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The thermal stability and morphological study of weathered and intact limestone

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Abstract: Limestone, a multifunctional sedimentary rock, operates as an important component in several scientific and economic sectors. Its versatility and diverse application underline the significance of completely knowing its morphology and thermal stability to enhance consumption and ensure optimal preservation. The aims of this paper are to understand how variations in microstructural characteristics impact thermal conductivity and heat transmission parameters, thereby uncovering fundamental mechanisms governing limestone's response to heat stress. Thus, the objectives of study are to investigate and analyze intact and weathered limestone rocks in terms of thermal stability (i.e.: temperature effects on limestone›s stability and weight) and morphology (i.e.: differences in surface morphology, porosity distribution, and microstructural features) using advanced techniques like Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM), respectively. From the thermal stability analysis, it revealed that weathered limestone showed the maximum peak weight loss of 4.54% per minute at 778.31°C, whereas intact limestone showed the highest weight decrease rate of 3.2% per minute at 734.45°C. It can be summarised that weathered limestone demonstrates a more intricate and rapid thermal deterioration profile in comparison to intact limestone. The morphology analysist revealed the different particle size distributions; weathered limestone had long, deep fractures with a distribution from 1.89μm to 31.0μm, while intact limestone showed a range from 1.39μm to 14.0μm. The presence of uneven shapes and a range of sizes of particles is indicative of the weathering and erosion processes that cause the limestone structure to break apart and disintegrate. The identified patterns and trends for each different limestone conditions explained the complex relationship between morphology and thermal stability that improve decision-making processes in multiple fields. In conclusion, it is important knowing limestone's morphology and thermal behavior to optimize consumption and assure good preservation. The findings have practical ramifications that go beyond theoretical comprehension, providing useful information for preservation and implementation in a variety of sectors and domains.

Keywords: Intact, limestone, morphological, thermal, weathered

INTRODUCTION

Limestone, a ubiquitous sedimentary rock, holds crucial relevance throughout geological, industrial, and architectural domains due to its abundance and unique qualities. Composed mostly of calcium carbonate ($CaCO_3$) with various impurities and secondary minerals; limestone undergoes continual alteration processes throughout its geological history, resulting in the production of both intact and weathered varieties (Müller, 2021). Intact limestone indicates the pristine state of the rock, keeping its original mineralogical and structural integrity. Conversely, weathered limestone experiences variations due to external forces such as weathering, erosion, and chemical reactions, resulting to changes in its physical and chemical properties (Hack, 2019). Understanding the delicate relationship between the morphology and thermal characteristics of limestone is vital for different scientific and practical applications. The morphology of limestone, including pore structure, grain size, and surface topography; directly determines its thermal performance. Changes

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in morphology generated by weathering processes can considerably alter the rock's thermal stability and heat transmission capabilities (Hashim, 2022).

Previous research has extensively examined the thermal behaviour and morphological evolution of limestone in varied settings. However, gaps in understanding continue, notably regarding the intricate interplay between shape and thermal stability in weathered and intact limestone (Jodry *et al*., 2023). This study intends to solve these gaps through a comprehensive comparative analysis of the thermal stability and morphology of weathered and intact limestone. Leveraging modern techniques such as Thermal Gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM), in order to explore the fundamental distinctions between these two versions and uncover the underlying mechanisms driving their thermal behaviour.

Limestone formation

Limestones are rocks that contain more than 50% carbonate minerals, at least 50% of which are aragonite or calcite. The colours of limestone range from white to grey to dark grey to yellow, green, blue, and occasionally even black (Silva *et al*., 2022). A mixture of clayey material, glauconite, or finely dispersed ferrous compounds causes a greenish tint, while the presence of ferric iron causes a reddish or brownish coloration (Müller, 2021). Compared to fine-grained limestones, which are typically indicative of deeper, potentially decreasing circumstances during early diagenesis, coarse-grained limestones typically exhibit lighter colours, which are linked with well-oxidized environments. Magnesium carbonates, dolomite, silica, glauconite, gypsum, fluorite, siderite, sulphides, iron and manganese oxides, phosphates, clays, and organic materials are among the several impurities found in limestone (Rajendran & Nasir, 2014).

Calcareous sandstone, shale and others are defined as having a $CaCO_3$ content of slightly less than 50%. Differential weathering frequently occurs in its carbonate portion, giving it the appearance of limestone. Insoluble quartz grains and other materials are typically inconspicuous and readily released during weathering processes. Certain calcareous aeolianites that contain less than 30% $CaCO_3$ go on to form karst landforms and other limestone characteristics. The majority of sedimentary carbonate rocks are the result of deposition in marine environments, with paralia and autogeosynclines serving as the main repository in neritic settings. Although it is not as common as that of banks, platforms, and shelves, calcium carbonate can also build up in deep water and in coral atoll structures encircled by an abyssal zone. The primary material that makes up limestone is the calcium carbonate ($CaCO_3$) mineral calcite. Modern seas contain large amounts of calcium carbonate in its dissolved state, but certain requirements must be satisfied for the mineral to precipitate as a solid (Silva *et al*., 2022). The primary biological process used to precipitate calcite from seawater. Calcite is used by a variety of marine creatures to form their shells and skeletons, which, when they die, fall to the seafloor, where they are buried and compacted into sedimentary rock. The bone pieces and grains may never make it to the seafloor, though, as calcite dissolves readily. Furthermore, the environments in which those marine species live regulate the deposition of limestone in particular geographical areas. Because limestone formation is restricted, its presence or absence in the geologic record provides information about the climate and geographic circumstances of the era (Kambakhsh *et al.*, 2024).

Batu Caves geological formation

The Batu Caves is a geographically distinct limestone hill, characterized by its dome shape, situated at coordinates 3.2379° N and 101.6840° E, with an elevation of roughly 390 meters above sea level. It is positioned around 11 kilometers northeast of Kuala Lumpur, as documented (Kiew & Rahman, 2021). The geological composition of the Batu Caves mostly consists of Silurian limestone, a rock formation dating back about 400 million years to the Paleozoic epoch. Following the initial deposition of the rock, it underwent a series of geological transformations, including uplift, compression, heating, and folding, which took place millions of years later during the Triassic period, approximately 200 million years ago. However, it is plausible that these processes commenced as early as the Devonian-Carboniferous period, around 300 million years ago. The majority of the limestone underwent a transformation into crystalline marble and then underwent uplift, resulting in the formation of the mountain ranges (Zabidi & Freitas, 2006). The limestone formation of Batu Caves exemplifies the intricate connections between geological processes and the passage of time. The place exhibits the exceptional artistic abilities of nature, featuring visually striking stalactites, stalagmites, and intriguing formations within the cave (Dodge-wan, 2015). Every curve, contour, and crack present in the limestone is a testament to the ancient history of the Earth, intricately imprinted inside the very structure of the cave. Limestone is a sedimentary rock composed of calcite minerals, chemically known as calcium carbonate ($CaCO_3$). Dolomite [Ca Mg (CO_3)] is another prevalent mineral found in limestone (Chowdhury *et al*., 1990). Frequently encountered impurities inside limestone are characterized by its microcrystalline, cryptocrystalline quartz, amorphous silica composition (SiO_2), clay, organic debris, and iron oxides. Limestone exhibits a distinctive characteristic as it possesses solubility even in mildly acidic aqueous environments, including carbonic acid from dissolving carbon dioxide in water (Tan, 2002).

The Batu Caves area located in Gombak District is shown in the geological map (Figure 1). The map showcases a complex interplay of sedimentary, metamorphic, and intrusive rock formations, centred around the renowned Batu Caves. The region features isolated continental basin deposits from the Late Tertiary period, composed of shale, sandstone, and conglomerate, which reveal the remnants of ancient sedimentary basins. Metamorphic formations, including schist, phyllite, slate, and limestone intercalations, dominate parts of the district, shaped by immense geological pressures and transformations over time.

Marine and continental deposits, consisting of clay, silt, sand, and gravel, highlight the influence of past marine and riverine processes. Pink zones represent acid intrusive rocks, remnants of magmatic activity near the area, while yellow zones of vein quartz indicate areas of mineral concentration formed by ancient fluid movements. Scattered water bodies, marked in blue, add ecological significance and diversity to the terrain.

Batu Caves, nestled within limestone formations, exemplifies the region's karstic landscape, blending natural history with cultural heritage. This map provides an understanding of Gombak's geological framework, showcasing its evolution and the dynamic processes that have shaped its iconic features. The Kenny Hill Formation, a younger sequence of metasedimentary rocks is composed of phyllite and quartzite and situated on top of the Silurian Kuala Lumpur Limestone. The Hawthornden Schist Formation is made up of fine-grained pyrite-bearing graphitic schists that have a dark color. The oldest rock formation in Kuala Lumpur is the Dinding Schist, which is Cambrian to Ordovician in age and is composed of schistosed conglomerate, calc-silicate and quartz-mica schists (Gobbett, 1965).

Weathered limestone grade in Batu Caves

The weathering of limestone in Batu Caves is a complex process influenced by various factors, including environmental conditions, rock properties, and the duration of exposure to weathering. These caves, located in Selangor, Malaysia, are a significant geological and cultural site, showcasing the interplay between natural weathering processes and human activity. Understanding the grade of weathered limestone in Batu Caves requires examining the specific mechanisms of physical, chemical, and biological weathering that affect this unique limestone formation.

a) Physical weathering

Physical weathering, also known as mechanical weathering, involves the breakdown of rocks without chemical alteration (Camuffo, 1995). In Batu Caves, this process is primarily driven by temperature fluctuations and water infiltration. Weathering in Batu Caves is not only driven by natural processes but also significantly influenced by human activities. Thousands of visitors frequent the site annually, engaging in various activities that contribute to the physical deterioration of the limestone. Additionally, fog plays a role in physical weathering by promoting moisture accumulation on the

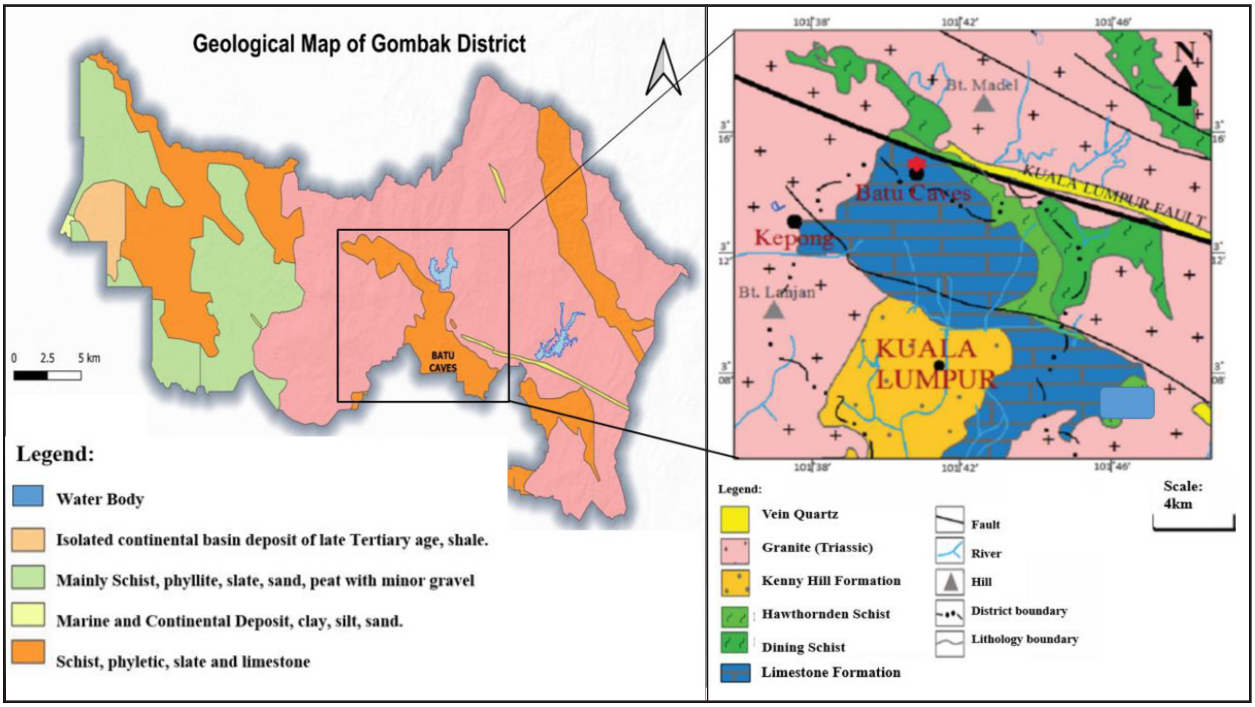

Figure 1: Geological Map of Batu Caves, Gombak, Selangor. (source: Added and modified from Goh *et al*., 2018).

Figure 2: The photos showing the type of weathering limestone (a) physical (b) chemical and (c) biological weathering limestone in Batu Caves, Malaysia.

rock surfaces, leading to increased erosion and mechanical breakdown. This impact of fog on physical weathering is illustrated in the accompanying Figure 2a.

b) Chemical weathering

Carbonation is a process of an atmospheric carbon dioxide (CO_2) combines with water to form carbonic acid (H_2CO_3) (Price & Velbel, 2003). This reaction leads to the gradual weakening and dissolution of limestone, contributing to the formation of karst landscapes, characterized by features such as caves, sinkholes, and limestone pavements. In Batu Caves, evidence of carbonation is visible in the smooth, rounded surfaces of limestone formations shown in Figure 2b.

$$CaCO_3 + H_2O + CO_2 = Ca\,(HCO_3)_2 \qquad \text{Equation (1)}$$

(Limestone + water + carbon dioxide = Calcium bicarbonate)

c) Biological weathering

Biological weathering involves the physical or chemical alteration of rocks by living organisms (Bland & Rolls, 2020). In Batu Caves, plant roots and microorganisms play a significant role in the weathering process. Plant roots can grow into fissures and crevices in limestone, exerting pressure as they expand over time, roots can cause significant physical damage to the rock, leading to its fragmentation and weakening. In the context of Batu Caves, the presence of vegetation contributes to the degradation of limestone structures. As plants mature, their roots penetrate deeper into the rock, exacerbating the weathering process shown in Figure 2c (Dontsova *et al*., 2020).

Weathering processes and impact on limestone

The process of weathering limestone entails the gradual disintegration and modification of its minerals and structure over a period of time. This process can be affected by a range of elements, such as climate, biological activity, and environmental circumstances (Benavente *et al*., 2021). Physical weathering, such as the repeated freezing and thawing of water and the wearing down of rock surfaces, can cause the formation of cracks and the enlargement of pore spaces in the rock. Chemical weathering, which occurs through reactions with acidic rainwater or atmospheric gases, can result in the dissolution of calcite and the subsequent creation of secondary minerals such as gypsum (Kambakhsh & Nik Norsyahariati, 2023). Organisms such as lichens and bacteria can speed up the deterioration process by producing organic acids and other byproducts through biological weathering. The parameters that play a role in the weathering mechanism of limestone are shown in Table 1.

Limestone morphological and thermal stability

Understanding limestone's morphology and thermal stability is critical to many fields, including engineering, geology, and materials science. Sedimentary rocks like limestone are commonplace and are used extensively in

Table 1: Various parameters cause weathering of limestone formation (Dans & Royaume, 1974).

Environmental Factors	Time Year	Rock Properties	Response
Temperature	Varying	Mineralogical composition	Discoloration
Moisture	Geological time	Fabric and grain structure	Decomposition
Chemical fluids	Different	Structural defects	Disintegration

construction, geological research, and industrial processes. Its structural characteristics and thermal behaviour significantly impact how well-suited it is for different uses and how it reacts to external stimuli (Beyer & Mrozek, 2022).

Morphology refers to the structural features of limestone, such as pore size distribution, texture, and crystal orientation. Scanning Electron Microscopy (SEM) is a potent method for analysing morphology, providing high-resolution imaging that is crucial for identifying microstructural characteristics (Zeng *et al*., 2017). Morphological characteristics affect the mechanical characteristics of limestone-based materials and also have a role in determining their thermal capacity, permeability, and vulnerability to weathering and damage (Noraini *et al*., 2022).

Thermal stability clarifies the temperature-dependent breakdown of limestone and is frequently assessed using methods such as Thermogravimetric analysis (TGA) (Radulović *et al*., 2017). Thermogravimetric analysis (TGA) is a valuable technique for comprehending limestone's thermal behaviour. The important insights on the material's sensitivity to temperature variations can be determined by graphing the TGA curve, which shows the rate of weight change, against temperature. Differential thermo-gravimetry (DTG) curve peaks indicate specific weight loss events and provide important insights into the underlying mechanisms and the impact of temperature on these processes. Prior TGA investigations of limestone have yielded important insights into its thermal properties and responses to temperature changes. It showed how TGA clarified key patterns of weight loss in limestone, revealing procedures like dehydration and the oxidation of organic materials to produce limestone and carbon dioxide from carbonates, particularly calcite (Li & Wang, 2022). Understanding thermal behaviour is crucial for cement production and other businesses that rely on limestone to optimize manufacturing procedures and guarantee product quality. Furthermore, thermal stability evaluations aid in the interpretation of the thermal history of historical artifacts and limestone formations in disciplines such as geology and archaeology (Niry *et al*., 2013).

These results highlight how crucial TGA is for understanding the complex thermal behaviours of limestone and how it reacts to its surroundings. The objective of this work is to gain a greater understanding of the thermal dynamics of limestone by utilizing these insights to examine the thermal stability of both intact and weathered limestone samples.

MATERIALS AND METHODOLOGY

Sample collection and preparation

Limestone rock is used as the principal material for this study. In the sample selection process, six limestone samples were retrieved; the first group consisted of three specimens of intact limestone taken from the exterior of Batu Caves, precisely pinpointed at GPS used (Brand: GARMIN, model: STAM Map 76csx), coordinates N 03°14'14.5" and E 101°40'58.4". Additionally, the second group comprised three intact limestone samples were gathered from a specific point within the cave's confines, identified by GPS coordinates N 03°14'17.7" and E 101°41'01.4", shown in Figure 3. The process of taking limestone samples according to the C-50 standard was selected from the areas that were physically deformed (ASTM, 2006).

The labelling and names of each limestone samples studied in this work are shown in Table 2 for future references in this paper.

After transferring the limestone samples to the laboratory, the preservation and identification of samples were prioritized, each sample was carefully labelled to ensure that the limestone sample remained unaltered and underwent no transformations upon arrival at the

Figure 3: The GPS locations of weathered limestone from outside Batu Caves (Location 1) and intact limestone sampling from inside (Location 2) Batu Caves.

Table 2: Labelling of limestone rock samples – intact and weathered limestone.

Samples	Labels / Names
Intact Limestone	
Sample 1	Intact – S1
Sample 2	Intact – S2
Sample 3	Intact – S3
Weathered Limestone	
Sample 1	Weathered – S1
Sample 2	Weathered – S2
Sample 3	Weathered – S3

Figure 4: The laboratory procedures in preparing the samples for characterising tests (a) limestone samples, (b) washing process and (c) drying process in the oven.

laboratory for analyses (Figure 4a). The first step to take is the washing process where the limestone samples need to be cleaned to eliminate any superficial impurities and pollutants. The process is important for ensuring that the subsequent examinations were carried out on unadulterated material (Figure 4b). Following thorough preparation, the samples underwent a finely regulated drying procedure. The procedure involved subjecting the samples to a constant temperature of 110°C for a continuous period of 24 hours. The drying method was conducted in accordance with the prescribed guidelines specified in ASTM D5731 (Conshohocken, 1995; Figure 4c).

After completing the preparing process, the limestone samples were subjected to reducing their particle size to achieve a uniform and granular state, which would aid in conducting further analyses. The reduction process entailed applying mechanical force using crushing and grinding techniques using pastel and mortar to attain a consistent distribution of particle sizes in the samples. In order to achieve a more precise particle size, the limestone samples that had been crushed and ground were meticulously placed into a sieve with a specified aperture size of 300µm. The purpose of this sieving operation was to maintain the uniformity of the particle size distribution and eliminate any data points that deviated significantly from the norm. This was done to improve the precision and reliability of the subsequent analytical methods.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of limestone weathering provides insights into the behaviour of this material under temperature variations and provides an understanding of its durability and stability in environmental circumstances. For this study of limestone thermal stability analyses, the TGA instrumentation (Brand: Mettler Toledo) was used. It works with high accuracy at a temperature between 25°C and 1000°C using a 10°C/min heating rate. The sample was put inside the machine at a precisely regulated temperature and increased it at a consistent rate, following ASTM E2402-19 (ASTM International, 2019). As the temperature increment took place, the limestone underwent transformations, and some of its constituents began to evaporate or decompose. The effect of those modifications changed into something observed in terms of weight loss, which can be minute even though sizable.

At the same time, the particular temperature at which these adjustments occurred were monitored and recorded. This fact-series technique became important because it provided essential insights into the limestone's thermal behaviour. It allowed to pinpoint the exact temperature factors at which weight reduction came about, signifying the onset of various tactics, which include the release of unstable additives or alterations within the limestone's shape.

Scanning electron microscopy (SEM) analysis

The surface morphology of limestone was determined by employing a scanning electron microscope (SEM) with a 5k accelerating voltage (Brand: Hitachi SU3500, modes 60-650Pa). The magnification range is within the values of 1000 and 50000X for limestone as specified by ASTM C1437 (ASTM International, 2009). The analysis was carried out to examine and evaluate the fine details of the mineral composition, possible microfractures, and surface shape of the limestone. From the examination of intact and weathered limestone, the aims are to shed light on characteristics, especially due to weathering processes.

RESULTS

Thermal stability analysis – Intact limestone

The results of thermal stability analysis for intact limestone samples were presented in this section and temperature thermogram in Figure 5 will be referred. For Intact - S1 sample, the pinnacle level for weight reduction, 3.1%/min, arrived at a steady warming pace of 728.75°C (Figure 5a). Followed by Intact - S2, the TGA results show the pinnacle level for weight reduction arrived at 2.4%/

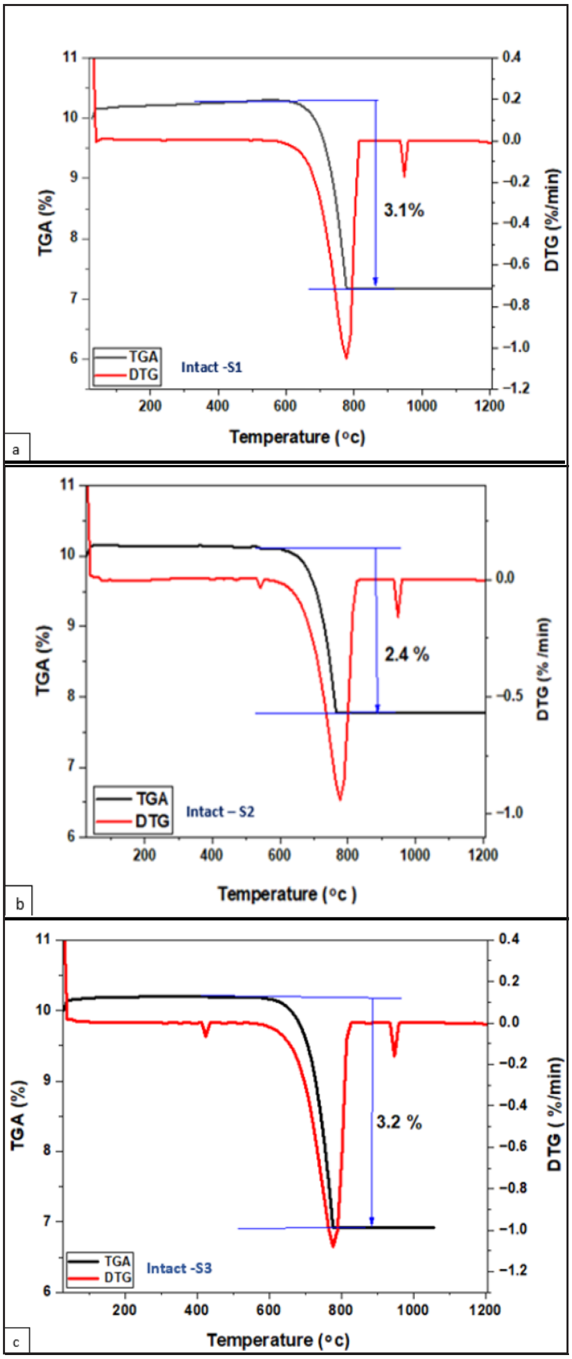

Figure 5: Thermogravimetric analysis of intact limestone samples (a) Intact – S1, (b) Intact – S2 and (c) Intact – S3.

min, happening at 772.90°C (Figure 5b). Sample Intact - S3 has shown the pinnacle level for weight reduction enrolled at 3.2%/min, happening at 734.45°C (Figure 5c).

From all the results (Table 3), it has described the warm way of behaving and disintegration profile of the subsequent limestone test, underscoring key temperature focuses and pace of weight reduction.

Thermal stability analysis – Weathered limestone

This section will present the results on thermal stability of weathered limestone while temperature thermogram will be referred as in Figure 6. The summarised values from the temperature thermogram were tabulated in Table 4.

The TGA analysis of sample Weathered-S1 show the pinnacle level for weight reduction arrived at 4.1%/min, happening at 778.47°C. This extensive figure discloses basic temperature spans and disintegration profiles, helping with the comprehension of the fourth limestone test's warm way of behaving (Figure 6a). For Weathered-S2 sample, the thermogravimetric analysis has revealed the slope variations in various regions of the thermogram (Figure 6b). The initial thermal event linked to moisture loss transpires within the temperature range of 200°C. Subsequently, a second loss reaction occurs between 300 – 650°C with a loss weight of 0.21%, which is associated with the magnesium carbonate decomposition that liberates CO_2. In a similar vein, decomposition is linked to the third thermal event; nevertheless, the substance that is dissociated is calcium carbonate, and the slope of the baseline changes occurs within the temperature range of 650 – 800°C. In the process of decomposition, both substances liberate carbon dioxide as magnesium and calcium oxides are formed. The pinnacle level for weight reduction was 4.54 %/min happening at 734.45°C. This curve gives itemized experiences into the temperature focuses and weight reduction qualities of the fifth limestone test.

Meanwhile, Weathered-S3 sample presents the initial thermal event linked to moisture loss transpires within the temperature range of 200°C (Figure 6c). Subsequently, a second loss reaction occurs between 375 – 650°C with a loss weight of 0.24%, which is associated with the magnesium carbonate decomposition that liberates CO_2. In a similar vein, decomposition is linked to the third thermal event; nevertheless, the substance that is dissociated is

Table 3: The results of the thermal analysis of samples of intact limestone.

Sample	Temperature Range (°C)	Weight Loss (%/min)	Peak Temperature (°C)
Intact – S1	27.40 -145.12	3.1	728.75
Intact – S2	28.42 -142.59	2.4	772.90
Intact – S3	27.18 -147.88	3.2	734.45

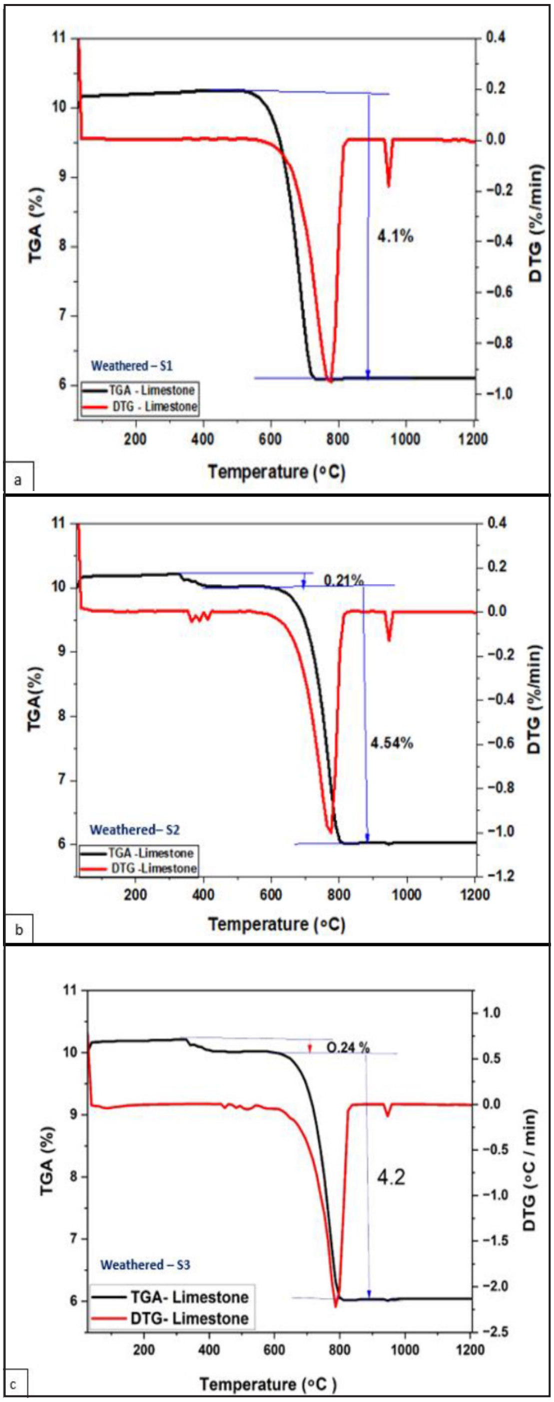

Figure 6: Thermogravimetric analysis of intact limestone samples (a) Weathered – S1, (b) Weathered – S2 and (c) Weathered – S3.

calcium carbonate, and the slope of the baseline changes occurs within the temperature range of 700 – 800°C. In the process of decomposition, both substances liberate carbon dioxide as magnesium and calcium oxides are formed. The pinnacle level for weight reduction was 4.2 %/min happening at 779.62°C.

Surface morphological characteristics - Intact limestone

The morphological characteristics of intact limestone images and data will be presented in this section. Intact limestone samples, as seen by Scanning Electron Microscopy (SEM) image (Figure 7), exhibit a morphology that suggests the characteristics in their original condition. In general, the images have revealed a surface that is smooth and uniform, with few surface imperfections or cracks visible at high magnification. The crystalline structure seems well-defined and unbroken, representing the clean structure of the limestone. Pores inside the intact samples are consistently distributed and very tiny in size, contributing to the overall compaction and low porosity of the limestone. Also, the surface features such as tiny scratches or abrasions, likely sustained through handling and preparation processes, further supporting the integrity of the complete limestone, and the colour remains consistent across all samples, generally showing a light grey.

The microscopy was conducted at 5.00kV with a 10.8mm x 5.00k SE aperture. The presence of larger particles, up to 10.0µm, was notable, indicating potential impurities or variations in composition (Figure 7a). For Intact-S2 sample, it has displayed a relatively narrow particle size distribution, with sizes ranging from 3.33µm to 11.0µm. The particles appeared more spherical in shape. The microscopy was conducted at 5.00kV with a 9.6mm x3.00k SE aperture. There was a distinct peak around 10.0µm, suggesting a prominent size mode in this sample (Figure 7b).

Finally, Intact-S3 sample has exhibited a particle size distribution spanning from 4.82µm to 10.0µm, with an irregular shape. microscopy was performed at 5.00kv with a 10.6mm x 5.00k SE aperture. the distribution showed multiple peaks at 5.31µm, 5.68µm, and 5.19µm, indicative of various size modes. the presence of smaller particles down to 4.76µm was observed as well (Figure 7c).

Table 4: Thermal analysis of samples of weathered limestone.

Sample	Temperature Range (°C)	Weight Loss (%/min)	Peak Temperature (°C)
Weathered–S1	28.90 -142.10	4.1	778.47
Weathered–S2	28.90 -142.10	4.54	778.31
Weathered–S3	28.42 -149.95	4.2	779.62

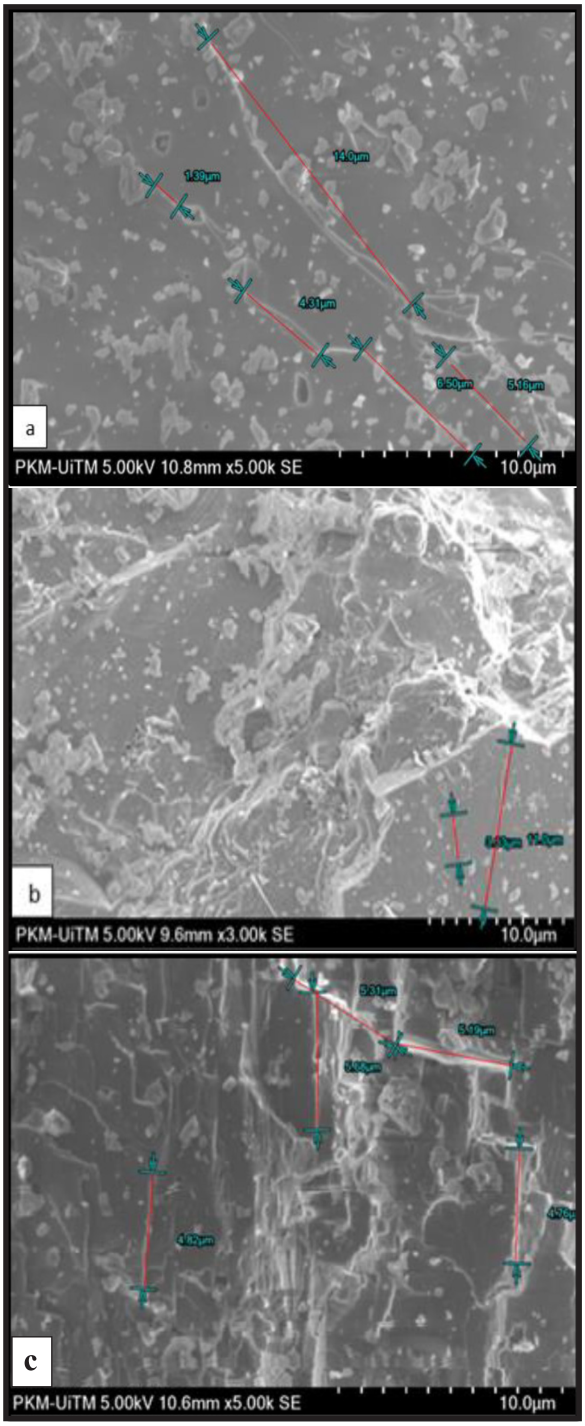

Figure 7: Microscopic examination of intact limestone of (a) Intact – S1, (b) Intact – S2, and (c) Intact – S3.

Table 5 shows the distribution of particle size for intact limestone samples. The assessment of Intact-S1sample has uncovered a different molecule size dissemination, with a reach spreading over from 1.39µm to 14.0µm. The particles appeared to be irregular in shape, with some clustering observed around 4.31µm.

Surface morphological characteristics - Weathered limestone

Conversely, the SEM images examination of weathered limestone samples (Figure 8) reveals a morphology characterized by significant changes brought about by weathering processes in the environment. Under magnification, the surface texture shows distinct traces of weathering and erosion. The texture seems rough and uneven. The broken and fractured crystalline structure shows how the composition of the limestone has changed and deteriorated over time. The weathered samples have larger, more irregular pores, which indicate the dissolution and leaching of mineral components brought on by external influences. Cracks, fissures, and weathering rinds are noticeable surface characteristics that attest to extended exposure to environmental factors. In addition, there are noticeable colour variations that range from lighter to deeper tones, which indicate the level of weathering and the existence of environmental pollutants.

The examination of Weathered-S1 sample has unveiled a wide-ranging particle size of fracture distribution, from 2.98 µm to 21.1 µm. The particles appeared irregular in shape. Microscopy was carried out at 5.00 kv with a 10.7mm x 3.00 k SE aperture. The distribution showed several peaks, particularly at 3.31µm, 3.78µm, 5.93µm, and 9.71µm. This diverse distribution suggests the presence of particles of various sizes and shapes (Figure 8a).

Weathered-S2 sample has displayed a wide-ranging particle size distribution from 1.49µm to 8.24µm. The particles were predominantly irregular in shape. Microscopy was conducted at 5.00kv with a 9.9mm x 3.00k SE aperture. The distribution revealed numerous peaks, specifically round 4.64 µm and 5.46µm, signifying multiple size modes. Moreover, the presence of smaller particles, down to 49µm, becomes evident (Figure 8b). Finally, Weathered-S3 sample showed a very long and deep fractures, demonstrating a particle length distribution

Table 5: Distribution of particle sizes for three samples of intact limestone.

Sample	Particle Size Range (µm)	Peak Particle Size (µm)	Additional Information
Intact–S1	1.39-14.0	4.31	Presence of larger particles, potential impurities or variations
Intact–S2	3.33-11.0	10	Relatively narrow distribution, distinct peak around 10.0µm
Intact–S3	4.82-10.0	5.31; 5.68; 5.19	Multiple size modes, presence of smaller particles

Table 6: Distribution of particle sizes for weathered limestone.

Sample	Particle Size Range (μm)	Peak Particle Size (μm)	Additional Information
Weathered-S1	2.98 - 21.1	3.31; 3.78; 5.93; 9.71	Diverse distribution with various sizes and shapes
Weathered-S2	1.49 - 8.24	4.64; 5.46	Multiple size modes, presence of smaller particles
Weathered-S3	1.89 - 31.0	1.89; 10.6. 9.6	Blended particle size distribution with various modes

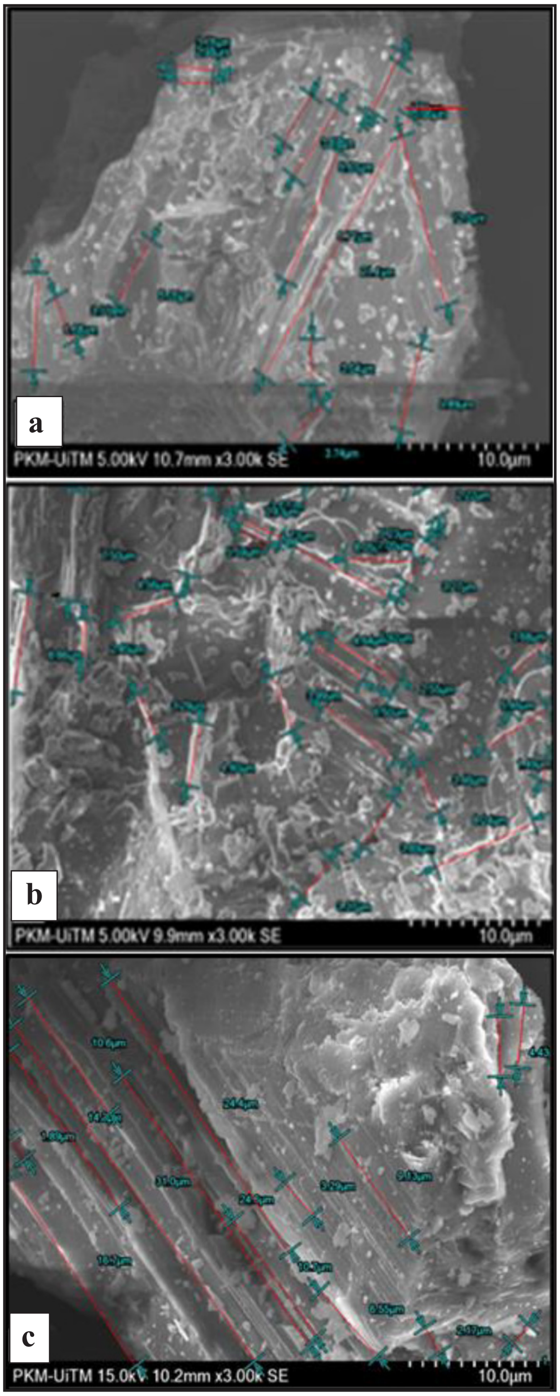

Figure 8: Microscopic examination of weathered limestone samples (a) Weathered-S1, (b) Weathered-S2 and (c) Weathered-S3.

ranging from 1.89 μm to 31.0 μm with an irregular form. Microscopy was carried out at 15.0 kv with a 10.2 mm x 3.00 k SE aperture. The distribution exhibited peaks at 1.89μm, 10.6μm, and 9.6, suggesting a blended particle size distribution with various modes (Figure 8c). Table 6 shows the distribution of particle size for weathered limestone samples.

Weathering-induced fractures and cracks in limestone samples

Based on SEM analyses, the results in the limestone sample exhibit a more uniform particle size distribution, suggesting less agglomeration among particles. This narrower distribution and relatively spherical particle shapes may make the sample more susceptible to fractures or cracks, as the uniformity in particle sizes could increase brittleness. The distinct peak at 10.0μm indicates a prominent size mode, potentially indicating areas of higher stress concentration.

Figure 9 illustrates the presence of fractures and cracks caused by air exposure in limestone samples and their correlation with the degree of weathering.

DISCUSSION

Thermal stability analysis of intact and weathered limestone

Weathered limestone samples usually show a greater weight loss, one of the reasons for increasing porosity. Limestone becomes more porous as a result of weathering

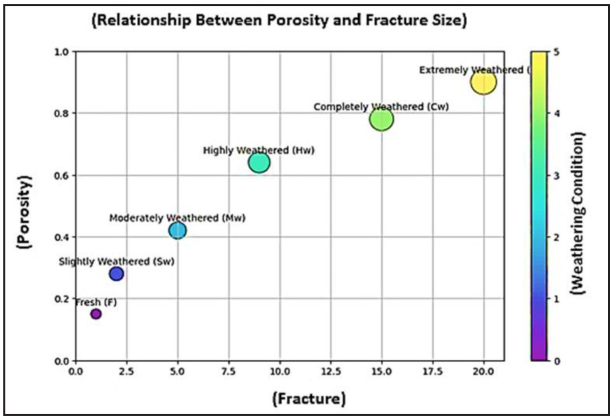

Figure 9: Data showing fractures and cracks caused by air in limestone samples and their relationship with the weathering grade.

processes such as dissolution, abrasion and chemical weathering. Compared to intact samples with lower porosity, these pores allow gases to escape during thermal fracture, resulting in greater weight loss.

Weathering can cause changes in the mineral composition of limestone that led to the leaching of some components or the production of secondary minerals and affect the thermal stability of the rock, which can lead to more weight loss when heated. Also, limestone often has more surface due to fracture and dissolution during weathering processes. More reactive sites are exposed by the larger surface area, which makes the rock more susceptible to thermal failure and causes more weight loss.

The thermal behaviour of limestone can be impacted by weathering-induced structural alterations such as microfractures, mineral recrystallization, and cementation. Elevated reactivity and faster breakdown could result from these modifications, which would increase weight loss. Overall, the higher weight loss seen in weathered limestone samples compared to intact ones during thermal stability analysis can be attributed to a combination of increased porosity, changed mineral composition, higher surface area, and structural changes brought on by weathering processes.

An investigation into the thermal characteristics of limestone via Thermal Gravimetric Analysis (TGA) yields significant knowledge regarding its attributes. The parameters analysed including weight loss, residue formation, peak temperatures, and peak weight loss rates can be accessed via TGA analysis.

Comparison of intact limestone samples indicates consistent thermal characteristics, with stable behaviour demonstrated across all intact limestone samples. Each sample displays uniform degradation dynamics, characterized by identical temperature ranges, inflection points, and peak weight loss rates. For instance, the range of weight loss for intact limestone samples differs minimally, with Intact-S1 sample has losing 3.1% per minute at 728.75°C, meanwhile, Intact-S2 sample has losing 2.4% per minute at 772.90°C, and Intact-S3 sample has losing 3.2% per minute at 734.45°C (Figure 10a). These data reveal a similar pattern of thermal breakdown in intact limestone, with small variances in temperature profiles and weight loss.

In contrast, the impact of weathering on thermal stability becomes clear. Weathered limestone samples demonstrate unique breakdown characteristics compared to their undamaged counterparts. Weathered-S1 sample has indicated an accelerated breakdown rate, with a peak weight loss rate of 4.1% per minute at 778.47°C. Meanwhile, Weathered-S2 sample has displayed heterogeneous degradation behaviour, demonstrated by a peak weight loss rate of 4.54% per minute at 778.31°C. Weathered-S3 sample has displayed a complex thermal degradation pattern, with a peak weight loss rate of 4.2% per minute at 779.62°C (Figure 10b). These data demonstrate that weathering produces structural alterations in limestone, resulting in varied thermal degradation characteristics.

The results align with the findings of Navarre *et al*. (2015), who observed that weathered limestone demonstrates a more intricate and rapid thermal deterioration profile in comparison to intact limestone. The TGA analysis verifies that weathering has a substantial impact on the thermal stability of limestone, rendering it more prone to disintegration at high temperatures.

Surface morphological comparative analysis of intact and weathered limestone

Particle size distributions with mostly irregular forms are revealed by SEM analysis of intact limestone samples (Intact-S1, Intact-S2, and Intact-S3). The particle size distribution curves for these samples show distinct peaks, which are suggestive of uniform particle sizes and shapes. Some samples also show bigger particles, which could indicate contaminants or compositional differences. On the other hand, a SEM image analysis of the weathered limestone samples (Weathered-S1, Weathered-S2, and Weathered-S3) shows cracked surfaces and wider particle size distributions with irregular forms.

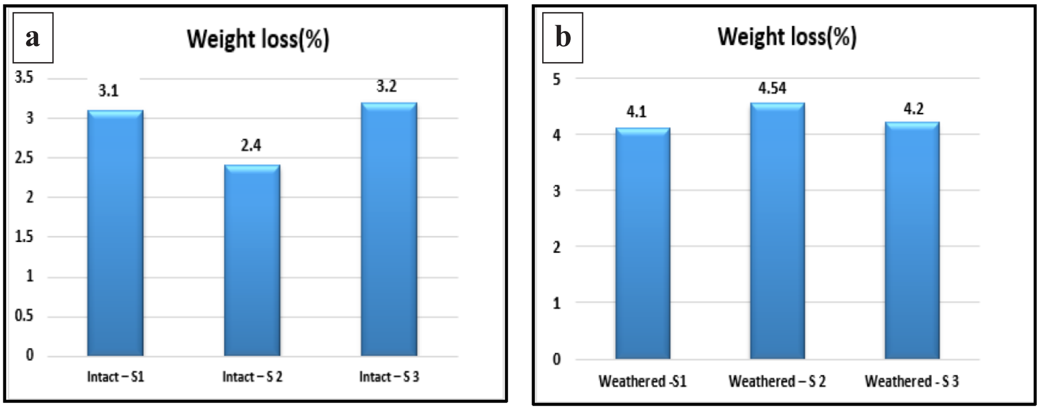

Figure 10: The thermal properties result on weight loss (a) intact limestone samples and (b) weathered limestone.

The presence of uneven shapes and a range of sizes of particles is indicative of the weathering and erosion processes that cause the limestone structure to break apart and disintegrate. In addition, the level of environmental degradation is highlighted by the discovery of smaller particles and extensive fractures in weathered samples. These findings are consistent with the research conducted (Navarre *et al*., 2015), who similarly noted higher porosity and irregular particle sizes in weathered limestone as compared to intact samples. The scanning electron microscopy (SEM) investigation supports earlier research by demonstrating that weathering has a substantial impact on the morphological properties of limestone, resulting in a more diverse and fractured structure.

Significance of the study

The value of this study rests in its extensive evaluation of the morphological and thermal stability variations between weathered and intact limestone. This study will contribute to the understanding of how environmental conditions and long-term exposure effect the integrity and usefulness of limestone in various applications.

a) Enhanced understanding of material properties:

By comparing the findings from SEM image and TGA data, an insight into how weathering processes alter the microstructural characteristics of limestone, such as particle size distribution and surface morphology was gained. The identification of long, deep fractures and increased porosity in weathered limestone, as opposed to the more uniform and compact structure of intact limestone, highlights the significant impact of environmental degradation.

b) Implications for industrial applications:

The thermal stability differences between weathered and undamaged limestone have important ramifications for businesses that use limestone in construction, manufacturing, and environmental cleanup. The higher peak weight loss rates seen in weathered limestone suggest that it is more prone to thermal breakdown, which could impair its performance in high-temperature environments. This knowledge is essential for making sound judgments about material selection and treatment techniques that improve durability and efficiency.

c) Impact on environmental and structural design:

The association between microstructural characteristics and thermal behaviour established by this work emphasizes the need of rigorous material characterization in the design and fabrication of high-temperature-resistant items. This knowledge allows engineers and architects to make more educated decisions regarding the materials they choose, potentially leading to more durable and sustainable buildings.

Finally, this study compares weathered and intact limestone, providing vital insights into how weathering affects thermal stability and morphology. The findings have practical significance for a variety of businesses, including construction, environmental remediation, and historic preservation. Understanding the intricate interaction between microstructural features and thermal behaviour might help us make better decisions and encourage innovation in the use and conservation of limestone. This study not only improves theoretical understanding, but it also provides practical recommendations for applying and preserving this adaptable substance in a variety of disciplines.

CONCLUSION

In this paper, a comparative investigation of the thermal stability and morphology of weathered and intact limestone rocks, acknowledging limestone's multifunctional role in numerous scientific and commercial areas. By applying modern techniques like Scanning Electron Microscopy (SEM) for morphological evaluation and thermogravimetric analysis (TGA) to analyse thermal deterioration behavior, the scientific information concerning limestone's thermal behavior and morphological qualities can be extended.

The study goal is to give useful insights into the complicated link between morphology and thermal stability in limestone. Through extensive TGA research, the effect of temperature on limestone's thermal stability was studied and evaluated the consequent weight reduction. Additionally, SEM morphological examinations offered significant information concerning microstructural characteristics in worn and undamaged limestone samples. Comparing surface morphology, porosity distribution, seams, fractures, and weight changes between weathered and undamaged limestone exposed new understandings about their structural nuances and thermal behaviour.

The major findings revealed considerable differences between weathered and intact limestone samples. Weathered limestone displayed the biggest peak weight loss, but intact limestone demonstrated the highest weight reduction rate. SEM findings further indicated unique particle size distributions across the two versions, with weathered limestone having lengthy, deep fractures compared to unbroken limestone.

These findings have practical consequences for numerous industries and domains, extending beyond theoretical knowledge. Understanding how shape and structure effect heat resistance is vital for decision-making in domains like as building, environmental cleaning, and historical preservation. By discovering patterns and trends that illuminate the delicate relationship between morphology and thermal stability; this study contributes to informed decision-making and promotes innovation across industries also it will give useful information for preservation and implementation in many sectors and domains, supporting informed decisions and promoting innovation.

In conclusion, this work underlines the need of thoroughly knowing limestone's morphology and thermal behaviour to optimize consumption and assure good preservation.

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AUTHORS CONTRIBUTION

The authors affirm their contributions to the paper as follows: study conception and design were led by HK and NNND; data collection: HK; analysis and interpretation of results: HK, NNND, draft manuscript preparation: HK, NNND and SI have contributed with ideas on the design of the experiment. This delineation of individual contributions underscores the collaborative effort and ensures transparency regarding each author's involvement in the research process.

CONFLICT OF INTEREST

The authors, HK and NNND declare no conflicts of interest related to the publication. HK has dual affiliations with the Department of Geology and Mine at Faryab University, Afghanistan, and the Department of Civil Engineering at Universiti Putra Malaysia, Malaysia. NNND is affiliated with the Department of Civil Engineering at Universiti Putra Malaysia, Malaysia and is the corresponding author. There are no financial or personal relationships that could be perceived as conflicts of interest.

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