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Analysis of Deterioration on Stone Surfaces: The Case of Kasimiye Madrasah

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Abstract

The durability of stone is important for traditional buildings to survive today. However, as a result of environmental and atmospheric factors, physical, chemical, biological and anthropogenic degradation occurs on stone surfaces. Detecting, classifying and taking appropriate measures against these degradations on stone surfaces is one of the factors that play a role in the survival of stone structures for a longer period. In this study, the deterioration of the facades of Kasımiye Madrasah in Mardin was analyzed. The deterioration of the building was classified and analyzed. Visual, mapping, and X-Ray Fluorescence Spectroscopy (XRF chemical analysis method) were used as analysis methods. The deterioration of the building was analyzed and classified by visual analysis. The type of deterioration and its ratio to the façade were examined using the mapping method. With the XRF analysis method on the deteriorated stone surfaces, the chemical components on the stone surface were examined and the effect causing the deterioration was examined. The study aims to determine the types and causes of deterioration in the building, to offer solutions, and to ensure that the building is transferred to future generations without losing its originality for many years in the light of this information.

Keywords: *Kasımiye Madrasah, stone deterioration, XRF chemical analysis method.*

Taş Yüzeylerinde Görülen Bozunmaların Analizi: Kasımiye Medresesi Örneğinde

Öz

Geleneksel yapıların günümüze kadar ulaşmasında taşın dayanıklılığı önemlidir. Ancak çevresel ve atmosferik etkenler sonucunda taş yüzeylerinde fiziksel, kimyasal, biyolojik ve antropojenik bozunmalar meydana gelmektedir. Taş yüzeylerde meydana gelen bu bozunmaların tespiti, sınıflandırılması ve bozunmalara karşı uygun önlemlerin alınması taş yapıların daha uzun süre ayakta kalmasında rol oynayan etkenlerden biridir. Bu çalışmada Mardin'de yer alan Kasımiye Medresesi'nin cephelerinde meydana gelen bozunmalar irdelenmiştir. Yapıda oluşan bozunmalar sınıflandırılmış ve analiz edilmiştir. Analiz yöntemi olarak görsel, haritalama ve X-Işınları Floresan Spektroskopisi (XRF kimyasal analiz yöntemi) yöntemi kullanılmıştır. Yapıda meydana gelen bozunmalar görsel analiz ile incelenmiş ve sınıflandırılmıştır. Bozunma türü ve cepheye oranı haritalama yöntemi kullanılarak incelenmiştir. Bozunma olan taş yüzeylerde yapılan XRF analiz yöntemi ile taş yüzeydeki kimyasal bileşenler incelenmiş ve bozunmaya neden olan etki irdelenmiştir. Çalışmanın amacı; yapıda meydana gelen bozunma türlerini ve nedenlerini tespit etmek, çözüm önerileri sunmak ve bu bilgiler ışığında yapının uzun yıllar boyunca özgünlüğünü kaybetmeden gelecek nesillere aktarılmasını sağlamaktır.

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Anahtar kelimeler: *Kasımiye Medresesi, taş bozunmaları, XRF kimyasal analiz yöntemi.*

1. Introduction

Due to its geographical location, Mardin has been home to many civilizations and civilizations, and throughout history, representatives of different cultures, civilizations, peoples, languages, and religions have lived together in peace (Alioğlu, 1989).

These civilizations that ruled in Mardin built structures with different functions. Madrasa buildings, one of these structures built in the city, have been used for educational and cultural purposes throughout history (Yardımlı, 2018). Limestone, one of the natural stones, was used in cultural heritage buildings in Mardin. When natural stones are exposed to internal and external factors such as adverse climatic conditions, user error, and traffic density, deterioration occurs on stone surfaces (Öcal, 2010; Dal & Öcal, 2013a; Dal & Öcal, 2013b). These deteriorations that occur on stone surfaces over time cause the durability and strength values of the stone to decrease (Semerci, 2017). The decrease in durability and strength values shortens the survival time of the structures for a long time. Taking measures to minimize deterioration and reduce damage is important for the life of structures (Douglas, Hughes, Jones, & Yarrow, 2016). The measures to be taken for these types of deterioration in buildings vary according to the types of deterioration and are different from each other (Dal & Öcal, 2017). It is important to correctly identify the deterioration that occurs in buildings, to classify the deterioration and to take precautions in order to deal with the deterioration separately (Arpacıoğlu, 2016). In some cases, the deterioration of the structures paves the way for the formation of another deterioration. In addition, regular inspection of the structures, selection of suitable stones, cleaning the structure and taking measures to increase its durability play an effective role in carrying the structure to the next years (Doehne & Price, 2010; Karkaş & Acun Özgünler, 2022).

The study aims to examine and identify the stone deterioration observed on the facades of Kasımiye Madrasah in Mardin and to ensure that the building survives longer by taking measures against deterioration. In this context, the stone deterioration observed in Kasımiye Madrasah was analysed in three stages. Firstly, it was visually examined and deterioration was systematically analysed as physical, chemical, biological and anthropogenic deterioration. In the second stage, after identifying the deterioration on the facades, the mapping method was used to determine the types of deterioration and their ratios in relation to all facades. The mapping method relied on software programmes (Autocad 2018 and Adobe Photoshop CS6). In the third stage, the chemical content of the stone was determined using the X-Ray Fluorescence Spectroscopy (XRF chemical analysis method). In light of the data obtained from the study, the aim is to form the basis for conservation projects to be carried out in the upcoming years (Biçen Çelik, 2021).

2. Material and Method

Natural stones have been used for different purposes and functions from the past to the present. The fact that it can be used without the need for binding materials has caused it to be preferred more than other main construction materials. The most important factor in the survival of traditional buildings, which are cultural heritage, is the high durability and strength values of the stone used in the building. When natural stones are faced with environmental and climatic factors, deterioration occurs on the surfaces of the stone (Ay et al., 2023a; Biçen Çelik et al., 2023; Umaroğuları & Kartal, 2021). In this study, natural stone deterioration in the Kasımiye Madrasah in Mardin is discussed. The deterioration on the stone surfaces of the building was analyzed, and the types and rates of deterioration, their diversity and causes were determined. The study includes the analysis of the deteriorated surfaces on the east, west and south facades of the building and the inner courtyard facades facing west and south as a result of environmental conditions.

Different methods were used to determine the types of deterioration that occurred in the Kasımiye Madrasah. The mapping method, which is one of the methods used, is an internationally recognized method and deterioration was detected and classified with these methods (Fitzner, Heinriches, & Kownatzki, 1997). After the deterioration of the building facades was visually detected, they were processed on the facades through AutoCAD 2018 and Adobe Photoshop CS6 programs and thus a mapping method was created. According to the data obtained, the types of deterioration on the facades and the ratio of deterioration to the entire facade were determined. In the study, the deteriorations were grouped as physical, chemical, biological and anthropogenic deteriorations. As a result of the classification, deterioration was handled separately. In addition to visual detection and mapping methods, chemical analysis method was also used. Among the chemical methods, X-Ray Fluorescence Spectroscopy (XRF chemical analysis method) was preferred. With this method, it was aimed to determine the chemical content of the degraded stone. SPECTRO xSORT / Portable Metal Spectrometer model device was used for XRF chemical analysis method. According to the XRF chemical analysis method, the ratios of CaO, SiO_2, Al_2O_3, SO_3, Fe_2O_3 and P_2O_5 compounds in the stone were determined, evaluated and analyzed with tables and graphs. As a result of the data obtained, the relationship between the deterioration and the components in the stone was determined. This study aims to form an important basis for the interventions to be made to the Kasımiye Madrasah.

2.1. Study Area Features

2.1.1. History of Mardin Province

The historian Ammianus Marcellinus first mentioned the name Mardin as "Maride" (Gabriel, 1940). The name Mardin was also referred to as Mâridin and Mârdê by different ethnicities (Noyan, 2008; Yousif, 2011). Mardin has been home to various cultures and ethnic origins throughout history due to its location on an important trade route (Silk Road) and its geographical and topographical defensibility (Alioğlu, 2000).

The first settlements in Mardin have artifacts dating back to 3000 BC (Aydın, Emiroğlu, Özel & Ünsal, 1999). In later years, different civilisations (Yıldız, 2007) and states (Aliveya, 2007; Biçen Çelik, 2021). It can be said that the Artuqids in the XIIth century had an impact on determining Mardin's identity (Dal & Öcal, 2017). After the Artuqids, Mardin came under the rule of Akkoyuncu, Karakoyunlu, Safavids and Ottomans, and there are traces of all civilisations in Mardin (Çağlayan, 2018; Dolapönü, 1972). Kasımiye Madrasah was built in the XIVth century and is among the religious buildings until today (Alioğlu, 2000). The satellite image of Mardin province was taken and processed on Google Earth and the location of Kasımiye Madrasah was marked and given in Figure 1.

Figure 1. Satellite image of Mardin (processed from Google Earth)

2.1.2. Geographical features of Mardin Province

Mardin is located in the Southeastern Anatolia Region of Turkey, neighboring Syria together with the provinces of Şanlıurfa, Diyarbakır, Batman, Şırnak and Siirt. Mardin Castle is located at the top of the city. The first settlements of the city were around the castle and then settlements started outside the castle on the high plateaus overlooking the Mesopotamian plain (Karataş, 2018) (Figure 2). In this region where the settlement is located, the buildings were built on sloping land. Access to the buildings is provided by steep ramps and stairs (Bekleyen, Dalkılıç & Özen, 2014).

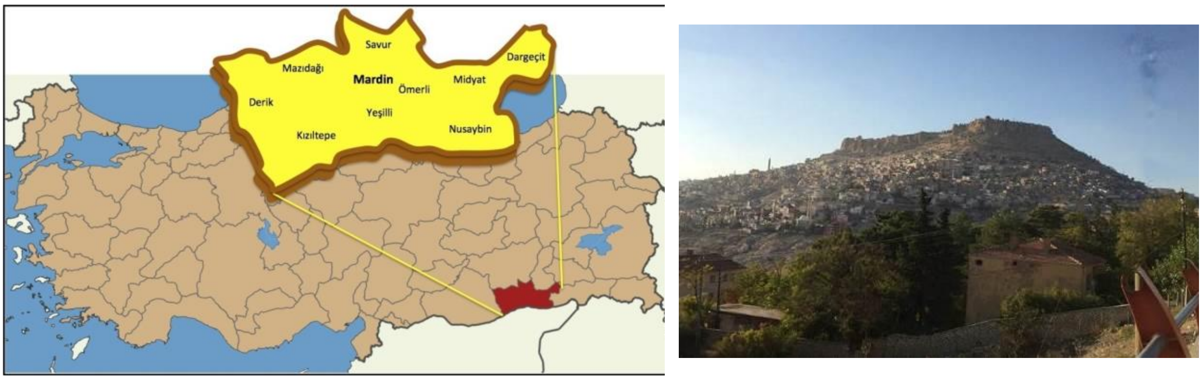


Figure 2. Mardin's location in Turkey (Dal & Öcal, 2017) and Mardin view (Biçen Çelik, 2019)

When the climate of Mardin province is examined, continental climate is observed in the center and Mediterranean climate is observed in the districts. Winter months are cold. In the summer season, it is dry and hot due to the effect of the pressure and wind coming from the desert. Looking at the annual average temperature values of the province, it is seen that the highest temperature value is 29.8 °C in July and the lowest temperature value is 3.0 °C in January (Table 1). When the climatic data of Mardin province between 1941 and 2022 are analysed, it is seen that the maximum average sunshine duration is 12.4 hours in July and the minimum sunshine duration is 4.5 hours in December. Due to the climatic characteristics of Mardin province, stone deterioration is frequently encountered (Karataş, 20018).

Table 1. Meteorological data evaluation of Mardin province (Measurement Period, 1941-2022) (General Directorate of Meteorology, 2023)

MARDİN	Average Temperature (°C)	Average Highest Temperature (°C)	Average Lowest Temperature (°C)	Average Sunbathing Time (hours)	Average Number of Rainy Days	Average Monthly Precipitation (mm)
January	3.0	5.8	0.6	4.5	12.11	115.9
February	4.2	7.4	1.4	5.1	10.61	103.2
March	7.9	11.6	4.6	5.9	11.70	97.7
April	13.5	17.4	9.8	7.3	10.28	81.1
May	19.5	24.0	15.1	9.7	7.35	47.3
June	25.6	30.6	20.3	12.1	1.54	6.5
July	29.8	35.0	24.6	12.4	0.48	3.2
August	29.6	34.7	24.7	11.4	0.24	2.3
September	25.3	30.1	20.8	10.3	0.70	4.0
October	18.6	22.9	14.7	7.7	5.12	33.8
November	11.1	14.5	8.1	5.9	7.66	71.9
December	5.4	8.2	2.9	4.4	10.80	108.7
Annual	16.1	20.2	12.3	8.1	78.6	675.6

2.1.3. Architectural features of Kasımiye Madrasah

Kasımiye Madrasah is located on the hill on the southwest side of Mardin. The construction date of the building is not known exactly. Gabriel's ideas about the construction date of the building and the madrasah are generally accepted (Altun, 1971). It is estimated that the madrasah was started at the end of the Artuqid period and completed during the Akkoyunlu period. Due to the similarity of the architectural style of Kasımiye Madrasah and Zinciriye Madrasah, it is estimated that the two buildings were built in the same period (Artuqid period) and by the same architect. The resemblance of the building is similar to the decoration of Zinciriye Madrasah. There is a belt with muqarnas outside the door and corner columns and a three-slice arch inside (Semerci, 2017).

The main portal, which is one of the most important parts of the building, resembles the portal of Zinciriye Madrasah. Its stones and stone decorations are quite worn. Therefore, the portal is enclosed in a frame with muqarnas. The entrance to Kasımiye Madrasah, one of Mardin's two-storey madrasas with a single courtyard, is through the main portal. The building consists of a domed square space over the mosque and barrel vaulted rooms. Madrasah rooms are located at the back of the courtyard. The ground floor of the building has a mausoleum, Hanafi masjid, Shafii masjid and 11 cells, while the first floor has 12 cells (Figure 3). To the left of the main entrance is the Hanafi masjid with onion slices and to the right is the tomb with a slice dome. The part of the entrance corridor opening to the courtyard is covered with a passion vault. When you enter the courtyard, there is an iwan with selsebil and cells with sliced domes located around the courtyard. The iwan in the courtyard is covered with a pointed vault. There is a mihrab in the centre of the southern part of the courtyard. On the left side of the mihrab is the tomb and on the right side is the Shafii masjid. The tops of the tomb and Shafii masjid are covered with a sliced trumpet dome. With the repair in 2007, the porch vaults on the ground floor were cut stone, but after the repair, the tops were plastered and turned into barrel vaults (Figure 3) (Çağlayan, 2018; Karataş & Peyker, 2023; Yeşilbaş, 2020). The building, which was restored in 1967, was allocated to the Governorship of Mardin in 1974 and started to be used as a museum. During the restoration of the madrasah in 2007, the stone surfaces were cleaned (Ergin, Biçen Çelik & Dal, 2019).

Kasımiye Madrasah has a total of seven facades, including four facades facing the inner courtyard, the south facade, which is the front facade, and the east and west facades, which are the side facades. Limestone was used as the main material of the building. Kabayonu stone was used on the eastern façade of the building and the western façade, except for the mosque part. The Hanafi masjid on the west façade and the south façade have cut stone (Figure 4).

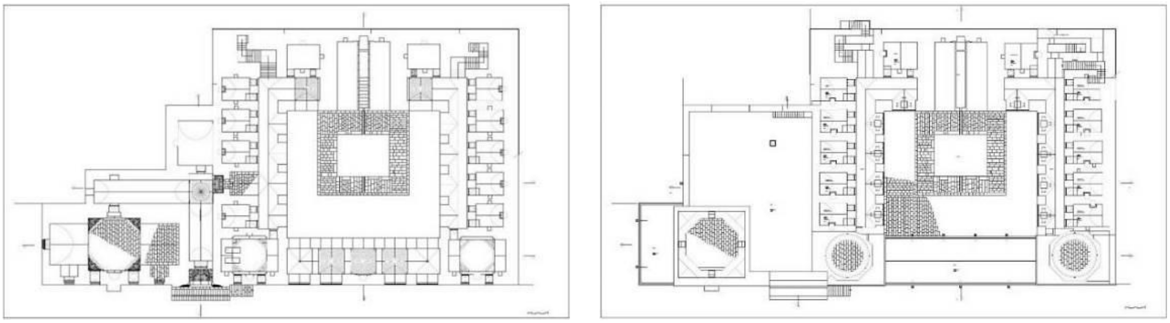


Figure 3. Floor plans of Kasımiye Madrasah

Figure 4. Facade photographs of Kasımiye Madrasah (Biçen Çelik, 2019)

3. Findings and Discussion

Determining the factors that cause stone deterioration is important for cultural heritage (Karataş & Peyker, 2023). Stone has been used and continues to be used in different forms and functions in the process until today (Tintin, 2012). Stone, which was used by the first people for defense purposes, was also used as a housing, decorative product and symbol in later periods, apart from giving messages and using gravestones (Sabbioni & Cassar, 2012).

Stone, which is preferred as a building material, degrades over time as a result of environmental and climatic factors such as pressure, temperature and wind (Dal, 2016). As a result of the deterioration, the structure and strength of the stone deteriorates significantly. In addition, these deteriorations sometimes prepare the environment for another deterioration and accelerate the process (Ergin, Biçen Çelik & Dal, 2020). If necessary precautions are not taken or incorrect applications are made, serious damages and significant destruction occur in the structures (Doehne & Price, 2010; Torraca, 1976; Yardımlı, Hattap, Khooshroo & Javadi, 2017).

The deterioration occurring in buildings is handled in four groups physical, chemical, biological, and anthropogenic deterioration.

Physical deterioration is characterized as the surface loss that occurs on the surface of the stone as a result of mechanical effects on the surface of the stone. These can be exemplified as fracture, crack, piece breakage, deformation, abrasion, cut, honeycombing, joint discharges (Dal & Yardımlı, 2021).

Chemical deterioration is the type of deterioration on the surface of the stone as a result of atmospheric events. Examples such as colour change, salting, crystallisation (blooming), crusting, blistering, sugaring and foliation are examples of chemical deterioration (Öcal & Dal, 2012).

Biodeterioration is the type of deterioration of organic substances caused by stone. Algae formation, plant formation, and bioaccumulation are examples of biodeterioration (Rivera, Ramos, Sánchez, & Serrano, 2018; Dal, Zülfikar & Dolar, 2020; Dolar & Yardımlı, 2017).

Anthropogenic deterioration is the deterioration caused by human destruction. Improper application, misuse and periodic wear can be given as examples of anthropogenic deterioration (Ay et. al, 2023b; Hattap, 2002).

In this study, the deterioration of Kasımiye Madrasah was examined under three different headings: visual examination, examination using the mapping method and examination using XRF chemical analysis method.

3.1. Visual Investigation of the Deterioration Occurring in Kasımiye Madrasah

The deterioration of Kasımiye Madrasah was analysed in four groups physical, chemical, biological, and anthropogenic deterioration. The physical deterioration of Kasımiye Madrasah as a result of environmental and climatic factors is shown in Figure 5. As a result of climatic factors, capillary cracks in the walls (Figure 5a), fragment breaks in the window openings (Figure 5b), fragment breaks in the inner courtyard (Figures 5c and 5d), abrasion caused by wind-borne dust on the south façade (Figures 5e and 5f), fragment breaks, capillary cracks and joint discharges on the main portal and west façade of the building (Figures 5h and g), and abrasion on the entrance staircase due to visitor flow (Figure 5).

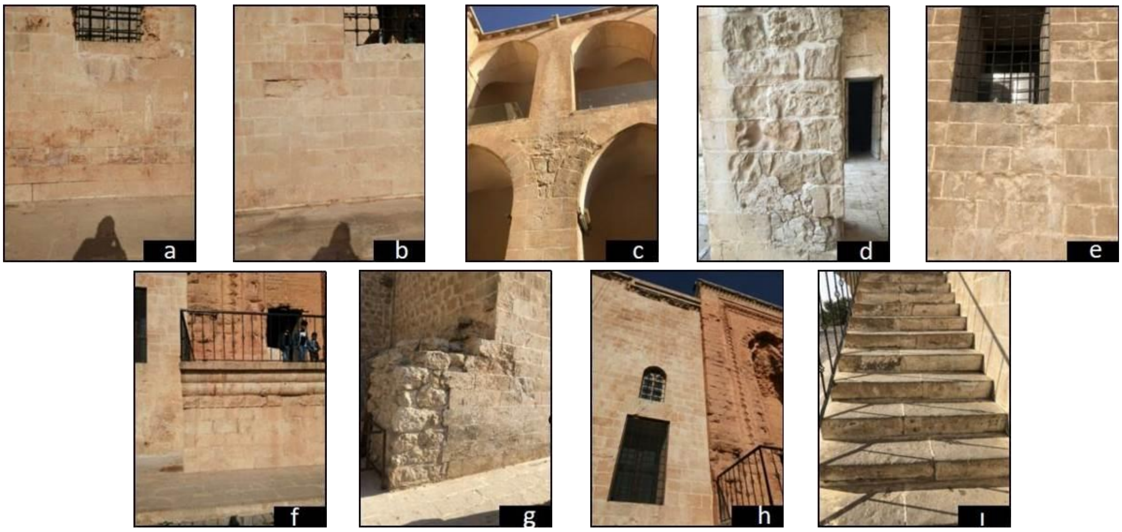


Figure 5. Physical deterioration of Kasımiye Madrasah (Biçen Çelik, 2019)

Salination and discoloration caused by climatic factors in Kasımiye Madrasah are shown in Figure 6. Salination is caused by the dissolution and evaporation of the salts in the limestone under the influence of humidity and temperature (Figure 6a, 6b and 6c) and discoloration is caused by the interaction of the minerals in the stones (Figure 6d, 6e and 6f) were observed.

Figure 6. Chemical deterioration in Kasımiye Madrasah (Biçen Çelik, 2019)

Biological deterioration occurring in Kasımiye Madrasah is shown in Figure 7. Plant formations are observed as a result of the interaction of the seeds that settle inside the capillary cracks with water (Dal &Yardımlı, 2019). Plant formations were observed on the south façade (Figure 7a) and east façade (Figure 7e) of the building, biochemical deterioration caused by bacteria settled on the stone surfaces (Figures 7b and 7c), deterioration caused by bird droppings (Figure 7d) and moss formations in the selsebilli iwan (Figure 7e).

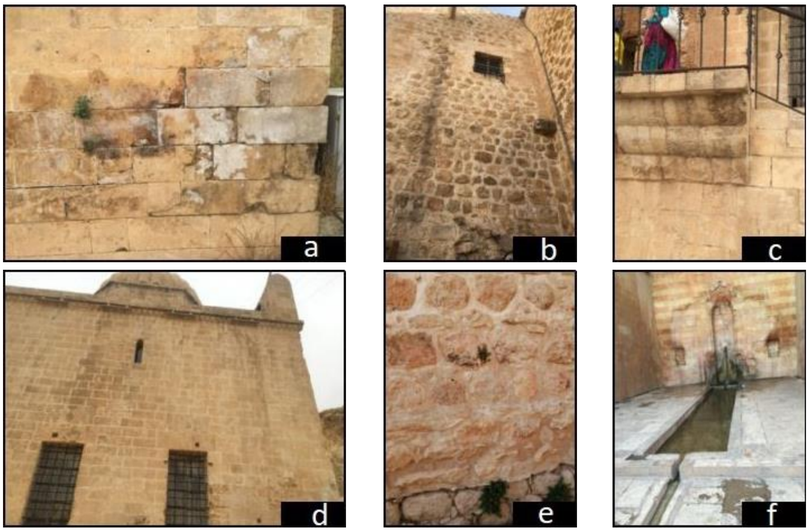


Figure 7. Biological deterioration in Kasımiye Madrasah (Biçen Çelik, 2019)

The deterioration of Kasımiye Madrasah as a result of anthropogenic impacts is shown in Figure 8. As a result of the damage caused to the building by unconscious users with sharp tools, deterioration was observed on different facades (Figure 8a, 8b and 8c).

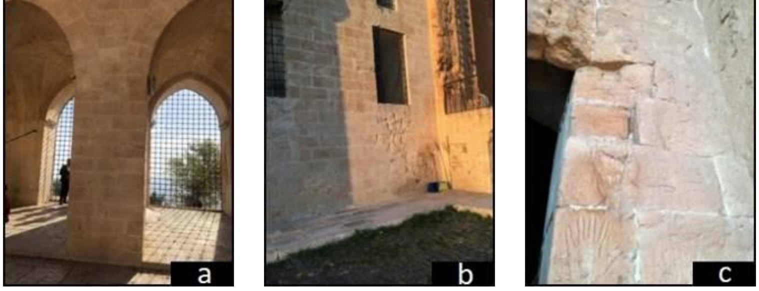


Figure 8. Anthropogenic deterioration of the Kasımiye Madrasah (Biçen Çelik, 2019)

3.2. Investigation of the Deterioration of the Kasımiye Madrasa by Using the Mapping Method

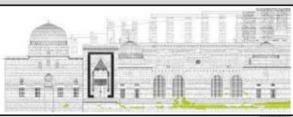
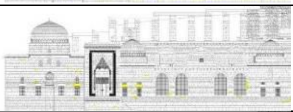
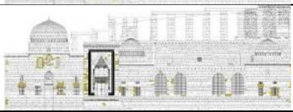
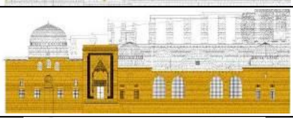
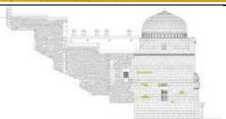
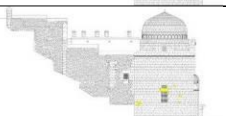
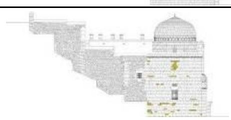
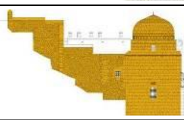
The deterioration of Kasımiye Madrasah is shown in the charts by mapping method. The façades of the building facing the south, east, west and inner courtyard, as well as the façades with the selsebil, were analysed. After observational analyses were made on the selected facades, the facades were photographed.

The types of physical deterioration that occurred in Kasımiye Madrasah are shown in Table 2. The types of deterioration such as joint discharge, fragment rupture, hairline cracks and surface loss were observed. When the facades are analysed separately, surface abrasion was the most common type of deterioration on all south, west and east facades, and on the facades facing south and west (83% and 20% respectively). The least common types of deterioration were capillary cracks on the south and west facades, joint discharge on the east facade, and capillary cracks on the courtyard facades facing south and west. When all facades were considered together, surface abrasion was the most common type of deterioration while capillary cracks were the least common.

The chemical deterioration of the building is shown in Table 3. Discoloration and salination were observed on all facades (100%). Bacteria formation was observed on the south façade at a rate of 5.6%, on the east façade at a rate of 18%, on the west façade at a rate of 7.9% and on the west-facing courtyard façade at a rate of 47% and was the least observed type of chemical deterioration in the building.

The types of biological deterioration observed in Kasımiye Madrasah are shown in Table 4. Plant formations are observed on the south and east facades of the building and mossing is observed on the facade facing the inner courtyard. Plant formations occupy 0.2% of the south façade and 0.1% of the east façade. Moss formation was observed at a rate of 1.8% on the south-facing courtyard façade.

Table 2. Physical deterioration of Kasımiye Madrasah

	Physical Deterioration Type	Facade Deterioration Ratio	Rate (%)
SOUTH FACADE	Joint Discharge		6.6
	Capillary Crack		1.9
	Fragment Breakage		8
	Surface Abrasion		100
WEST FACADE	Joint Discharge		0.9
	Capillary Crack		0.6
	Fragment Breakage		2.5
	Surface Abrasion		100

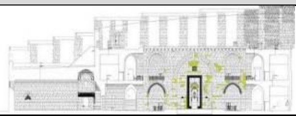
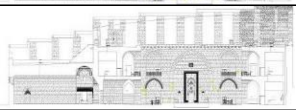
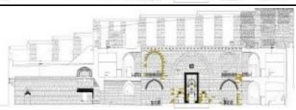
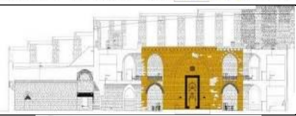
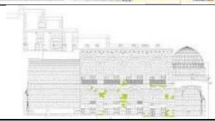
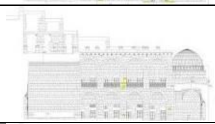
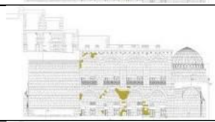
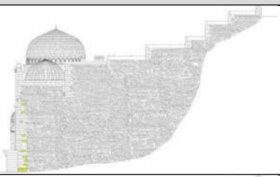
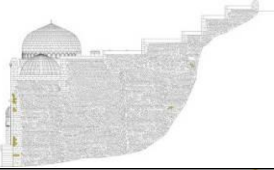
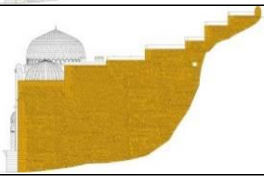
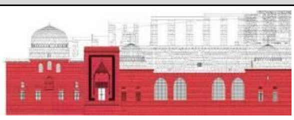
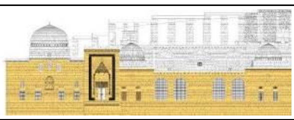
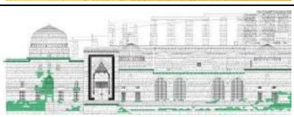
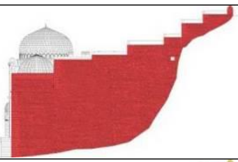
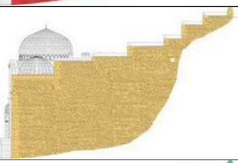
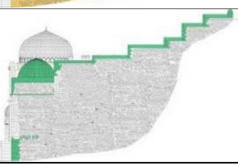
	Physical Deterioration Type	Facade Deterioration Ratio	Rate (%)
SOUTH FACING COURTYARD FACADE	Joint Discharge		11
	Capillary Crack		1.2
	Fragment Breakage		10
	Surface Abrasion		83
WEST FACING COURTYARD FACADE	Joint Discharge		8.1
	Capillary Crack		1.2
	Fragment Breakage		13
	Surface Abrasion		20

Table 2. Physical deterioration of Kasımiye Madrasah (contiuned)

	Physical Deterioration Type	Facade Deterioration Ratio	Rate (%)
EAST FACADE	Joint Discharge		0.5
	Fragment Breakage		0.7
	Surface Abrasion		100

The deterioration of Kasımiye Madrasah as a result of anthropogenic impacts is shown in Table 5. The use of sharp tools on the south, south-facing courtyard façade and west-facing courtyard façades and the use of paint on the south façade were observed. The use of sharp tools was 0.4 percent on the south facade, 0.9 percent on the south-facing courtyard facade and 1.6 percent on the west-facing courtyard facade. The rate of paint use observed on the south façade is 0.1%.

Table 3. Chemical deterioration of Kasımiye Madrasah

	Chemical Deterioration Type	Facade Deterioration Ratio	Rate (%)
SOUTH FACADE	Colour Variation		100
	Salitisation		100
	Bacteria Formation		5.6
EAST FACADE	Colour Variation		100
	Salitisation		100
	Bacteria Formation		18

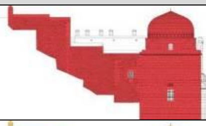
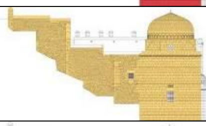
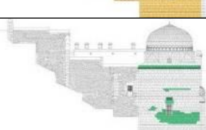
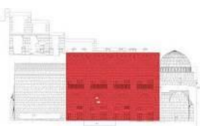
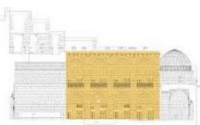
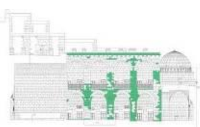
	Chemical Deterioration Type	Facade Deterioration Ratio	Rate (%)
WEST FACADE	Colour Variation		100
	Salitisation		100
	Bacteria Formation		7.9
WEST FACING COURTYARD FACADE	Colour Variation		100
	Salitisation		100
	Bacteria Formation		47

Table 4. Biological deterioration of Kasımiye Madrasah

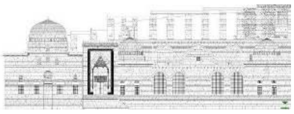
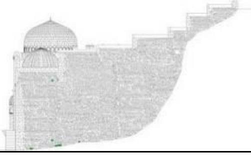
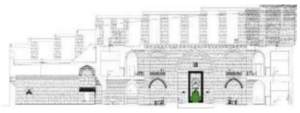
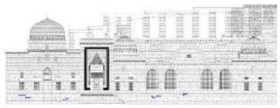
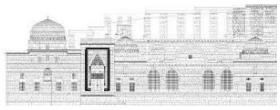
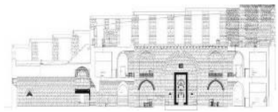
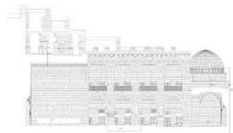
	Biological Deterioration Type	Facade Deterioration Ratio	Rate (%)
SOUTH FACADE	Plant Formation		0.2
EAST FACADE	Plant Formation		0.1
SOUTH FACING COURTYARD FACADE	Moss Formation		1.8

Table 5. Anthropogenic deterioration of the Kasımiye Madrasah

	Antropogenic Deterioration Type	Facade Deterioration Ratio	Rate (%)
SOUTH FACADE	Sharp Instrument Use		0.4
	Paint Usage		0.1
SOUTH FACING COURTYARD	Sharp Instrument Use		0.9
WEST FACING COURTYARD	Sharp Instrument Use		1.6

3.3. Investigation of the Deterioration of the Kasımiye Madrasah Using XRF Chemical Analysis Method

All types of deterioration occurring in the Kasımiye Madrasah were analysed with the codes determined by X-Ray Fluorescence Spectroscopy (XRF chemical analysis method). The codes determined (Table 6), the representations of the selected stones on the plan (Figure 9) and on the facade (Figure 10) are given below. The main purpose of analysing the materials of historical buildings is to obtain information about the production technology as well as the physical and chemical composition of the materials (Karataş, Alptekin & Yakar, 2022).

Table 6. Stones selected for the use of XRF chemical method for the deterioration of the Kasımiye Madrasah

Stone Code	Type of Deterıoratıon	
A0	Clean Stone	
A1a	Abrasion	Physical Deterioration
A1b	Capillary Crack	
A1c	Joint Discharge	
A1d	Fragment Breakage	
A2a1	Colour Variation	Chemical Deterioration
A2a2	Salitisation	
A2b	Bacteria Formation	
A2c	Microorganism Formation	Biological Deterioration
A3a	Sharp Instrument Use	Anthropogenic Deterioration

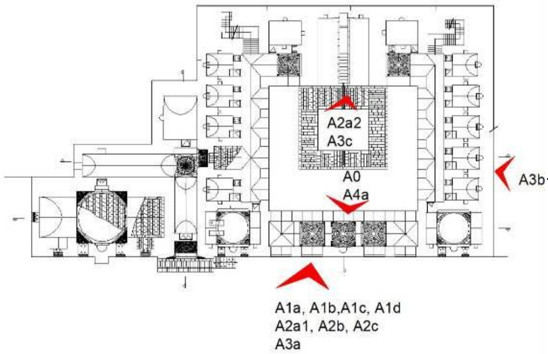
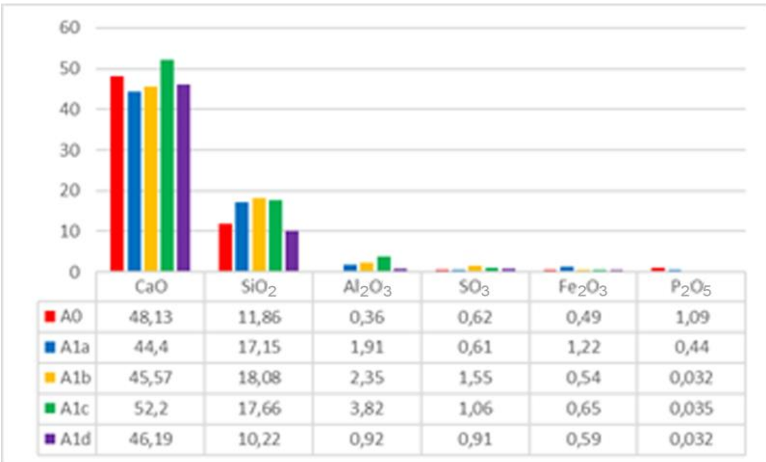


Figure 9. The plan representation of the stones selected for the use of XRF chemical method for the deterioration of the Kasımiye Madrasah

Figure 10. Demonstration of the stones selected for the use of XRF chemical method for the deterioration of Hatuniye Madrasah on the facade

The results of the analysis of the physical deterioration in Kasımiye Madrasah according to XRF analysis method are given in Table 7. According to the analysis results, changes in SO_3, SiO_2 and CaO ratios are remarkable. An increase in SO_3 occurred in A1b stone. The increase in SO_3 ratio is due to the air pollution of the stone. It can be said that the strength of the stone increases with the increase in SiO_2 ratio. While the SiO_2 ratio was 11.86% in A0 stone, this ratio was 18.08% in A1b stone. The clays decomposed on the stone surface cause the SiO_2 ratio to increase. Changes are observed in the stones due to daily and annual temperature differences and different minerals in the stones. Physical deterioration such as capillary cracks, surface abrasions and fragment fractures were observed in Kasımiye Madrasah (Karataş, Alptekin & Yakar, 2023).

Table 7. XRF chemical analysis results of physical deterioration observed on the facades of Kasımiye Madrasah

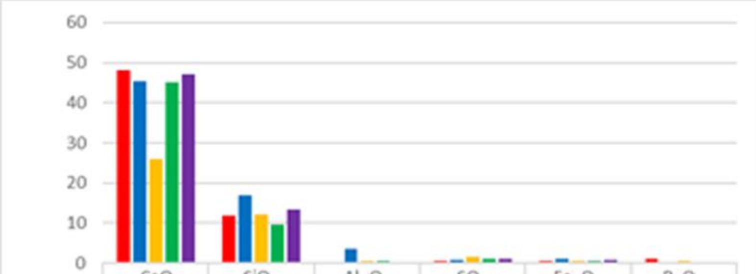


	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	P_2O_5
A0	48,13	11,86	0,36	0,62	0,49	1,09
A1a	44,4	17,15	1,91	0,61	1,22	0,44
A1b	45,57	18,08	2,35	1,55	0,54	0,032
A1c	52,2	17,66	3,82	1,06	0,65	0,035
A1d	46,19	10,22	0,92	0,91	0,59	0,032

The results of XRF chemical analyses of the chemical deterioration in Kasımiye Madrasah are shown in Table 8. According to the results obtained, it is seen that the CaO ratio decreased in stone A0 compared to other stones. Since the SO_3 ratios in A2a2 and A2b stones are high, it can be said that they are affected by air pollution. While the SiO_2 ratio was 11.86% in A0 stone, this ratio increased to 17.04% in A2a1 stone. This increase is due to the carbonated silica and marl (clayey limestone) content in the structure of the stone. When other compounds are examined, it is seen that there are no serious changes (Table 8).

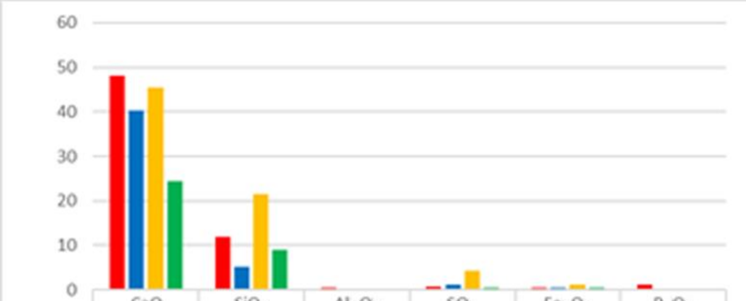
The results of the analysis of biodeterioration in Kasımiye Madrasah are given in Table 9. According to the analysis results, a decrease in CaO ratio was observed. It can be said that the reason for the decrease in CaO ratio in stone A3c is the interaction of acids secreted by bacteria. The change in the SiO_2 ratio in stone A3b draws attention. While this ratio was 11.86% in stone A0, it was measured as 21.44% in stone A3b. No significant changes were observed in other compounds (Table 9).

Table 8. XRF chemical analysis results of chemical deterioration observed on the facades of Kasımiye Madrasah



	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	P_2O_5
A0	48,13	11,86	0,36	0,62	0,49	1,09
A2a1	45,45	17,04	3,61	0,85	0,95	0,033
A2a2	26,03	12,07	0,5	1,48	0,55	0,43
A2b	45,08	9,49	0,66	1,14	0,54	0,081
A2c	47,05	13,46	0,1	1,03	0,83	0,19

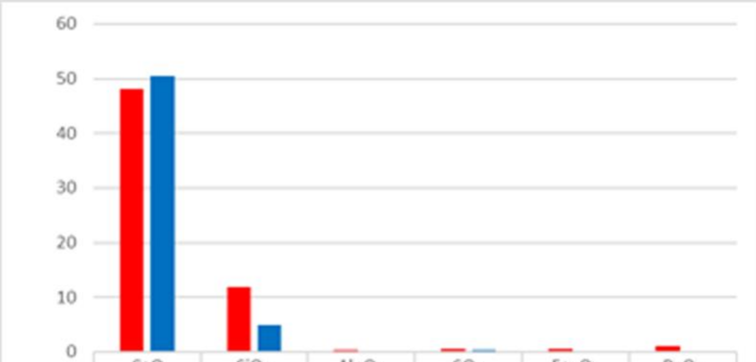
Table 9. XRF chemical analysis results of biological deterioration observed on the facades of Kasımiye Madrasah



	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	P_2O_5
A0	48,13	11,86	0,36	0,62	0,49	1,09
A3a	40,25	5,26	0,15	1,04	0,53	0,026
A3b	45,35	21,44	0,11	4,29	1,16	0,037
A3c	24,41	8,86	0,056	0,53	0,56	0,02

When the anthropogenic deterioration in Kasımiye Madrasah was analysed by XRF chemical analysis method, an increase in CaO ratio and a decrease in SiO_2 ratio were observed. While the SiO_2 ratio was 11.86% in stone A0, this ratio decreased to 4.99% in stone A4a. Clay deposits were observed from the degraded stone surfaces (Table 10).

Table 10. XRF chemical analysis results of anthropogenic deterioration observed on the facades of Kasımiye Madrasah



	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	P_2O_5
A0	48,13	11,86	0,36	0,62	0,49	1,09
A4a	50,4	4,99	0,1	0,41	0,25	0,033

4. Conclusion and Suggestions

Stone, which is used as a building material, takes place in every aspect of our lives in different forms and functions. When the historical buildings in Mardin are examined, it is seen that limestone is used as the main material of the building. Limestone is exposed to deterioration over time due to its structure. In this study, the stone deterioration of Kasımiye Madrasah was discussed and analysed. The deterioration was analysed by using visual analysis, mapping method and XRF analysis methods.

As a result of the investigations, it was observed that the rate of chemical deterioration in the structure was higher, while anthropogenic deterioration was the least. Capillary cracks, abrasion, joint discharge and fragment rupture were observed as physical deterioration. Discoloration and salination were observed as chemical deterioration; bacterial growth, plant growth and algae species were observed as biological deterioration. In anthropogenic deterioration, which is characterised as damage to the structure consciously or unconsciously by humans, sharp tools and paints were used in the structure.

Table 11. Deterioration on the facades of Kasımiye Madrasah

Kasımiye Madrasah	**Physical Deteriorations**				**Chemical Deteriorations**			**Biological Deteriorations**		**Anthropogenic Deteriorations**	
	Abrasion	Capillary Crack	Joint Emptying	Fragment Breakage	Colour Variation	Salitisation	Bacteria Formation	Plant Formation	Moss Formation	Sharp Instrument Use	Paint Usage
South Facade	+	+	+	+	+	+	+	+	-	+	+
East Facade	+	+	+	+	+	+	+	+	-	-	-
West Facade	+	+	+	+	+	+	+	-	-	-	-
South Facing Courtyard Facade	+	+	+	+	+	+	+	-	+	+	-
West Facing Courtyard Facade	+	+	+	+	+	+	+	-	-	+	+

When analysed on the basis of façade, capillary cracks, abrasion, joint discharges and fragment breakage, which are physical deterioration types, were observed on all façades. Apart from physical deterioration, chemical deterioration such as discoloration, salting and bacterial growth were also observed on all facades. Among the biological deterioration types, plant formation was observed on the south and east facades of the building, while moss formation was observed on the south-facing courtyard facade. The use of sharp tools and paint in anthropogenic deterioration types is observed on the south and west-facing courtyard facades of the building, while the use of sharp tools is observed on the south-facing courtyard facade (Table 11).

According to the results of XRF chemical analyses performed in Kasımiye Madrasah, chemical changes in selected stones were examined. According to the results obtained, the changes in CaO, SiO_2 and SO_3 values in the stones are remarkable. According to the results of the analyses, while the CaO ratio was 48.13% in the clean stone A0, this ratio decreased to 24.41% in the stone A3c. While the SiO_2 ratio was 11.86% in stone A0, this ratio increased to 21.44% in stone A3b. The increase is because the building stone is limestone with carbonated silica and marl content (Table 12).

Table 12. XRF chemical analysis results of the deterioration observed on the facades of Kasımiye Madrasah

Component	A0	A1a	A1b	A1c	A1d	A2a1	A2a2	A2b	A2c	A3a	A3b	A3c	A4a
CaO	48.13	44.4	45.57	52.2	46.19	45.45	26.03	45.08	47.05	40.25	45.35	24.41	50.4
SiO_2	11.86	17.15	18.08	17.66	10.22	17.04	12.07	9.49	13.46	5.26	21.44	8.86	4.99
Al_2O_3	0.36	1.91	2.35	3.82	0.92	3.61	0.5	0.66	0.1	0.15	0.11	0.056	0.1
SO_3	0.62	0.61	1.55	1.06	0.91	0.85	1.48	1.14	1.03	1.04	4.29	0.53	0.41
Fe_2O_3	0.49	1.22	0.54	0.65	0.59	0.95	0.55	0.54	0.83	0.53	1.16	0.56	0.25
P_2O_5	1.09	0.44	0.032	0.035	0.032	0.033	0.43	0.081	0.19	0.026	0.037	0.02	0.033

According to the data obtained as a result of the analyses, it was determined that physical and chemical deterioration were the most frequently observed types of deterioration in all facades of Kasımiye Madrasah. Capillary cracks, abrasion, joint discharge and fragment rupture among the physical deterioration types; discoloration, salting and bacterial formation among the chemical deterioration types were observed in all of the facades examined. When the XRF analysis results were analysed, it was observed that when the clay ratio increased, the deterioration also increased. There is an inverse relationship in silica ratios. As the amount of silica increases, deterioration decreases. When the overall structure is examined, the increase in clay and carbonate ratio caused an increase in the deterioration. As a result of the decomposition of the clay on the surface of the stone, an increase in the calcium and silica ratios in the structure of the stone was also observed.

As stated by Halaç and Akdağ (2018), in order for the building to survive for a longer period of time, deterioration should be accurately detected and measures should be taken against them. Detection of deterioration and taking measures for the protection of traditional buildings is an important phenomenon.

The results of the data and analyses obtained from this study should be used to provide effective solutions for building conservation projects planned to be carried out in the coming years. Taking early measures to reduce or stop the structural deterioration of the building is important for the building to survive for a longer period of time. It is important to accurately detect and evaluate the deterioration and develop improvement techniques in order to transfer the buildings to future generations.

Acknowledgements and Information Note

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Author Contribution and Conflict of Interest Disclosure Information

1st author 40%, 2nd author 20%, 3rd author 20% and 4th author 20% contributed. There is no conflict of interest.

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