

2.4 INVESTIGATION OF THE MINERALOGICAL-PETROGRAPHICAL AND GEOCHEMICAL PROPERTIES OF DARENDE (MALATYA) REGION LIMESTONE

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ABSTRACT

In this study, the geological, mineralogical-petrographic and geochemical properties of limestone marbles belonging to the Alacakaya company in Darende/Malatya Hacılar Sıragöz Village were examined. Marble production is obtained from Cretaceous aged Kırankaya limestone. Limestones generally have thick layers, cracks and occasionally dissolution gaps. This situation negatively affects marble production. Limestones, which are generally massive in appearance, have acquired a fractured and fissured structure. The cracks detected in the stages within the marble quarry are generally located N40°W/80°NE. Polarizing microscope examinations were carried out to determine the mineralogical and petrographic properties of limestones. As a result of polarizing microscope examinations, it was observed that micritic textured calcite minerals formed the matrix of the rock, and also coarser-grained secondary (Spary) calcites settled in the microfractures and cracks in the limestone. In addition, to a lesser extent, calcite and opaque minerals with a brecciated structure have been detected in limestones. Fossil species such as Algae, Coral and Discoclylina Sp. have been identified in the limestones. When the major (main) element, minor (trace) element and rare earth element (REE) analysis results were examined, CaO was observed as the main element in all samples. CaO values vary between 52.68% and 55.72%. It was observed that the contents of other main oxide elements remained below 1% in all samples. It was determined that the Sr element was more enriched than other trace elements, and the Zn element was more enriched than other trace elements in some limestone samples.

KEYWORDS: Limestone, Mineralogy Petrography, Darende, Malatya

INTRODUCTION

The use of natural stones begins with human history. Human beings initially used rocks for the production of hunting weapons for nutrition and defense, and later for housing and protection. Natural stones have become an important industrial product because they are durable, have various color options, can be shaped and polished. Natural stones or marbles have been used throughout history in entire buildings or in decorating these structures (Kulaksız et al. 2012). The regions with significant potential in our country are Marmara, Western Anatolia, Southern Anatolia and Central and Northern Anatolia Regions. There are many travertine, marble and building stone quarries within the borders of Malatya and Elazığ provinces. The names of the marble fields where production is made throughout the province of Malatya are as follows. In the region, Darende (Hacılar, Irmaklı, Başkaya, Üçpınar, Geniz and Göllüce Villages); There are marble

deposits in Hasançelebi travertine, Kuluncak marble, Arguvan travertine, Akçadağ (Hançerli, Ören, Ortaköy, Gürkaynak and Dedeyazı Villages) locations. Within the scope of this study, the marble field operated by Alacakaya marble in the region located approximately 10 km away from Darende district of Malatya province was determined as the study area (Figure 1). Limestones appear in color tones ranging from light cream to dark cream. There are 3 stages opened in the marble quarry. In the studies carried out, sampling was done to reflect all levels. Detailed analysis and examinations were made on the marble samples taken and the mineralogical and geochemical properties of the marbles were determined.

MATERIAL METHOD

The limestone (beige) marble quarry within the borders of Hacılar Village in Darende District of Malatya Province was chosen as the study area. Using the TS EN 12670 (2004) standard, limestone marbles were examined in terms of grain size, texture, mineralogical composition and rock group with a Leica DM 2500P model polarizing microscope. The ground test samples prepared for XRD analysis were photographed on the Shimadzu brand XRD-6000 model XRD device between 2° and 70°. Total abundance ratios for major and trace elements were analyzed with a 0.1 g sample using an ICP emission spectrometer and treated with lithium metaborate and dilute nitric acid. Total fire loss was measured after 1000 °C heat treatment. Trace element and rare earth element values were analyzed by ICP-MS on a 0.1 g sample by lithium metaborate/tetraborate fission and dilute nitric acid treatment. Detection limits for major element are 0.002-0.1 wt%, and detection limits for trace element and rare earth element analyzes are 0.1-8 ppm and 0.005-0.1 ppm, respectively. Chemical analyzes were carried out in the Canadian (ACME) laboratory.

RESULTS

Geological Setting

The study area is located on the 1/25000 scale Elbistan K 38-C3 sheet around the Darende district of Malatya province (Figure 2). General geology, petroleum geology, tectonics and paleontology studies have been carried out in and around the study area, and Akkuş (1970,1971), Kurtman and Akkuş (1974), Kurtman (1978), Örcen (1986) and Şafak (1990) are some of them. The study area includes Cretaceous, Tertiary and Quaternary aged units. The units that make up the Cretaceous are; ophiolitic rocks and the massive limestone blocks (Geniz Limestone) found with them are the Ulupınar Formation and Kırankaya Limestone, which consists of weakly cemented coarse elastics. Tertiary aged units unconformably overlie the Cretaceous. These are, from bottom to top, the Yenice Formation consisting of sandy limestones with marl and marl interlayers, the Asartepe Formation represented by layered limestone and marls, the Balaban Formation consisting of gypsum conglomerates, and the Darende Formation consisting of marls with gypsum and sandstone interlayers. Plio-Quaternary is represented by the Çaybaşı Formation, which consists of conglomerates of different origin. The youngest units in the field are Quaternary alluvial units. Limestones, which constitute the main subject of the study and are considered marble, are located within the Kırankaya limestones (Figure 3). Limestones generally consist of thin and medium-thick layered limestones. It is light yellow or off-white in color (Akkuş 1971).

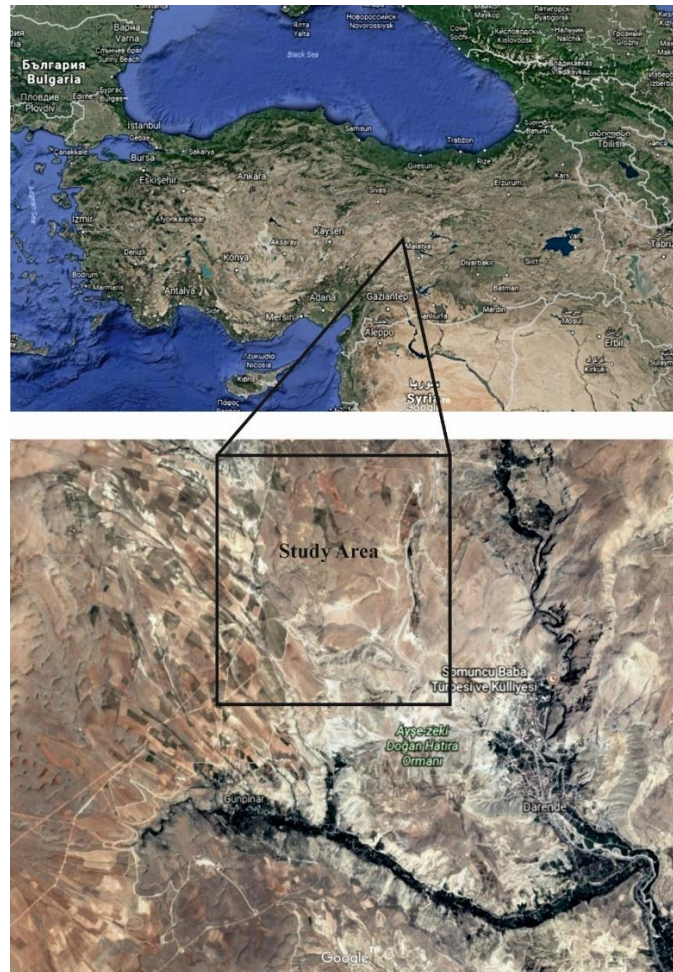


Figure1 Locator Map of the Study Area

MINERALOGICAL INVESTIGATIONS

Polarizing microscope analyzes

Most of the limestone samples consist of cream, beige and greyish-beige colored micritic limestones. In addition to beige colored micritic limestones, brecciated limestones are also encountered. Beige - white colored limestones: generally represented by micritic limestones containing oolites and algal shells (Figure 4). The limestones remaining in the quarry are generally beige, cream, grayish-beige in color. Oolite and occasionally pellet clasts, fossil shells such as algae and coral, and rock fragment sections were observed in thin sections made on limestone samples. Brecciated and nodular limestones and sparite-veined micritic limestones constitute the main rock types. Limestones are mostly micritic, occasionally sparitic and contain bioclasts. In sparitic veined micritic limestones, micritic limestone clasts and secondary sparitic calcites are seen to be connected to each other. During polarizing microscope examinations, grain size measurement results were measured as $1.9\ \mu\text{m}$ - $11.2\ \mu\text{m}$ in primary calcite grains and $300.4\ \mu\text{m} \pm 405.17\ \mu\text{m}$ in secondary calcite grains, respectively.

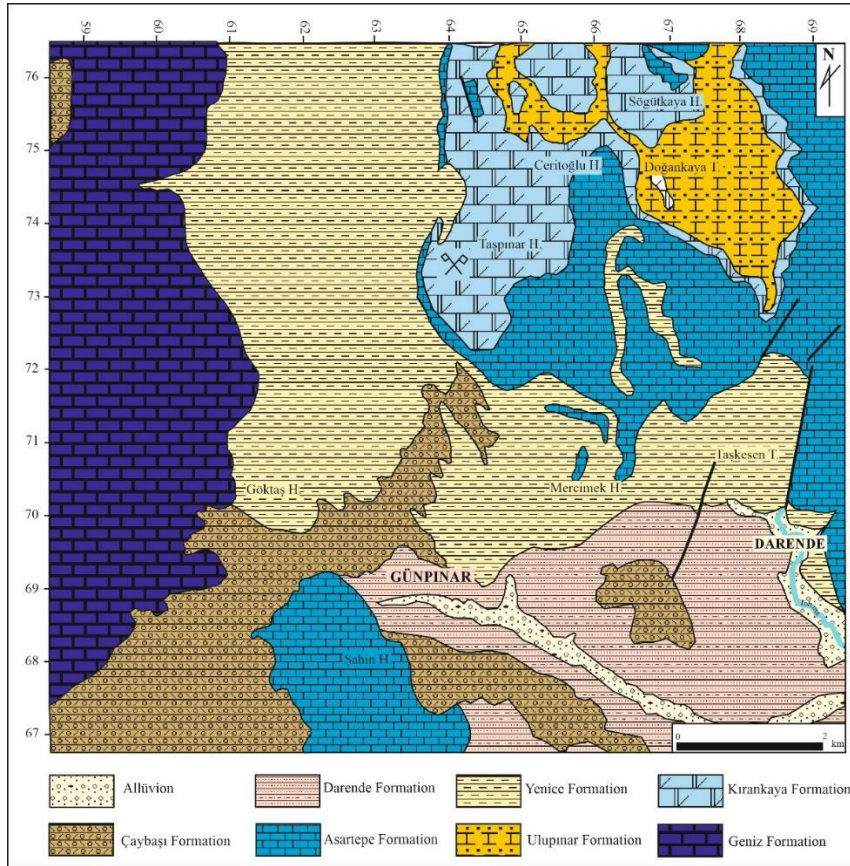


Figure2 Geological map of the study area.



Figure3 General view of the limestone quarry where block marble is produced.

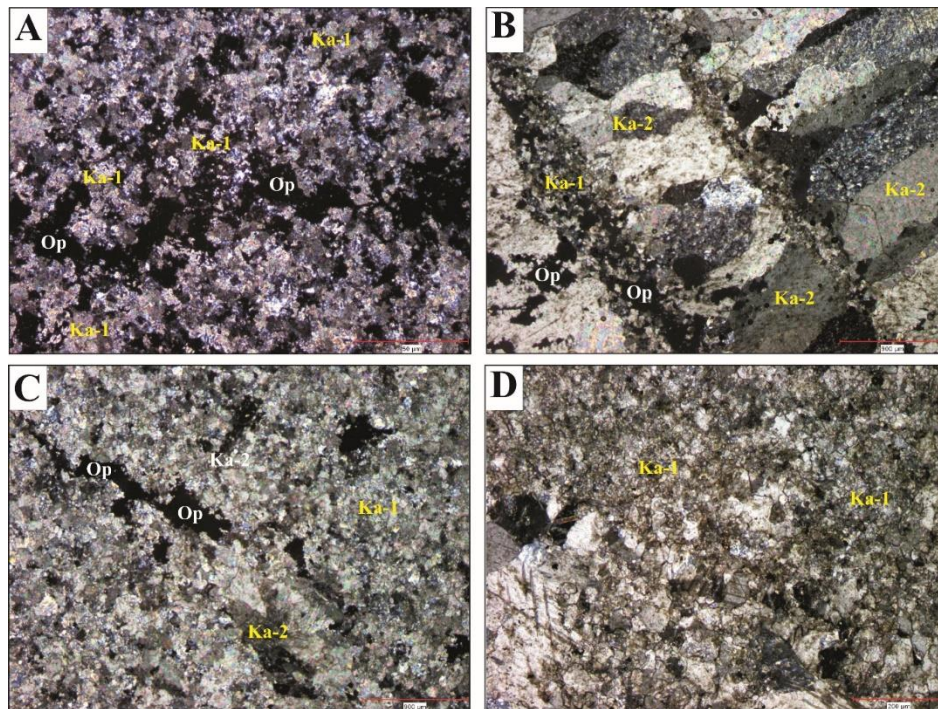


Figure 4 Polarizing microscope image of limestone marbles. Primary and secondary (Secondary calcite crystals are observed. The matrix generally consists of carbonate micrites. Additionally, opaque minerals have been observed in microcracks in some places. Ka1: Primary calcite, Ka-2: Secondary (Secondary calcite), Opaque mineral: Op.

XRD Analysis

XRD images were taken between 2° - 70° with the Shimadzu brand XRD-6000 model XRD device at AKU TUAM Center. When XRD images taken on limestone samples were examined, it was seen that calcite mineral was dominant in all samples (Figure 5).

Geochemistry

Major, trace and rare earth element (REE) analyzes were performed on a total of 26 limestone samples taken for geochemical studies. Graphs showing the major, trace and rare earth element (REE) analysis results of all samples taken are given in Figure 6. Major (Ca, Mg) and trace elements (Sr, Na, Mn and Fe) provide very important information about the diagenesis processes, chemical properties and mineralogical properties of carbonate rocks (Rao and Naqvi, 1977). In the diagenesis of limestones and dolomites, their fabric properties are related to the Mg /Ca ratio and salinity in the solution (Folk and Land 1975). Strontium and original carbonate mineralogy varies with facies and salinity (Veizer and Demovie, 1974). Sodium is considered as a possible salinity index of precipitation and salinity. Minor Mg and trace (Fe, Mn, Sr) elements are incorporated into carbonate minerals during precipitation and are reintroduced during diagenesis. Stratigraphic variations are related to Sr, Na and Mn deposition environments and diagenesis (Rao, CP, 1990). To understand the precipitation and chemical environment of chemicals, representative limestone samples were collected from the limestone quarry operated by Alacakaya Mermer in Darende district. Samples were taken on the stove mirror and step surfaces. Representative samples were taken to represent the marble quarry. Limestones generally vary in beige, cream and light brown colors. The main oxide elements on the samples were SiO_2 , Al_2O_3 , TiO_2 , Fe_2O_3 , MgO, CaO, Na_2O ,

K₂O, P₂O₅ and trace elements such as Loss of Fire (LOI), Sr, Mn, Ba, Rb, Cr, Ni, V, Cu, Co, Sc, U, Th, Cs, Zr, Hf, Nb, Ga, Pb and Y and Rare Earth Elements (REE) were analyzed.

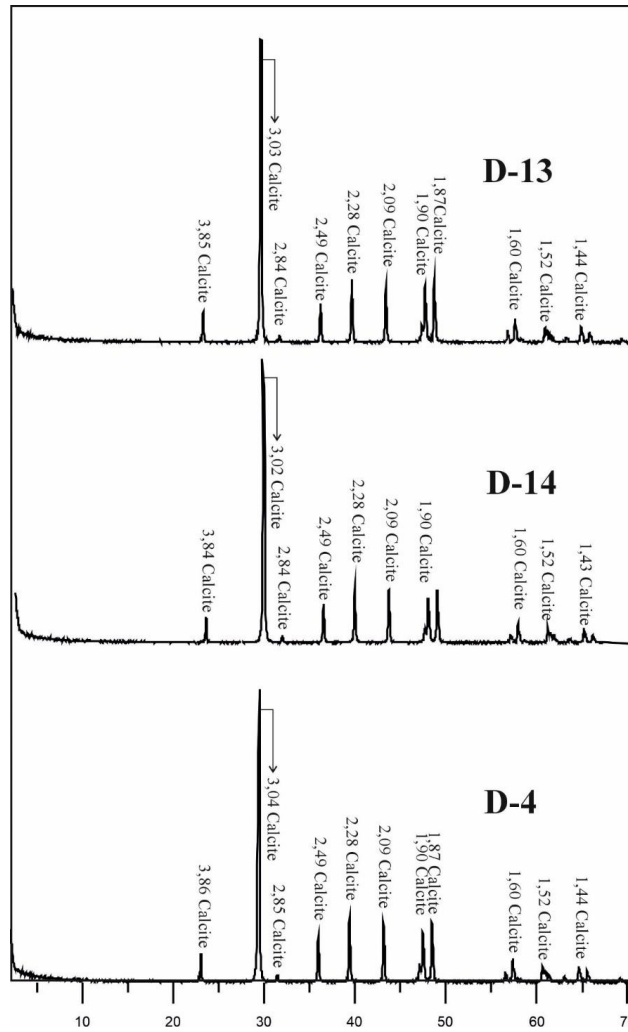


Figure 5 XRD graphs of some Limestone samples.

Limestone samples have high Ca contents but very low Mg contents. CaO wt% contents vary between 52.68% and 55.77%, and MgO wt% contents vary between 0.12% and 0.66%, with an average of 0.26%. The Ca/Mg ratio ranges of the samples vary between 83% and 464%. In all limestone samples, the contents of main oxide elements such as SiO₂, Fe₂O₃, Al₂O₃ and MgO remained below 1%. Since the ionic ratio of Sr and Ca elements are similar, Sr element has the highest values among trace elements.

DISCUSSION AND CONCLUSION

Limestone marbles, which constitute the main subject of this study, are cream and light brown colored limestones seen in Hacilar Village and its surroundings within the borders of Darende (Malatya) district. The unit, known as Kirankaya Limestone in the literature, spreads over very wide areas in the region. There is a marble quarry operated by Alacakaya Marble Company, which operates economically in this region. Within the scope of the study, this marble quarry was studied in detail and systematic limestone samples were taken. Cretaceous aged Kirankaya Limestones are thick-layered, massive in appearance and contain abundant cracks and joint systems. In this respect, the block yield of marbles seems low. In polarizing microscope and XRD images, the main

component in all samples is calcite mineral. There are two different calcite mineral formations in limestone: primary and secondary. Primary calcites generally form matrix (dough). The matrix consists of calcite minerals in micrite size. In addition, larger secondary calcite minerals were observed in the rock as micro veins or stylolite. In addition, the presence of algae, coral and *Discocyclina* Sp fossils were also detected in the rock. According to petrographic examinations of limestone samples, limestones are tightly packed biomicrite according to Folk (1959) and wackestone according to Dunham (1962). When the major (main) element, minor (trace) element and rare earth element (REE) analysis results were examined, CaO was observed as the main element in all samples. CaO values vary between 52.68% and 55.72%. It was observed that all other oxide elements remained below 1%. It was determined that Sr trace elements and Zn elements were more enriched in some samples than other trace elements. Since Zn enrichment in limestones is important, it would be useful to examine this situation in more detail in another study.

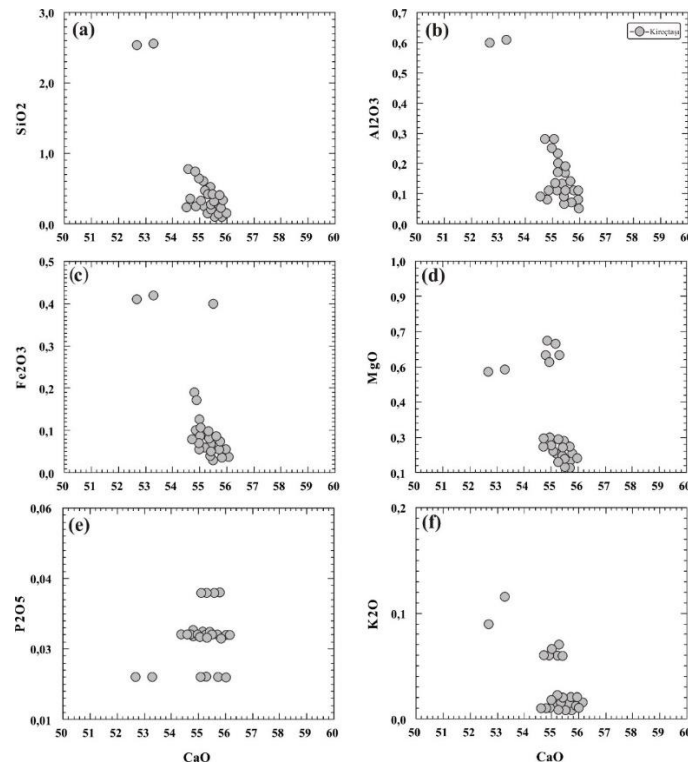


Figure6 Binary haker diagrams of Darende Limestone samples.

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REFERENCES

- Akkuş, M. F. (1970). Darende-Balaban havzasının (Malatya, Anadolu) jeolojik ve Stratigrafik incelenmesi . Maden Tetkik ve Arama Enstitüsü Dergisi, 1–80.
 Akkuş, M. F., 1971. Darende-Balaban havzasının (Malatya, ESE Anadolu) jeolojik ve stratigrafik incelenmesi, MTA Dergisi, No: 76, Ankara, 1-60.

- Dunham, R.J. 1962, Classification of Carbonate Rocks according to Depositional Texture. American Association of Petroleum Geologists, 1, 108-121.
- Folk, R.L. and Land, L.S. 1975. Mg/Ca ratio and salinity: two controls over crystallization of dolomite. *Bull. Geol. Soc. Am.*, 59: 60–68.
- Kulaksız, S., Özçelik, Y., Bayram, F., Engin, İ. C., 2012, Doğal Taş (Mermer) Maden İşletmeciliği Ve İşleme Teknolojileri, TMMOB Maden Mühendisleri Odası, Ankara.
- Kurtman, F, Akkuş, M.F. (1974): Malatya-Gürün havzasının jeolojisi ve petrol olanakları. Türkiye İkinci Petrol Kongresi Tebliğler, Ankara
- Kurtman, F. 1978. Gürün Bölgesinin jeoloji ve tektonik özellikleri. MTA Dergisi, No: 91, Ankara, 1-12
- Örçen, S., 1986. Medik-Ebreme (KB Malatya) dolayının biyostratigrafisi ve paleontolojisi, MTA Dergisi, No: 105-106, Ankara 39-74.
- Rao, C.P. and Naqvi, I.H. 1977. Petrography, geochemistry and factor analysis of a Lower Ordovician subsurface sequence, Tasmania, Australia. *J. Sedim. Petrol.*, 47: 1036–55.
- Rao, C.P., 1990, Petrography, trace elements and oxygen and carbon isotopes of Gordon Group carbonates (Ordovician), Florentine Valley, Tasmania, Australia: *Sedimentary Geology* (In press).
- Şafak, Ü., 1990. Malatya kuzeybatısının (Medik Ebreme yöresi) Üst Lütésiyan ostrakod faunası, Ç. Ü. Müh. Mim. Fak. Derg., C: 5, No: 135-156.

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