Perhaps this is the reason why slates are not present in the studies and scientific literature about fire damage performance [1–6,18–24]. This lack of representation might be due to slate's particular role in buildings. After a fire, the rocks making up the structural portion of a building are analyzed in order to first determine the extent of the damage inflicted, and then act accordingly in order to preserve them. Slate, however, is treated differently, as it is more functional to simply substitute the slate shingles with new ones. Perhaps because of this, architects and restorers tend not to be concerned about the state of the roof, which is seen as being composed of consumable rocks. However, an important part of Europe's architectural heritage is built with roofing slates coming from exhausted quarries. Nowadays, the main source for replacement slates are the Spanish quarries, which produce more than 75 % of the global production, supplying material for new and historical buildings throughout Europe. However, before discarding roofing slate shingles after a fire, architects and restorers should first assess their condition, since it is very likely that the original quarry has been exhausted.

The study of the fire behavior of roofing slates is undoubtedly a matter of interest for general research into stone weathering. This study provides data on the mineral and colorimetric evolution of different types of roofing slates along a thermal ramp ranging from 100 to 900 °C.

2. Methods and samples

The samples in this study were selected with a mind to covering the full range rocks most commonly used as roofing slates (Table 1). Each sample consisted of a fresh 2-cm-thick slab, cut into 6 smaller square pieces with 5–cm edges. The size and dimension of the samples were chosen so that the measurement of the variation in water absorption would be easier and more precise than if samples cut from thin slate plates were used. These pieces were considered aliquots, since they came from the same slate specimen. The pieces were numbered and separated into groups, each group being composed of one piece from each sample. Samples were collected directly from the companies when possible (BRA, ITL, ECA, VXE), or ordered by mail (BUR, ALT). For the first group of samples picked up directly at the supplier, several additional pieces of slate shingle were also taken in order to perform bending strength tests.

2.1. Mineralogical and elemental determination

The XRD and XRF analyses were conducted at the University of Oviedo's Scientific Services Department, in Spain. Samples were dried at 40 °C for two days and then pulverized. XRD analysis was done using a

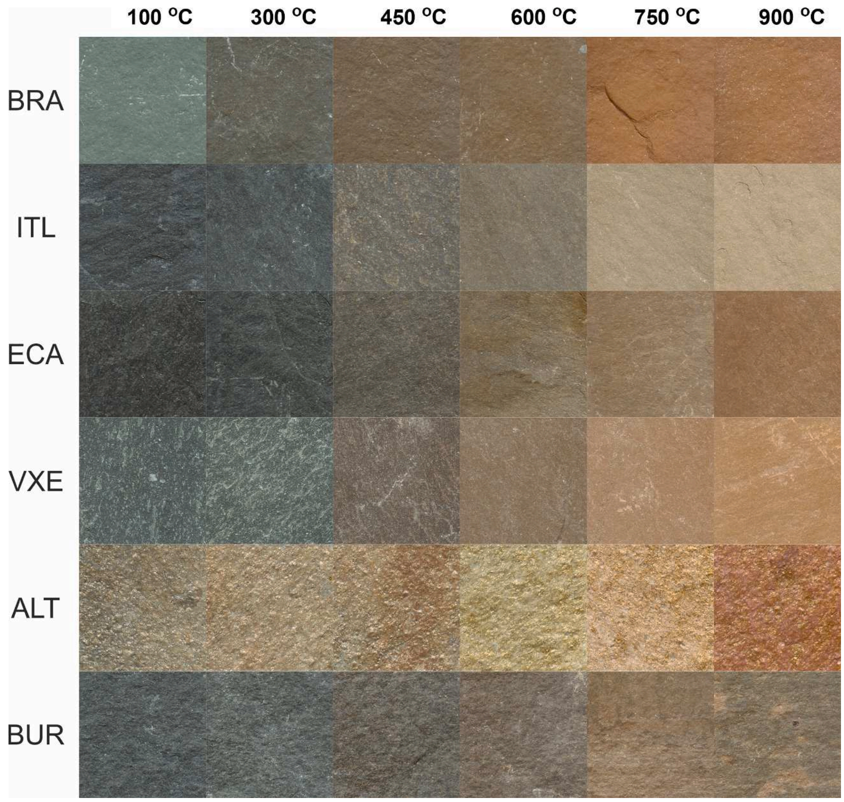

Fig. 1. Aesthetic changes in the surface of the samples over the course of the heating test.

Philips PW 1830 diffractometer, with a Cu cathode and a wavelength of $K\alpha = 1.5405$ Å. The angular scan was recorded from 2° to 60° 2θ with a Phillips PW 1710 digital recorder. Semi-quantification of the mineral phases was performed using XPowder software (v. 2004.04.44 PRO). In order to determine changes in the crystallinity and mineralogical composition, the XRD was carried out at each temperature interval (100, 300, 450, 600, 750 and 900 °C), thus making it a thermo-XRD. XRF analysis was performed with a Phillips PW spectrometer, with a Sc-Mo X-ray tube and a PR 10 scintillation gas detector. This analysis was only performed on the fresh samples in order to characterize their initial composition.

2.2. Heating test

Each group was subjected to a different temperature: 300, 450, 600, 750 and 900 °C. For this study we used a Thermconcept KL 5/11 muffle furnace, with a chamber volume of 7 l, located at the laboratory of the Geology Department of Ghent University, Belgium. This model can reach temperatures of up to 1100 °C. In order to replicate the sudden temperature increase of a domestic fire, the furnace was pre-heated to the desired temperature, at which point the samples were introduced for 24 h. The samples were left to cool at room temperature. After this, the samples were scanned with a CanoScan LIDE 300 desk image scanner for subsequent image analysis. In order to measure the water absorption, samples were weighed, then submerged in distilled water for 24 h, after which they were weighed again. Thin sections of the blocks were obtained from fresh and heated samples at 450 and 900 °C, and examined using a transmitted light petrographic microscope.

2.3. Thermogravimetry

Thermogravimetric (TG) and Differential Thermal (DTA) analyses were carried out at the National Museum of Natural History in Madrid, Spain, using the Simultaneous Thermal Analyzer (STA) 6000 from Perkin-Elmer thermal analyzer in N_2 atmosphere, located in the Museum's laboratories. The heating rate was 10 °C/min, from room temperature up to 1000 °C, with alumina as the reference material for the DTA.

2.4. Mechanical resistance: bending strength

For the determination of the bending strength according to the test procedure detailed in the European Standard for roofing slates, EN 12326, 16 190x125-mm tiles of samples ECA, BRA, ITL and VXE were used. Eight tiles of each sample were tested without heating to determine the bending strength value under normal conditions, and the other eight tiles were annealed in the furnace at 750 °C for 24 h, replicating the conditions of a domestic fire. For samples ALT and BUR it was not possible to obtain such tiles from the producers. ALT is a quartzite, and BUR is a slate of volcanic origin. These rocks are split into thicker tiles (8 to 20 mm) than a standard roofing slate (4 to 6 mm), and the main production of the quarries is focused on flooring, paving and walling. Mechanical tests were performed at the Laboratory of the Roofing Slate Producers Association, in Sobradelo de Valdeorras, Galicia, Spain. This lab is certified by the Spanish Association of Normalization (AENOR) to perform the EN 12326 tests.

2.5. Water absorption

Finally, water absorption was measured according to the EN 12326 standard. This parameter indirectly indicates the potential damage caused by the freeze–thaw cycles, and, together with the bending strength, defines the mechanical behavior of the roofing slates. Water absorption was measured for each sample at each temperature.

3. Results

As the heating cycles progressed, all samples exhibited two effects:

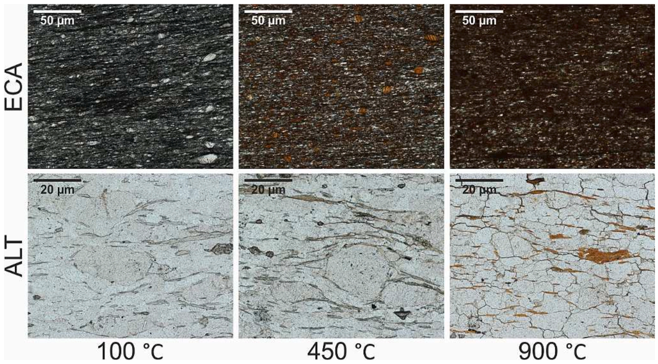

Fig. 2. Optical microscope images of the evolution of the oxidation processes induced by temperature increase. This oxidation mainly affects the phyllosilicates.

an aesthetic shift to a reddish hue, and a drastic reduction in bending strength. As pointed out before, this aesthetic change is common in natural rocks subjected to fire, due to the oxidation of Fe^{2+} by firing. In roofing slates, this effect is clearly visible. All samples took on a reddish hue (Fig. 1), this change being most evident from 450 °C onwards for slates with a compositional predominance of clays and phyllosilicates (Fig. 2). A small proportion of oxidized Fe^{3+} is enough to give the characteristic reddish hue, as it is seen in sample ALT, which has a small proportion of FeO (2.6 %). Samples with a high carbonate content (ITL, VXE and BUR) also displayed whitish tones.

The XRD mineralogical determination found the typical minerals for roofing slates (Fig. 3). However, it has to be taken into account that the thermo-XRD mapping from Fig. 3 is an approximation of the mineralogical characterization resulting from XRD patterns at each temperature Since these rocks come from the metamorphism of pelitic sediments, the main minerals (quartz, feldspar and phyllosilicates, mainly muscovite) are common for all of them (Fig. 3). Regarding elemental composition, all samples are mainly composed of SiO_2, Al_2O_3 and Fe_2O_3, except ITL, which has a significant proportion of calcium.

The TG and DTA analyses, complemented with the thermo-XRD, provided the exothermic, endothermic and weight differences. The joint graph (Fig. 3) highlights the physicochemical processes that occurred during the heating test. Sample BRA maintains a gradual weight loss with temperature, up to 2 %. Around 550 °C it displays a smooth exothermic peak, coinciding with an increase in weight loss, due to the release of hydroxyl groups from the phyllosilicates (mainly illite and muscovite). This release continues until the disappearance of the phyllosilicates, coinciding with an increase in cryptocrystalline silica and hematite at high temperatures. ITL exhibited a severe loss of weight (14 %) between 700 and 780 °C, due to the presence of calcite, which completes its thermal decomposition: $CaCO3(s) \rightarrow CaO(s) + CO2(g)$. The first exothermic peak around 750 °C would correspond with the formation of CaO (portlandite), but shortly after 900 °C a second

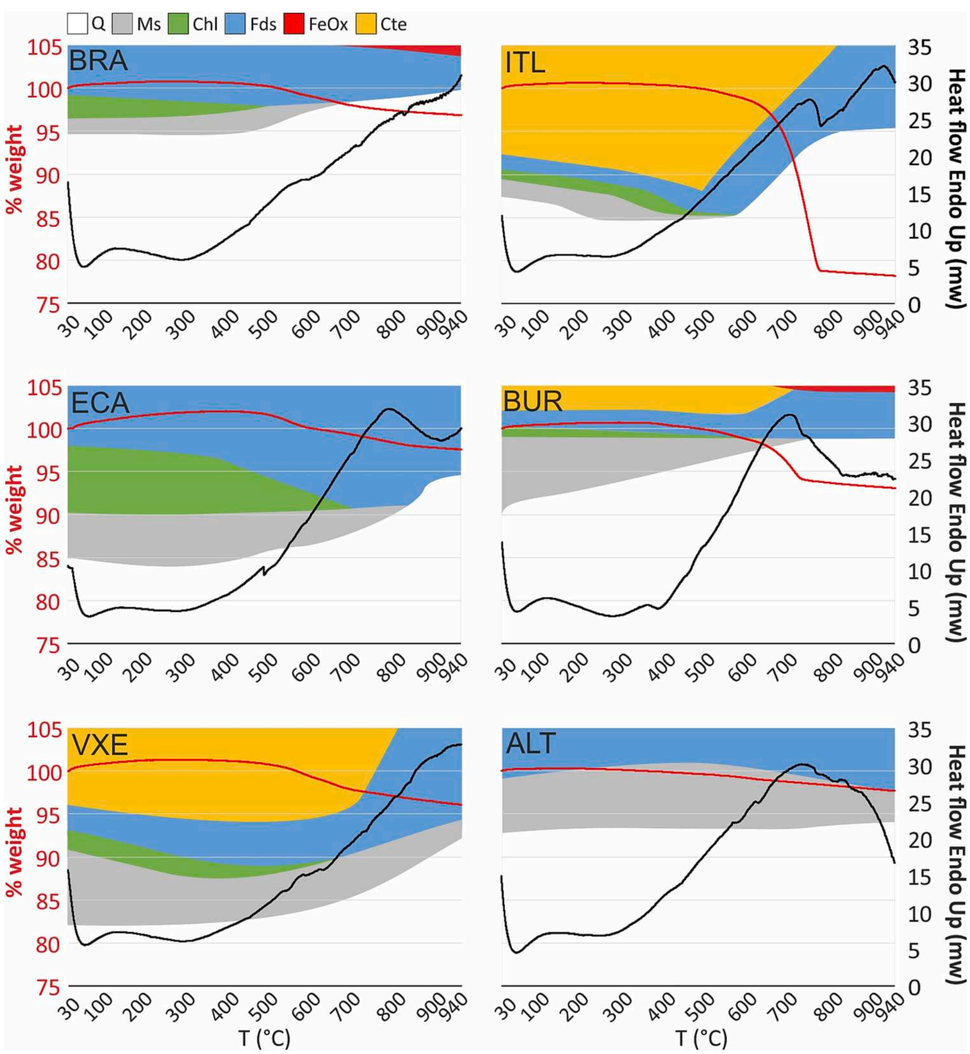

Fig. 3. Combined TG, DTA and thermo-XRD diagrams. Abbreviations: Q: Quartz; Ms: Muscovite; Chl: Chlorites; Fds: Feldspars; Fe Ox: Iron Oxides; Cte: Carbonates.

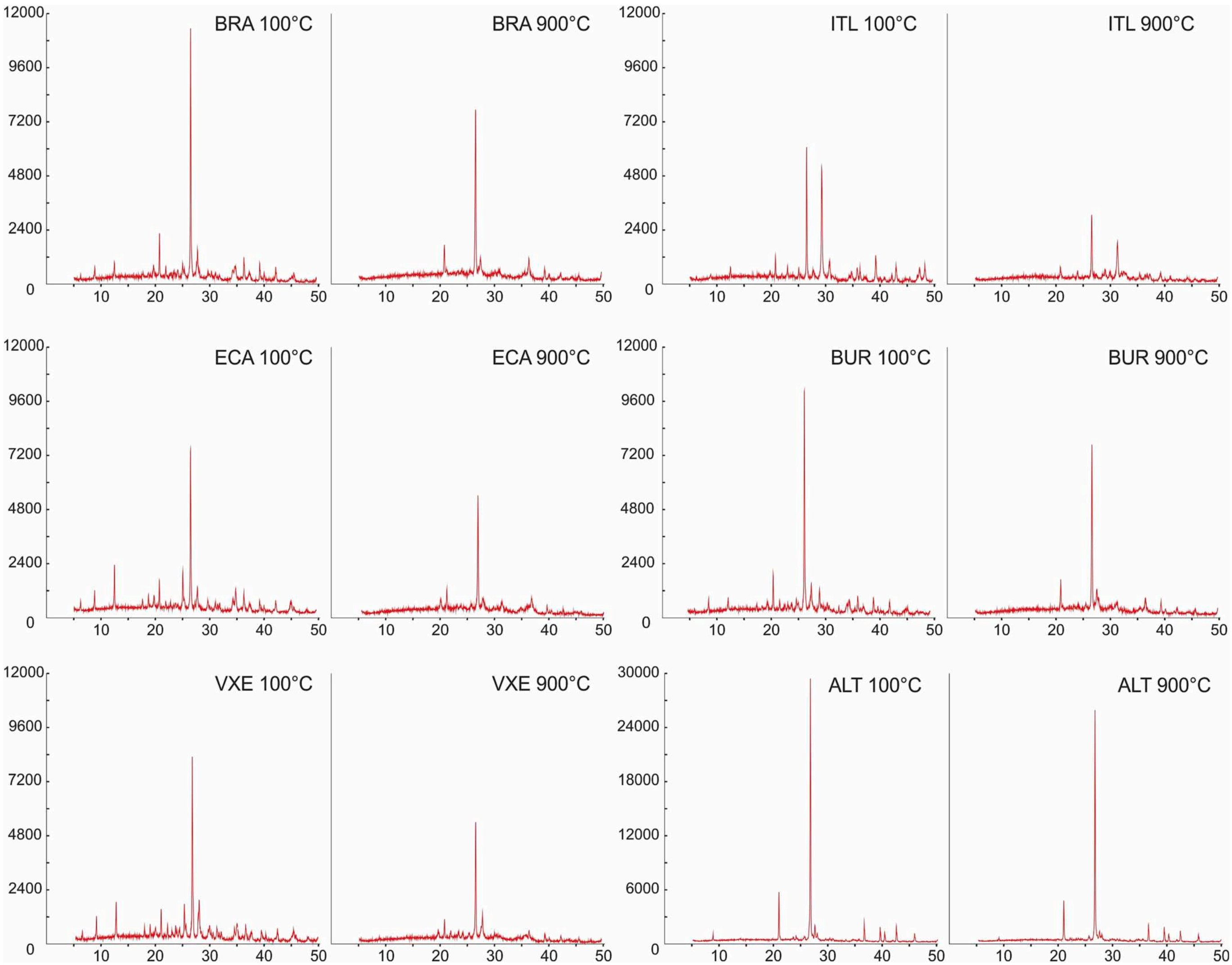

Fig. 4. Evolution of crystallinity, represented by the intensity of the peaks, over the course of the heating tests.

exothermic peak is observed, caused by the crystallization of anorthite, formed by the fusion of muscovite and chlorite glasses, combined with an excess of free calcium in the system. ECA slate also maintains a gradual weight loss with temperature, up to 2 %. It is richer in illite and chlorite phyllosilicates, which delays the release of hydroxyls by interfering with the kinetics of the release of water vapor. In any case, the complete thermal destruction of the phyllosilicates coincides, at the exothermal peak at 800 °C, with neoformations of cryptocrystalline silica and calcium-type refractory feldspars. It is also observed that the depletion of illite and chlorite fusion products slows down the growth of the refractory cryptocrystalline silica and feldspar at the end of the thermal experiment. BUR slate gradually loses up to 8 % of its weight until 730 °C due to the disappearance of phyllosilicates. Before this, around 300 °C, some of the muscovite hydroxyl groups are released, followed by a rapid molecular decomposition of this mineral, yielding an abundant release of silica as microcrystalline quartz. At the same time, the chlorite also breaks down, releasing also iron oxo-hydroxides until 600 °C. These iron oxo-hydroxides immediately recrystallize to hematite in the temperature range of 600 °C to 940 °C. At higher temperatures this process is expected to continue, giving the sample a characteristic reddish color. VXE phyllite also displays a progressive weight loss of around 4 %, due to the same process of thermal disintegration of the phyllosilicates, together with the output of hydroxyls and neoformation of large amounts of refractory feldspars and crystalline silica. No

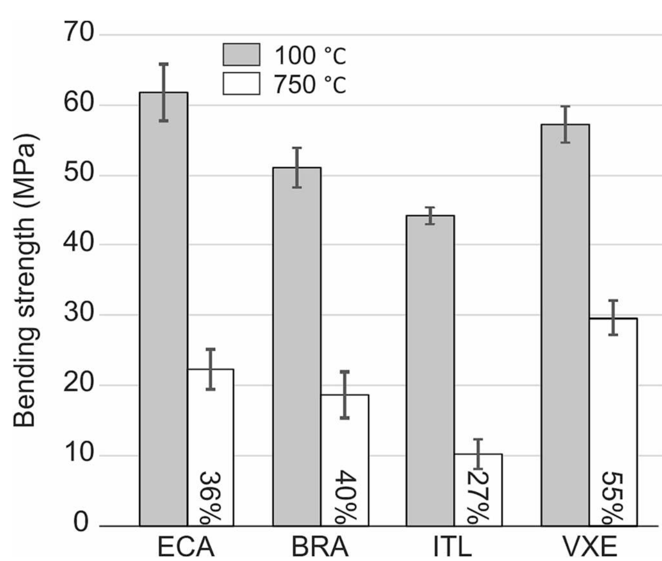

Fig. 5. Variation in bending strength at 100 °C and 750 °C.

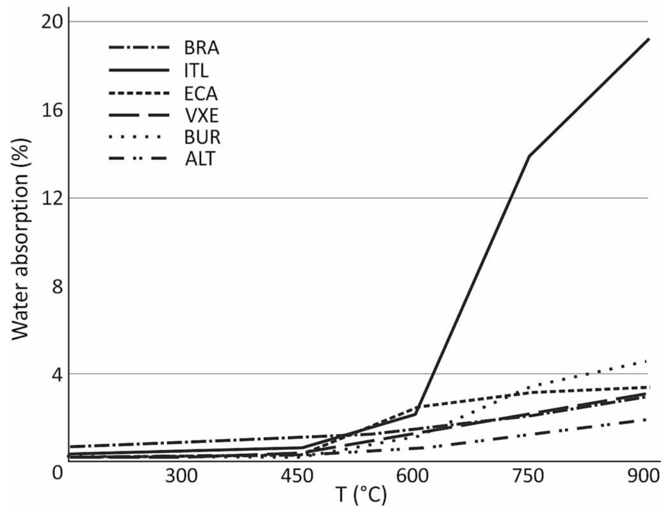

Fig. 6. Water absorption increase with temperature.

presence of high-temperature hematite is observed in this sample. Finally, ALT maintains a gradual weight loss with temperature, reaching 3 % at 940 °C, attributed to the release of hydroxyl groups. The decomposition of muscovite gradually releases silica-quartz. Around 900 °C a second exothermic peak is observed, which can be attributed to the formation of anorthite. The shape of the XRD diagrams before and after heating shows initial and newly formed phases (Fig. 4). However, some residual phases remain such as the case of the peak around 27 2Ø angle which match both, quartz and illite and given that above 700 °C illite is melted, the only remaining contributors are quartz or high temperature silica polymorphs. All the slate samples proved to be resistant to combustion, and no toxic or hazardous smoke was released during the heating test.

The bending strength test, performed with samples BRA, ITL, ECA and VXE, demonstrated that heating brought about a major decrease in this parameter (Fig. 5). This drastic reduction is mainly due to the formation of cracks generated during the dehydroxylation processes of the phyllosilicates. The remobilization and sudden volume increase of the interlaminar water, now transformed into gas, creates a sudden pore pressure within the rock matrix that causes cracks to form. This effect is more intense in rocks with low pore space, since there is less space to accommodate the new gaseous phase. This effect is clearly visible by the abrupt changes in the slope of the TG curves. On the other hand, the differential stresses created by the different thermal expansion coefficient of the slate-forming minerals is a process that can also generate cracks, but this effect is more likely to take place after long periods of thermal exposure, rather than during a sudden event such as a fire. Additionally, samples containing carbonate are more likely to form cracks and void spaces, since carbonate starts to break down at 650 °C. Consequently, the carbonate slate ITL displayed a reduction of up to 27 % in its bending strength. At the other end of the spectrum, the phyllite VXE exhibited the lowest reduction (55 %) in bending strength. Phyllite is more compact and crystalline than slate, making its structure more resistant to the effects of heating. The water absorption of the samples throughout the heating tests points in the same direction. The capacity to absorb water is directly linked to the open spaces available to host molecular water. The water absorption gradually increases in all samples, but for the carbonate slate ITL it shoots up shortly after reaching 600 °C (Fig. 6).

4. Conclusions

The effects of thermal increase on different roofing slate lithologies (metalutite, slate, phyllite and mica schist) can be grouped into two main groups: aesthetic changes and decrease in mechanical resistance. Regarding aesthetic changes, all samples acquired a reddish hue due to the oxidation of the Fe^{2+} to Fe^{3+}, caused by firing. Additionally, samples with carbonate minerals took on a whitish hue. The TG and DTA analyses showed the release of the hydroxyl groups of the phyllosilicates (muscovite, illite and chlorite), which at the annealing end leads to a complete loss of these hydrous minerals. Iron oxides (hematite) started forming in samples BRA and BUR at temperatures above 600 °C, more or less the same temperature at which carbonates begin to disappear.

Regarding mechanical behavior, there is a general decay in the bending strength, caused by the formation of cracks in the rock matrix due to the different thermal expansion coefficients of the minerals, and the voids created by the disappearance of carbonates. These alterations lead to a reduction in bending strength of between 27 and 55 %, depending on the specific lithology of the roofing slate. Consequently, we can conclude that the constructive properties of roofing slates are significantly affected by an increase in temperature to 900 °C, the same range reached by domestic fires. Therefore, the reutilization of roofing slates affected by fire is not recommended. On the other hand, roofing slates proved to be a non-combustible material and did not release any toxic or hazardous fumes during the heating tests.

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CRediT authorship contribution statement

V. Cárdenes: Conceptualization, Methodology, Investigation, Writing – original draft, Visualization, Supervision. **A. Rubio-Ordóñez:** Conceptualization, Software, Validation, Formal analysis, Writing – review & editing. **J. García-Guinea:** Methodology, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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