CHARACTERISTICS OF LIMES PRODUCED FROM MARBLES AND LIMESTONES

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ABSTRACT

CHARACTERISTICS OF LIMES PRODUCED FROM LIMESTONES AND MARBLES

In this study, characteristics of lime produced from some marbles and limestones were investigated in order to compare their effects on the lime mortars. For this purpose, limestones that contain low and high amounts of diatoms and marbles quarried from the city of Muğla and the Marmara island were selected as samples.

The calcination temperatures of the stones were found to be around 800 °C by TGA analysis. Considering their calcination temperatures, they were heated to 850 °C in a laboratory furnace, then slaked and carbonated. Before and after these processes, mineralogical and chemical compositions, and microstructures of the products were investigated by XRD and SEM-EDS analysis.

The hydraulic properties of carbonated limes were evaluated by determining weight loss at the temperatures between 200-600^{o}C due to the loss of the structurally bound water of hydraulic products and weight loss at the temperatures over 600^{o}C due to carbon dioxide released during the decomposition of calcium carbonates by TGA.

The effects of limes on the properties of mortars were investigated by producing lime mortars and comparing their compressive strengths during one year carbonation in laboratory condition. Mortars were prepared with one part (in weight) of lime and three parts (in weight) of marble aggregates.

The results of the study indicated that the lime produced from limestone containing high amounts of diatoms is highly hydraulic due to formation of calcium silicate whereas the others are non-hydraulic. The mortars prepared from lime containing high amounts of diatoms were found to be relatively high in compressive strength due to its hydraulicity.

The results show that the production of hydaulic lime composed mainly of calcium silicate at a relatively low calcinations temperature (850 °C) is possible. Considering this result, it can be concluded that hydraulic lime could be produced by the calcining of limestone containing diatoms in historic kilns.

ÖZET

MERMER VE KİREÇ TAŞLARINDAN ELDE EDİLEN KİREÇLERİN ÖZELLİKLERİ

Bu çalışmada, farklı mermer ve kireç taşlarından elde edilen kireçlerin özellikleri ve elde edilen kirecin kireç harçları üzerine etkisi incelenmiştir. Bu sebeple, Urla bölgesindeki bazı tarihi binalarda kullanılmış, yüksek ve düşük miktarda diatom içeren 2 tip kireç taşı ile Muğla ve Marmara Adası'ndan çıkarılan mermerler üzerinde çalışma yapılmıştır.

Mermer ve kireç taşların kalsinasyon sıcaklıkları TGA analizleri ile yaklaşık 800 °C olarak belirlenmiştir. Belirlenen kalsinasyon sıcaklıklarına göre taşlar öncelikle 850 °C de laboatuar fırınında yakılmış, daha sonra söndürülüp karbonatlaşmaya bırakılmıştır. Tüm bu süreçlerin öncesinde ve sonrasında örneklerin, mineralojik ve kimyasal kompozisyonları ile mikro yapıları XRD ve SEM-EDS analizleriyle belirlenmiştir.

Karbonatlaşmış kireç örneklerin hidrolik özelliklerini belirlemek amacıyla TGA analizlerindeki ağırlık azalışları gözlenmiştir. 200-600 °C arasındaki ağırlık azalışı su kaybına bağlıyken 600 °C üzerindeki ağırlık azalışı ise karbon dioksit gazının açığa çıkmasıyla açıklanmaktadır.

Kirecin kireç harçları üzerine ektisini görmek amacıyla, elde edilen farklı tip kireçlerden kireç harçları hazırlanmış ve hazırlanan kireç harçlarının mekanik özellikleri bir senelik karbonatlaşma süreci boyunca laboratuar ortamında yapılan testlerle belirlenmiştir. Harçların hazırlanmasında 1 ölçek kirece karşılık 3 ölçek mermer agregaları kullanılmıştır.

Bu çalışmanın sonuçları, yüksek oranda diatom içeren kireç taşından elde edilen kirecin kalsiyum silikat oluşumuna bağlı olarak yüksek hidrolik özelliklere sahip olduğunu göstermektedir. Diğer örneklerden hazırlanan kireçler ise hidrolik özellikler taşımamaktadır. Bununla beraber, yüksek oranda diatom içeren kireç ile hazırlanan harçlar daha yüksek basınç mukavemetlerine sahiptir.

Sonuçlar yüksek oranda kalsiyum silikat içeren hidrolik kireçlerin düşük sıcaklıklarda elde edilebileceğini göstermektedir. Bu sonuç diatom içeren kireç

taşlarının yakılması sonucu hidrolik kireç elde edilebilmenin mümkün olduğunu kanıtlamaktadır.

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CHAPTER 1

INTRODUCTION

Lime is the most frequently used traditional material in building industry for more than three thousands years. The earliest civilizations such as Incas, Mayas, Chinese, Egyptians, ancient Greeks and Romans used lime for mortar binder in brick or stone masonry and for rendering the masonry surfaces (Boynton 1966, Cowper 2000). Today, it is still the most conventional material used in modern building industry.

In this chapter, the process of lime production is described to discuss the effects of its characteristics as binders on the lime mortars which is the main aim of this study. For this purpose, calcination of limestone, slaking of quicklime, carbonation of lime and the factors influencing the processes of calcination of calcareous stone and slaking and carbonation of lime are shortly defined in this section.

1.1. Raw Materials of Lime

Lime is produced by calcining (heating) of calcareous stones which are primarily composed of calcium carbonate ($CaCO_3$) and then hydration of the calcination products (Boynton 1966, Eckel 1928, Holmes and Wingate 1997). The most abundant type of calcareous stone is limestone in variable forms of calcareous stones in nature. Some of the most common types of calcareous stones are marble, travertine, chalk, tufa, glass stone, Iceland spar, coquina, marl, oyster shell, stalactites and stalagmites, and varying forms of limestone (Boynton 1966, Davey 1961, Eckel 1928).

Marble is the most dense metamorphic stone type formed under the high temperatures and pressure (Boynton 1966, Holmes and Wingate 1997). It has several types in color, purity and composition (Boynton 1966, Holmes and Wingate 1997). Travertine is a dense and hard stone type formed by chemical deposition of calcium carbonate ($CaCO_3$) in natural hot-water springs (Boynton 1966, Holmes and Wingate 1997). Chalk occurs in shallow water such as lakes and seas and contains some parts of shells, animals and calcareous algae (Holmes and Wingate 1997). It is a soft, fine-grained stone which has different forms in color and purity (Boynton 1966).

Iceland spar that is very difficult to find such a pure type in nature is a pure calcareous stone which contains about %99.9 of calcite ($CaCO_3$) (Boynton 1966). Marl is a type of calcareous stone which contains high amounts of clay and sand particles (Boynton 1966). Stalactites and stalagmites are other types of calcareous stones which are formed by deposition of calcium carbonate in cold groundwater and found on the roofs and floors of caverns (Boynton 1966).

1.1.1. Limestones

Limestones are the most important raw material sources of lime, which are the sedimentary rocks, composed mainly of calcite ($CaCO_3$) and magnesite ($MgCO_3$) (Boynton 1966, Holmes and Wingate 1997). They exist in four different mineralogical forms, which are calcite, aragonite ($CaCO_3$), magnesite, and dolomite ($CaMg(CO_3)_2$) (Boynton 1966,Holmes and Wingate 1997). In nature, limestones are founded with the massive forms of these minerals. It is very difficult to find the limestone in such an ideal, pure form of calcite. Usually, they consist of varying amounts of impurities such as; SiO_2, Al_2O_3, Fe_2O_3, sulphur, phosphate, alkalis, etc. (Boynton 1966 , Davey 1961, Eckel 1928). Limestone having different crystal forms and compositions are the main factors which affect the quality and property of lime (Boynton 1966,Holmes and Wingate 1997).

Fundamentally, limestones can be classified into 3 groups. According to their mineralogical composition, they are high calcium limestone containing from %95 to % 100 $CaCO_3$, magnesian limestone containing from %5 to %35 $MgCO_3$, and dolomitic limestone containing from %35 to %46 $MgCO_3$ (Boynton 1966, Gay and Parker 1932, Holmes and Wingate 1997).

Another classification into two groups, can be made according to the origins of limestones (Wingate 1985). These are organic and chemical limestones. Organic limestones occur in nature, by accumulation of shells, corals, and remains of organisms layer in oceans, seas and lakes. Some examples of limestones that are of organic origin are marl, chalk, calcareous ooze, fossiliferous limestone (Wingate 1985). Chemical limestones are formed by precipitation reactions of calcium with carbonate ions.

The most common types of limestones used for production of lime are argillaceous limestone, bastard limestone, bituminous limestone, brecciate limestone, calcitic limestone, carbonaceous limestone, cement stone, chemical-grade limestone, compact limestone, coral limestone, cherty limestone, dolomitic limestone, ferruginous limestone, fossiliferous limestone, glauconic limestone, high calcium limestone, hydraulic limestone, Indiana limestone, lias limestone, lithographic limestone, magnesian limestone, metallurgical grade limestone, oolitic limestone, phosphatic limestone, pisolitic limestone, shell limestone and siliceous limestone. (Boynton 1966, Davey 1961, Eckel 1928, Holmes and Wingate 1997).

1.2. Calcination Process of Calcareous Stones

Lime is produced by calcining of limestone at temperatures over 800 °C in a %100 CO_2 atmosphere at 760 mmHg pressure (Boynton 1966). In the calcination process, limestone decomposes by expelling carbon dioxide gas (CO_2) and converts to calcium oxide (CaO). This product is called as “quicklime” (Boynton 1966, Boynton 1984, Holmes and Wingate 1997). In the process, there are three main requirements which are heating the stone to its dissociation temperature, providing for minimum temperature for a certain duration, and expelling the CO_2 gas from the stone (Boynton 1966**).**

When a pure limestone (calcite) is heated to its dissociation temperature, it loses 44% of molecular weight by expulsing of CO_2 (Boynton 1966). The composition and quantitative dissociation of reaction are as follows;

$$\underset{100}{CaCO_3} + \text{heat} \rightarrow \underset{56}{CaO} + \underset{44}{CO_2} \qquad \textbf{(Reaction 1.1)}$$

In dolomitic and magnesian limestone, there will be greater loss, compared to calcite. If a dolomitic limestone containing 60% $CaCO_3$ and 40% $MgCO_3$ is heated, it loses 47.36% of molecular weight by driving off CO_2 (Eckel 1928). This affects the quantity of quicklime (CaO). The more $MgCO_3$ content is in a limestone, the less is the CaO that formed in burning process (Eckel 1928**)**.

The dissociation temperature of limestone varies according to the type of the limestone (Boynton 1966, McClellan 1970). The most important factors that affect the dissociation temperature are chemical purity and physical characteristics of limestone

(Boynton 1966, McClellan 1970). The dissociation temperature for a pure limestone which is primarily composed of $CaCO_3$ is 898 °C for 760 mm pressure for a 100 % CO_2 atmosphere. (Boynton 1966). However, for dolomitic and magnesian limestone the temperature changes according to the ratio of $MgCO_3$ to $CaCO_3$ (Boynton 1966). While dissociation of the pure magnesium carbonate ($MgCO_3$) is accomplished at 402–480°C, the dolomitic limestone decomposes at higher temperatures, (dense, fine crystalline type at 500°C**;** fairly crystalline type at 650°C ; and highly crystalline type at 750°C) (Boynton 1966) .

The size of the limestone pieces influences the time required for the calcination process (Boynton 1966, Boynton 1984). The calcination of large stones is completed in longer time compared to smaller ones; because the reaction begins at outer surfaces of the stone and then develops into inner sides. The greater the size of the stone, the greater time is required for the calcination (Boynton 1966, Boynton 1984, Hassibi 1999).

1.2.1. Lime Kilns

Calcination is carried out in lime kilns. In ancient times, to supply the limestones easily used in calcination, the kilns were built near limestone quarries. (Davey 1961, Eckel 1928) . The main substances burnt as source of energy were charcoal and wood used for calcination of limestones (Davey 1961) . There were two basic types of lime kilns which were, flare kilns and continuous kilns.

In flare kilns limestones were burnt with the heat and flames without any contact with fuel. This is called intermittent burning (Davey 1961) . The burning process was carried out 1.5 or 2 days at temperature lower than 900 °C (Callebaut 2000).

In running kilns continuous burning was carried out. Limestones and fuel took place alternately in the kilns and calcined one then the other successively. The calcination process was completed entirely about in a week.

Quicklime produced in flare kilns were more pure and whiter when compared to quicklime produced in running kilns. Therefore, flare kilns increased the quality of the produced quicklime (Davey 1961) . Today, ring kiln and rotary kilns are used for calcination of both lime and portland cement. Since oil and gas are the main energy source, it is possible to reach high temperatures in modern types of kilns. Therefore, both C_2S and C_3S are present in some 19 th century lime mortars (Callebaut 2000).

1.2.2. Factors That Affect the Properties of Quicklime

The chemical composition, the surface area, the porosity, the pore size distribution, the size of crystals of limestone affect the properties of produced quicklime (Eades and Sandberg 1970, McClellan 1970).

Chemical composition: Properties of quicklime are mainly affected by chemical composition of the raw material (Eades and Sandberg 1970, McClellan 1970). If a pure limestone composed with high percentages of calcium carbonate is used as a raw material, quicklime that is rich in calcium will be produced. When argillaceous limestones having high percentages of siliceous and argilleceous material are calcined at high temperatures (over 950 C), hydraulic compounds such as calcium aluminates - silicates are formed. The formation of hydraulic compounds depends on the silica-lime and the alumina-lime reaction, which increase hydraulic properties of lime (Cowper 2000, Davey 1961, Eckel 1928).

Physical characteristics of the raw material: Physical characteristics of the limestone also affect the properties of quicklime (Eades and Sandberg 1970, McClellan 1970). The limestone that has high porosity produces more porous quicklime, while the one that has low porosity forms less porous quicklime. The high porous quicklime is more rapidly hydrated with water than that of less porous one (Moropoulou et al. 2001).

Calcination conditions: The calcination temperature, the retention time and the fuel used in the calcination are the other factors that influence the properties of quicklime. The optimum temperature for the calcination process is 900 °C (Boynton 1966, Cowper 2000, Davey 1961). When the limestone is calcined at the temperature of 900 °C, the produced quicklime will have a large surface area, and high porosity which increase the chemical reactivity (Boynton 1966, Cowper 2000, Davey 1961). If a limestone is calcined at a temperature lower than 900 °C, the produced quicklime will be under-burnt which is the result of the incomplete process (Boynton 1966, Boynton 1984). On the other hand, when the calcination temperature is higher than 900 °C, the quicklime will be hard-burnt (Boynton 1984, Gillott 1967, Holmes and Wingate 1997). Moreover, exposed to higher temperatures at 1400 °C or over it will produce less reactive quicklime which is called dead-burnt lime having a dark color, low porosity, high density and a small surface area (Boynton 1984, Gillott 1967, Boynton 1984, Gillott 1967, Swallow 1995).

The retention time of calcination influences the properties of the quicklime. If the limestone is calcined more than its optimum duration, the quicklime will be hard-burnt or dead-burnt. In contrast, a short retention time produces an under-burnt quicklime (Potgier et al. 2002).

1.3. Hydration (Slaking) of Calcined Limestones

The hydration of quicklime with water, known as slaking, is a highly exothermic reaction. During the hydration reaction, the calcium oxide combines with water and forms 'lime hydrate' or 'hydrated lime' ($Ca(OH)_2$) (Reaction 1.2) (Boynton 1966, Wingate 1985).

$$\underset{\text{Quicklime}}{CaO} + \underset{\text{Water}}{H_2O} \rightarrow \underset{\text{Lime}}{Ca(OH)_2} + \text{heat} \qquad \textbf{(Reaction 1.2)}$$

Upon the reaction, the surface area and the volume of produced lime are higher than the quicklime's (Boynton 1966 , Eckel 1928, Holmes and Wingate 1997, Oates 1991, Wingate 1985). The degree of expansion changes with the chemical compositions of quicklime (Boynton 1966, Eckel 1928, Holmes and Wingate 1997, Wingate 1985). The pure quicklime having low amounts of magnesium oxide and other impurities expanses in volume by over 3 times. However, the impure quicklime will show less expansion (Boynton 1966, Holmes and Wingate 1997, Wingate 1985). Moreover, if the pure quicklime is slaked within the total amount of water at once, which is required for a complete hydration, the expansion will be 3.5 times in volume. Nevertheless, if it is slaked step by step, the volume of the lime will increase about 1.7 times (Eckel 1928).

1.3.1. Factors Influencing the Characteristics of Lime

The hydration process and the quality of lime change with the properties of quicklime such as impurity, porosity, pore size distribution, crystals size, MgO content and some external factors such as slaking temperature, amount of water, water quality, water/lime ratio, slaking temperature, agitation rate, and aging of lime putty.

Effects of the MgO content: The MgO content is one of the factors that have an important effect on the hydration reaction of quicklime and the properties of lime. The rapid and the intense slaking process decreases with the increasing amount of the magnesium oxide content in quicklime (Boynton 1966, Eckel 1928). The dolomitic quicklime needs more pressure for a complete slaking than high calcium quicklime that slakes at the atmospheric pressure (Boynton 1966, Eckel 1928). Similarly, the evolution of heat will be less in slaking of quicklime that contains high amounts of magnesium oxide. The greater the MgO component is in quicklime, the less heat is evolved during the slaking process (Boynton 1966, Eckel 1928). When one kilogram of pure quicklime is slaked, 123.5 cal of heat is produced. On the other hand, the dolomitic type produces 95.8 cal of heat during the hydration of one kilogram of quicklime.

Effects of Porosity: The porosity of quicklime is one of the most important factors influencing the process of hydration (Boynton 1966, Schlitt and Healy 1970). The high porous quicklime slakes rapidly compared to the low porous one (Boynton 1966, Schlitt and Healy 1970).

Effects of impurities: The impure quicklime which contains impurities in high amounts, slakes very slowly (Schlitt and Healy 1970). The impurities clog the pores of the quicklime and prevent the quicklime-water reaction (Schlitt and Healy 1970).

Effects of Water: The lime water ratio is the other important factor influencing the properties of the lime. The formation of different hydrated forms such as dry hydrate, putty, slurry, milk of lime depends on the amount of water used in the slaking process (Boynton 1966, Boynton 1984).

Effects of Water quality: The impure water including sulfates and sulfites retards the hydration process of quicklime by forming the gypsum and the calcium sulfite hemihydrate on the surface. These compounds block the reaction of quicklime with water (Boynton 1966, Dornap 1977, Hassibi 1999, Holmes and Wingate 1997). The other impurities such as chlorides and sugars have both advantages and disadvantages. In one hand they have an accelerating effects on the hydration reaction (Boynton 1966, Dornap 1977, Hassibi 1999, Holmes and Wingate 1997). On the other hand, chlorides are the source of soluble salts, which are the cause of the deterioration. To achieve an accomplished and successful hydration process, the water that is used in the reaction should be excessively pure (Boynton 1966, Dornap 1977, Hassibi 1999, Holmes and Wingate 1997).

Effects of temperature: The slaking temperature has an important factor that effects the hydration reaction of the quicklime (Boynton 1966, Hedin 1963). If the slaking temperature is high, the slaking process will take place rapidly (Boynton 1966, Hedin 1963). However, extremely higher slaking temperatures damage the plastic properties of the lime (Cowper 2000). Therefore, in order to achieve an effective hydration process, the reaction should be performed at a temperature between 71 $^{\circ}$C and 93 $^{\circ}$C (Boynton 1966).

Effects of stirring: The stirring has an accelerating effect on the slaking process of the quicklime by providing a rapid diffusion of water into quicklime (Boynton 1966, Dornap 1977). A slow agitation has an unfavorable effect on the slaking of quicklime, which causes incomplete hydration reaction (Boynton 1966).

Effects of aging: Aging has a favorable effect on the quality of the lime (Carrington and Swallow 1996, Lynch 1998). Both the plasticity and the water retention capacity of the lime are increased upon aging (Cowper 2000). During the aging process, the crystals size of the lime reduces and the surface area increases. A high surface area develops a faster carbonation process (Rodriguez et al. 1998).

1.4. Carbonation Process of Lime

Carbonation is a hardening process of the hydrated lime with the carbon dioxide gas. During the carbonation process, CO_2 diffuses through the lime and dissolves in the water present on the surface of lime and forms the carbonic acid. The carbonic acid reacts with the lime and then the calcium carbonate is formed (Reactions 1.3-1.4) (Holmes and Wingate 1997, Moorehead 1986, Van Balen and Van Gemert 1994).

$CO_2 + H_2O \rightarrow H_2CO_3$ **(Reaction 1.3)**

$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O + 74kj$ **(Reaction 1.4)**

1.4.1. Factors Influencing the Carbonation Reaction

The rate of the carbonation depends on CO_2 concentration, air pressure, and moisture content of the lime, temperature, relative humidity and thickness of specimen. Their effects are shortly described in this section.

CO_2 gas concentration: High concentration of CO_2 gas speeds the carbonation reaction of lime, which is directly proportional to concentration of CO_2 (Moorehead 1986). However, in a 100% CO_2 atmosphere, rapid carbonation takes place on the surface of the lime and the further carbonation is prevented (Moorehead 1986).

Moisture content: The moisture content of the lime is an important factor that influences the absorption of CO_2 gas from the atmosphere (Cazalla et.al. 2000, Van Balen and Van Gemert 1994). The carbonation reaction develops more rapidly in optimum saturated conditions. On the other hand, in dry or fully saturated conditions, the reaction becomes slower. (Moorehead 1986).

Temperature: High temperatures increase the rate of the chemical reaction. But, it decreases the solubility of the carbon dioxide and the hydrated lime in the water. Therefore, the optimum value for the carbonation temperature is about $20^{\circ}C$ (Van Balen and Van Gemert 1994).

Relative Humidity: The carbonation of the slaked lime is accelerated with increasing relative humidity between the range of 25% and 95%. (Cazalla et al. 2000, Swenson and Sereda 1968).

Permeability: Low permeability has a retarding effect on the rate of carbonation reaction which reduces the speed of absorption of CO_2 gas from the atmosphere. The slow rate of carbonation takes place in the low permeable lime (Moorehead 1986).

Thickness of the lime: The carbonation reaction begins on the surface of the lime and progresses to the inside. Hence, the increase in the thickness of the lime decreases the rate of penetration of carbon dioxide gas into lime, where the reaction develops (Moorehead 1986).

Lime concentration: The rate of the carbonation reaction is directly proportional to the amount of the lime that will be carbonated. If the calcium hydroxide concentration is increased, the time needed for the carbonation reaction will increase and the rate will be slower (Moorehead 1986).

Use of the aged-lime putty: The aging of the lime putties directly affect the carbonation process (Cazalla et al. 2000). Aged putties have smaller portlandite crystals while non-aged putties have larger ones. Smaller portlandite crystals transform into calcite crystals more rapidly compared to larger ones due to having a higher surface area (Cazalla et al. 2000, Henisch 1988). Therefore, aged putties exhibit rapid and extensive carbonation reaction.

1.6. Types of Lime

Limes can be classified into two fundamental types according to their hydraulic character (Cowper 2000, Eckel 1928, Vicat 2003). These are; non-hydraulic limes, those that are composed mainly of calcium oxide and magnesium oxide in different ratios, and hydraulic limes, those that contain active compounds of calcium silicates and aluminates in addition to CaO and MgO (Cowper 2000).

1.6.1. Non-hydraulic Limes

Non-hydraulic limes can be classified into three groups according to the amount of calcium oxide content. They are fat limes, lean limes, and magnesian limes (Cowper 2000, Eckel 1928, Vicat 2003).

Fat limes contain over 95 % of calcium oxide (CaO) and 5 % of impurities such as magnesia (MgO), silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3), etc. They slake rapidly, show great expansion in volume about 3 times, and evolve heat in a great extent during the slaking process (Cowper 2000, Eckel 1928, Vicat 2003). Magnesian limes contain over 30% of MgO (Cowper 2000, Eckel 1928, Vicat 2003). When compared to fat limes, this type of limes slake slowly and expand less in volume. Therefore, the resulting product of magnesian limes will be less, if equal amount of lime is slaked of these groups. Although magnesian limes are less plastic, they are much more durable than fat limes. Lean limes contain over 5% of impurities such as silica, alumina, iron oxide etc. (Cowper 2000, Eckel 1928, Vicat 2003).

1.6.2. Hydraulic Limes

Hydraulic limes can be classified in two groups, which are natural hydraulic limes and hydraulic limes. Natural hydraulic limes are produced from limestones which contain a high percentage of siliceous and argilleceous material. These types of limestones are composed of CaO, MgO and some other impurities such as alumina, iron and silica. If argillaceous limestones, which are impure and contain a high percentage of siliceous or argillaceous material, are used as a raw material for lime production, these impurities react with the quicklime during the calcination process at a high temperature and calcium aluminates-silicates are produced (tricalcium silicate: $3CaO.SiO_2$, dicalcium aluminate: $2CaO.Al_2O_3$) (Boynton 1966,Cowper 2000, Lea 1940). These compounds are set and harden in the water and increase the strength of the lime mortar. (Boynton 1966,Cowper 2000, Lea 1940). Therefore, such limes have been used as binders for mortars in water constructions such as bridges, drainage systems, cisterns, foundations etc. (Cowan 1977, Davey 1961).

Hydraulic lime is also produced by adding of silicates (clay minerals) into the pure powdered limestone. If these mixtures are heated at a temperature between 950-1250 ° C, hydraulic limes are produced (Boynton 1966, Cowper 2000, Lea 1940). They slake very slowly when compared to non-hydraulic limes and expanse less in volume during the slaking process (Cowper 2000, Lea 1940). While non-hydraulic limes harden with CO_2 only, hydraulic limes harden by CO_2 gas and by water (Cowper 2000, Lea 1940).

Hydraulic limes can be classified into three groups. They are eminently hydraulic limes, moderately hydraulic limes and feebly hydraulic limes (Cowper 2000). Eminently hydraulic limes set in water rapidly about in 2-4 days. Moderately hydraulic limes set in water in 15-20 days while feebly hydraulic limes set over 20 days (Cowper 2000).

Hydraulic limes can also be classified by hydraulic and cementation indices. They are the ratio of the total percentage of silica and alumina to the percentage of lime. The high index values show the more hydraulic capacity of lime. Followings are the formula of the indices (Vicat 2003).

$$\text{Hydraulic index} = (\%Al_2O_3+\%Fe_2O_3+\%SiO_2) / (\%CaO+\%MgO)$$

$$\text{Cementation index} = (2.8\%SiO_2+1.1\%Al_2O_3+0.7\%Fe_2O_3) / (\%CaO+1.4\%MgO)$$

Feebly hydraulic limes have 0.1 to 0.2 of hydraulic index. Eminently and moderately hydraulic limes have values of 0.2 to 0.4. (Cowper 2000).

1.7. Aim of the Study

Mortars used as bonding agent for bedding and jointing masonry units and rendering masonry surfaces are composed of binders and filling materials (Cowan 1977, Davey 1961). Historically, several kinds of mortars were used in the construction of buildings. Mud is the oldest known mortar, used in construction of the first collective settlements in Mesopotamia 10.000 years ago (Davey 1961). Gypsum is a binding material long used in the mortars of brick vaults and arches due to its quick setting and high mechanical strength (Davey 1961, Middendorf 1998). Lime mortars have been the most widely used in the construction of the buildings since their first known use in Eygpt in 4000 B.C. (Cowan 1977, Vicat 1997).

Lime mortars can be classified as non-hydraulic and hydraulic. Non-hydraulic mortars are produced by mixing fat lime with inert aggregates and hardened only by the carbonation of lime due to the carbon dioxide in the air.

Hydraulic mortars are produced either by mixing fat lime with the aggregates containing amorphous active silicates and aluminates such as pozzolans, or by mixing hydraulic lime with the inert aggregates. Hydraulic mortars are hardened by both the carbonation of lime and the reaction between the lime and pozzolans in the presence of water. This reaction produces calcium silicate hydrates and calcium aluminate hydrates, which set under water and impart high strength to the lime mortars (Lea 1970). For this reason, such mortars were extensively used in the construction of foundations placed in waterlogged grounds and for drainage systems, cisterns, bridges, etc. (Cowan 1977, Davey 1961). Romans successfully improved the use of hydraulic lime mortars produced by combining lime and pozzolanas in masonry structures (Cowan 1977, Davey 1961).

The determination of historic lime mortar characteristics became an important subject in the second half of the 20th century due to the extensive damage to historic building materials that was caused by cement-based mortars used in their restoration. The studies on historic lime mortars and plasters are compiled by Hansen et al. (Hansen et al. 2003) in a bibliography which provides an extensive source for conservators and conservation scientists.

Among the studies of historic lime mortars, the achievement of hydraulic properties of historic mortars is usually described as the process of mixing pozzolanic aggregates with the high calcium lime (Franzini et al. 1999, Moropoulou et al. 2001). However, the possibility of the use of the natural hydraulic lime in historic mortars has not been thoroughly considered.

The first production of hydraulic lime was found around the second half of the 18th century (Vicat 1997). This type of lime is obtained by the calcination of limestone with high amounts of clay substances, forming calcium and aluminium silicates at temperatures between 950° C and 1250° C. Even though such temperatures could not be reached before the 18th century, the possibility of achieving hydraulic properties of lime by heating limestone containing silica at relatively low temperatures has not been taken into consideration.

In a previous study (Çizer 2004), the hydraulic characteristics of lime mortars used in the walls and brick domes of some Ottoman baths are examined to determine whether hydraulicity of the mortars originates by mixing pozzolanic aggregates with fat lime or by the use of natural hydraulic lime. The results indicate that the lime used in the stone masonry of Ottoman baths was non-hydraulic but brick dome mortars was hydraulic.

In this study, taking into cosideration the kiln conditions of the 15th century, the possibility of obtaining non-hydraulic and hydraulic lime at a relatively low temperatures are examined. For this purpose some types of marbles and limestones are heated at a relatively low temperature (850 °C), then slaked and carbonated.

Lime mortars are prepared with mixing of limes produced by marbles and limestones and agregates produced from Marmara marble in order to compare their compressive strengths during one year carbonation in laboratory condition.

Then, characteristics of marbles and limestones after calcining, slaking and carbonation are indicated by XRD, SEM, EDS and TGA analyses.

CHAPTER 2

EXPERIMENTAL METHODS

In this study, different types of marble and limestone were used in the production of lime for the purpose of investigating the lime quality on the mortar properties. Marbles quarried from the Marmara Island and the city of Muğla, white and grey colored limestones quarried in Urla region were selected as samples for the study. The microstructure and mineralogical compositions of the marbles and limestones were determined before and after their heating, slaking, and carbonation processes. Mortars were prepared with one part (in weight) of lime and three parts (in weight) of marble aggregates. The characteristics of mortars were compared by determining their compressive strength after one year carbonation. In this section, experimental methods used in this work are described.

2.1. Marble and Limestone Samples

Marbles quarried from the city of Muğla and the Marmara Island were selected as marble samples in the production of lime. Limestones that contain low and high amounts of diatoms used in the walls of historic buildings in Urla region were selected as limestone samples (Teomete 2004). The definitions of the stone samples are given in the following table (Table 2.1).

Table 2.1.Definitions of stone samples.

Stone	Definition
M-M.	Marmara marble
Mu-M.	Muğla marble
W-L	White limestone
G-L	Gray limestone

2.2.Determination of Bulk Densities and Porosities of Stones

Bulk densities and porosities of marbles and limestones were determined by using RILEM standard test methods (RILEM 1980). The samples were first dried in an oven at temperatures about 103 ºC at least for 24 hours, then they were weighed by a precision balance (AND HF-3000G) to determine their dry weights (M_{dry}). Following these tests, the samples were saturated with water in a vacuum oven (Lab-Line 3608-6CE Vacuum Oven) and then weighed. Bulk densities and porosities of the stones were determined by dry weight, total saturation with water under vacuum and the hydrostatic weight method.

$$D\ (g/cm^3) = M_{dry} / (M_{sat} - M_{arch})$$
$$P\ (\%) = [(M_{sat} - M_{dry}) / (M_{sat} - M_{arch})] \times 100$$

where;

D = Density (g/cm^3)
P = Porosity (%)
M_{dry} = Dry weight (g)
M_{sat} = Saturated weight (g)
M_{arch} = Archimedes weight (g)
$M_{sat}-M_{dry}$ = Pore volume (g)
$M_{sat}- M_{arch}$ = Bulk volume (g)

2.3.Preparation of Stone Samples for Calcination

Small pieces of stones were used in the calcination process. The coarse pieces of marble and limestones were grinded by using a ball mill machine. Following the grinding process, the pieces of stones were sieved, to be ordered according to their particle sizes. The fraction between 250 - 125 mesh were used in the calcination process of the stones.

2.4. Determination of Calcination Temperatures of Stones

Calcination temperatures of marbles and limestones were determined by thermogravimetric analysis (TG/DTG) using Shimadzu TGA-21. The thermogravimetric analysis was carried out in a static nitrogen atmosphere at a temperature range of 50-1000°C with a controlled heating rate of 10°C/min. During the heating process, TGA instrument recorded the loss of hygroscopic (adsorbed) water (< 120°C) and the loss of structural carbon dioxide gas resulted from the decomposition of the calcium carbonate (>600°C).

2.5. Calcination Process of the Samples

The calcination temperature and the carbon dioxide content of limestone and marble were first determined by TGA analysis. After determining the calcination temperatures of stones by the TGA analysis, the calcination of the marbles and limestone samples were carried out in a laboratory furnace considering the calcination temperatures of the stones. About five grams of ground sample was heated in the crucible at 850 ºC which was above the calcination temperatures of stones for 12 hours until all calcium carbonate is converted into calcium oxide. Calcined samples were then kept in a desiccator before the slaking. Weight losses due to the release of the carbon dioxide gas at this temperature were precisely determined to find out the percentage of the calcium carbonate content in the compositions of the stones.

The reason for choosing the temperature of 850 ºC for the calcination process was to investigate the possibility of production of hydraulic lime from limestones at a relatively low calcination temperature.

2.6. Slaking and Carbonation of Calcined Stone Samples

The calcinated limestone (quicklime) was hydrated with distilled water in the glass beaker until lime putty was produced. The lime putty was then spread out on glass slides and carbonated for a month in the laboratory. During the carbonation process, lime was wetted with distilled water. After a month, the samples were dried in an oven at a temperature of 40 ° C for 24 hours.

2.7. Determination of Mineralogical Compositions of Unheated and Calcined Stones (quicklime), Slaked and Carbonated Lime

Minerological compositions of the unheated and heated limestones and marbles (quicklime), slaked and carbonated limes were determined by XRD and FT-IR analyses which were carried out on dry powdered samples. XRD analyses were performed on finely ground samples of less than 53 µm. X-ray diffraction patterns were taken with Cu K∝radiation by using a Philips X-Pert Pro X-ray model Diffractometer.

For the IR analysis, 0.3-0.5 milligram of dry powdered samples were mixed with 80 milligram of spectral grade KBr and pressed into pellets by about 10 tons/cm^2 pressure. Spectral measurements were executed by a Spectrum BX II FTIR spectrometer (Perkin Elmer). It was operated in the absorbance mode. The IR spectra was taken between 400-4000 cm^{-1} with a 4 cm^{-1} resolution.

2.8. Determination of Microstructural and Chemical Compositions of Unheated and Heated Stones (quicklime), Slaked and Carbonated Lime

Chemical compositions and the microstructural properties of the unheated and heated limestone and marbles (quicklime), slaked and carbonated lime were determined by Philips XL 30S-FEG Scanning Electron Microscope (SEM) equipped with X-Ray Energy Dispersive System (EDS).

SEM-EDS analysis was used in the determination of elemental compositions of the stones. For this analysis, samples were ground to the fineness of less than 53µm and then pressed into pellets. SEM-EDS analyses were carried out in three different zones of each specimen.

The microstructures of the samples were determined on coarse samples by SEM analyses.

2.9. Determination of Hydraulicity of Lime by TGA

Thermogravimetric analysis (TG/DTG) was performed on carbonated samples by using Shimadzu TGA-21 thermogravimetric analyzer in order to determine hygroscopic water, structurally bound water and carbon dioxide contents to evaluate hydraulicity of the lime. Their hydraulicities were evaluated by determining weight loss at the temperatures between 200-600^{o}C due to the loss of the structurally bound water of hydraulic products, such as calcium silicate hydrates and calcium aluminate hydrates, and weight loss at the temperatures over 600^{o}C due to carbon dioxide releases during the decomposition of calcium carbonates by using a Shimadzu TGA-51 (Moropoulou et al. 2001).

The thermogravimetric analysis was carried out in a static nitrogen atmosphere at a temperature range of 50-1000°C with a controlled heating rate of 10°C/min.

2.10. Preparation of Lime Mortars

Lime mortars were perapared with different types of limes produced by marbles and limestones in order to compare their characteristics by measuring the compressive strenghts during 12 months carbonation.

Marble pieces were used as aggregates for preparing the mortars. The reason for selecting marble aggregates was that it does not react with lime. Hence, the main purpose was to observe only the effects of different limes on the mortar characteristics.

In preparation of mortars, the quicklime - aggregate ratio in weight was 1/3 and the particle size of the aggregates were between 1000-2000, 500-1000, and 250-500 mesh in size in equal quantities. The main reason of using quicklime in the peraparation of mortars was to provide a homogenous mixture and a strong binding between the lime and the aggregates. The amount of water that was used in preparing of mortar was more than the amount of water which was needed for slaking of quicklime.

Mortar mixtures were prepared by the Kitcheneaid mini mixer and put into moulds of 4.5x5 cm in sizes, which is produced from PVC. After 48 hours waiting period, the mixtures were set off the moulds and waited for about 28 days in desiccators of which relative humidity was at %100 and temperature at 25°C. After 28 days, samples were left in the room conditions. The compressive strengths of the mortars were then determined after 3, 6, 9 and 12 months waiting periods.

2.11. Determination of Uniaxial Compressive Strengths of Mortars

The determination of uniaxial compressive strength of mortars were determined by Shimadizu AG-I Mechanical Test Instrument. The Instrument automatically computed, displayed and recorded test results using a software system. Maximum 15 kN force was applied with 1mm/min. speed. The strokes were recorded under loading. The relationship between the strokes and load by a graph was automatically displayed on the test condition monitor. This graph was composed of a curve of which the peak point gave the maximum force (F) under which the specimen failed. As a result, uniaxial compressive strenghts represented by ‘σ’ were calculated by using this graph with the following formula.

$$\sigma = F/A$$

where;

F : Failure load (kN)

A : Area onto which loading was applied (mm^2)

2.12. Determination of Modulus of Elasticity of Mortars

The modulus of elasticity is the rate of change of strain as a function of stress. It provides required information about how well a material can resist deformation under the action of external forces (Airapetov 1986). The modulus of elasticity (E) is formulated as follows.

$E = \text{Stress} / \text{Strain} = \sigma / \varepsilon = (\triangle F/A) / (\triangle l/l_o)$

where;

$\triangle F$: Failure load (kN)

A : Area onto which force was applied (mm^2)

$\triangle l$: Change in thickness of the sample along its vertical axis (mm)

l_o : Initial thickness of the sample (mm)

Stress (σ) is the ratio of force to the area where the force is applied. Strain (ε) corresponds to the change in thickness of samples under the action of the applied force (Airapetov 1986). When a compression force is applied onto a solid material, the force is transmitted through its body and causes it to become deformed along the direction of the applied force (Airapetov 1986). The decrease in thickness is denoted by $-\triangle l$. Here, the minus sign refers to contraction in dimension. This change in dimension is called strain and denoted by $\triangle l/l_o$ (Airapetov 1986).

Relationship between deformation and applied force is expressed by a stress-strain curve. Slope of this curve ($\tan\theta$) gives the modulus of elasticity of that material (Airapetov 1986). Therefore, the modulus of elasticity was calculated using the slopes of the stress-strain curves obtained from the results of the compression strength tests.

CHAPTER 3

RESULTS AND DISCUSSION

In this chapter, the physical, microstructural, mineralogic and chemical properties of the marbles and limestones used as samples are presented and the results are discussed at the beginning. Next, the properties of the quicklimes which were formed by calcinations of the stones, the lime produced within the hydration processes, and the final products after the carbonation processes and the differences among them constitute the main part of the chapter. Moreover, hydraulic capacities of carbonated limes are included . Finally, carbonation processes of the mortars which were produced from these limes, and their differences observed in their mechanical properties are discussed.

3.1. Densities and Porosities of Marbles and Limestones

Basic physical properties such as densitiy and porosity values of the stones were determined by using RILEM standart tests. According to the test results , Marmara and Muğla marbles have high density and low porosity values (Table 3.1). When compared to values of density and porosity of white limestones, it was observed that the grey limestone was less dense and a more porous stone (Table 3.1).

Table 3.1. Density and porosity values of marbles and limestones.

Sample	Density (g/cm3)	Porosity (%)
Mar-M	2.7	0.2
Mu-M	2.7	0.4
W-L	2.5	2.4
G-L	2.2	11.3

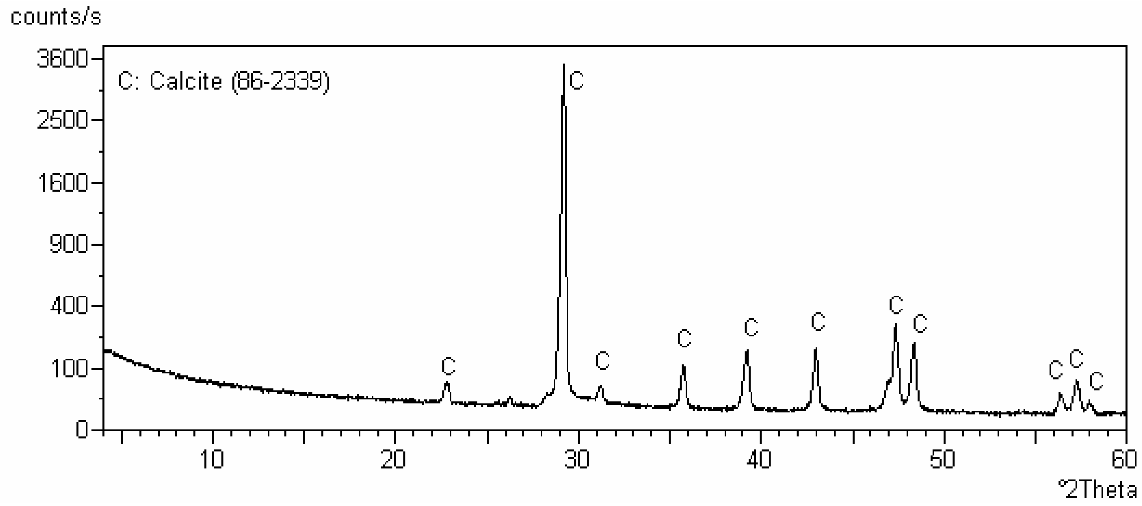
3.2. Mineralogical Compositions of Marbles and Limestones

Mineralogical compositions of marbles and limestones were determined by XRD and IR analyses. In XRD patterns of Marmara marble, only peaks of calcite minerals were observed. It indicates that the Marmara marble is composed of pure calcite crystals. However, it is detected both calcite minerals peaks and the most intense dolomite minerals peaks in XRD diffraction patterns of the Muğla marble. It shows that Muğla marble was composed mainly of calcite crystals, and dolomite minerals in lower amounts. In XRD patterns of white limestone, only the calcite peaks were observed. On the other hand, in the XRD patterns of grey limestone, peaks of calcite and less intense peaks of quartz minerals were observed. These results indicate that white and gray limestones were composed of mainly calcite crystals.

Table 3.2. Minerals determined by XRD analysis in marbles and limestones.

Sample	**Calcite**	**Dolomite**	**Quartz**
Ma-M	+++	-	-
Mu-M	+++	+	-
W-L	+++	-	-
G-L	+++	-	+

(a)



(b)

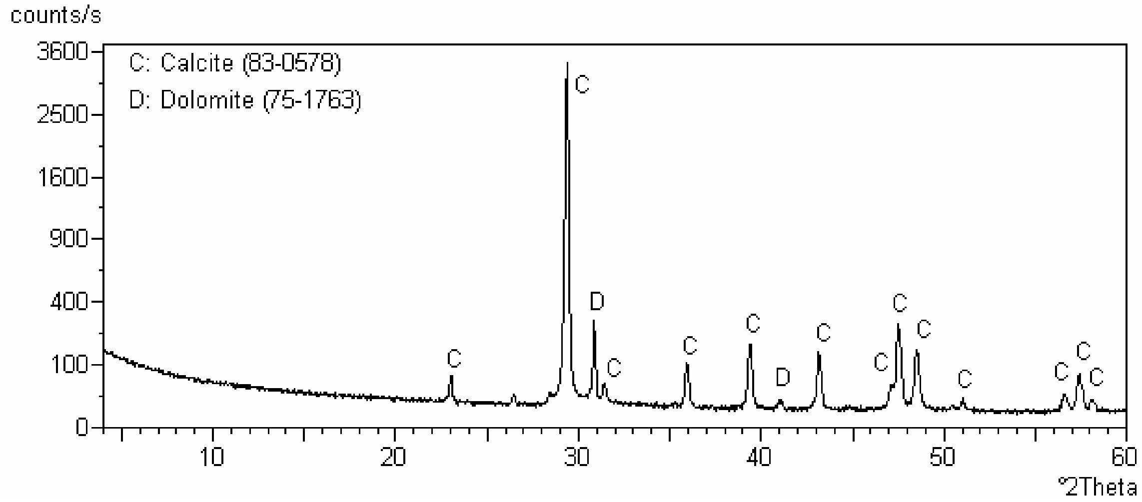


Figure 3.1. XRD patterns of (a) Marmara and (b) Muğla marbles.

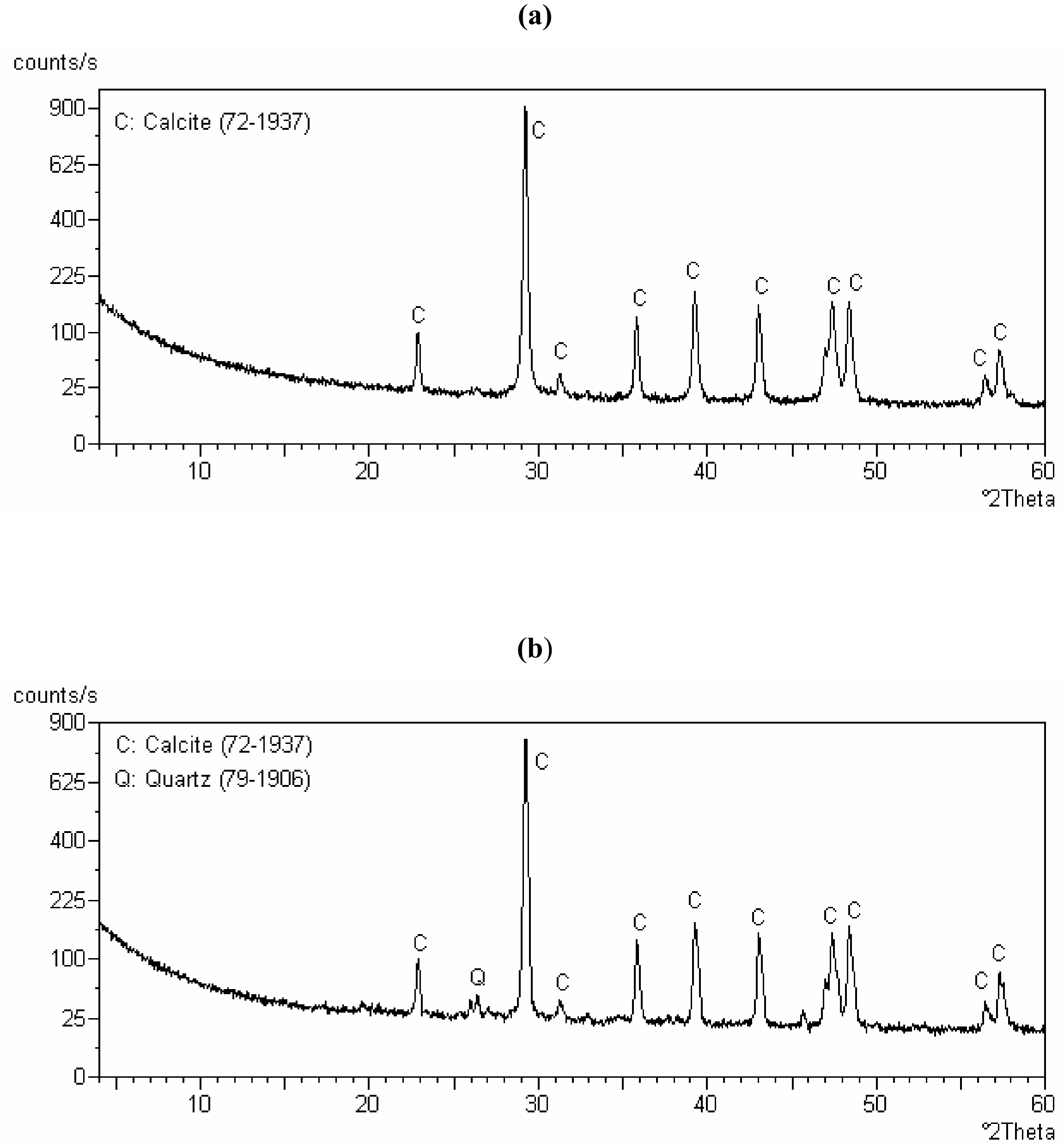
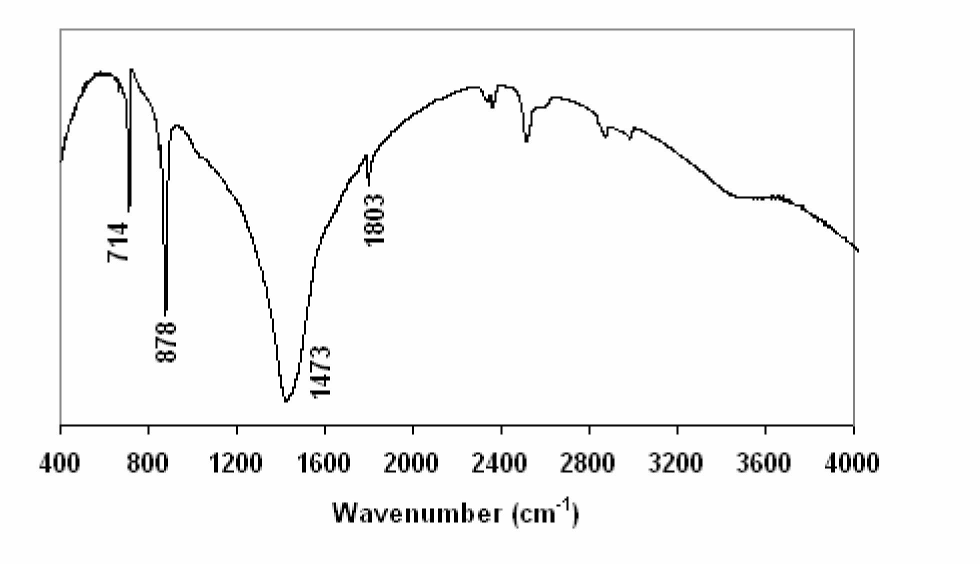
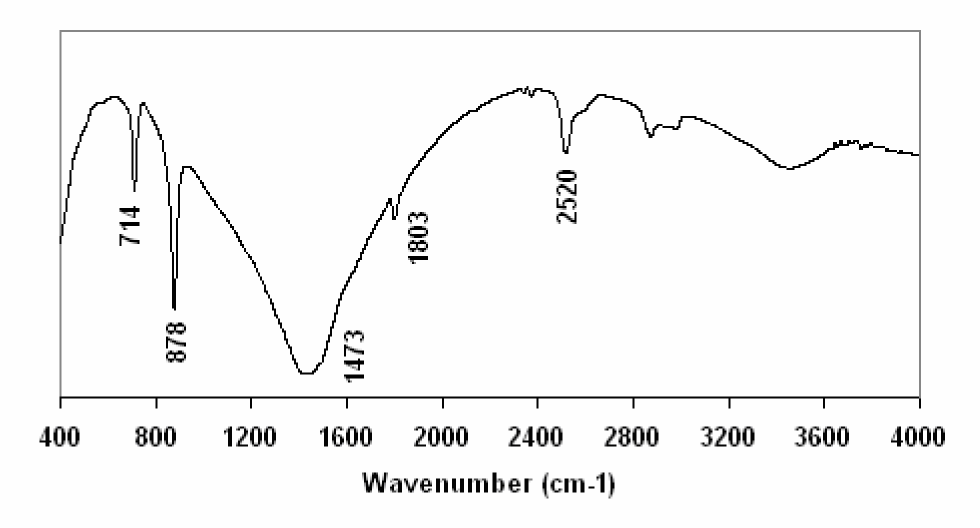


Figure 3.2. XRD patterns of (a) white and (b) grey limestones.

Mineralogical compositions of marbles and limestones were also determined by FT-IR analysis. In the FTIR spectrum of all marbles and limestones, the main $CaCO_3$ bands at 714, 878, 1473, 1803, 2520, 2883 and 2990 cm^{-1} were observed (Figures 3.3, 3.4). In addition, in the FTIR spectrum of the grey limestone , Si-O stretching vibrations at 1050 and 470 cm^{-1} (Gadsden 1975 ,Yu et al. 1999) due to the deformation of SiO_4 tetrahedra of the disordered silica (Figure 3.4(b)) were observed. The presence of silica peaks in IR spectrum of the grey limestone but its absence in XRD spectrum shows the existence of amorphous or poor crystalline silica in its composition.

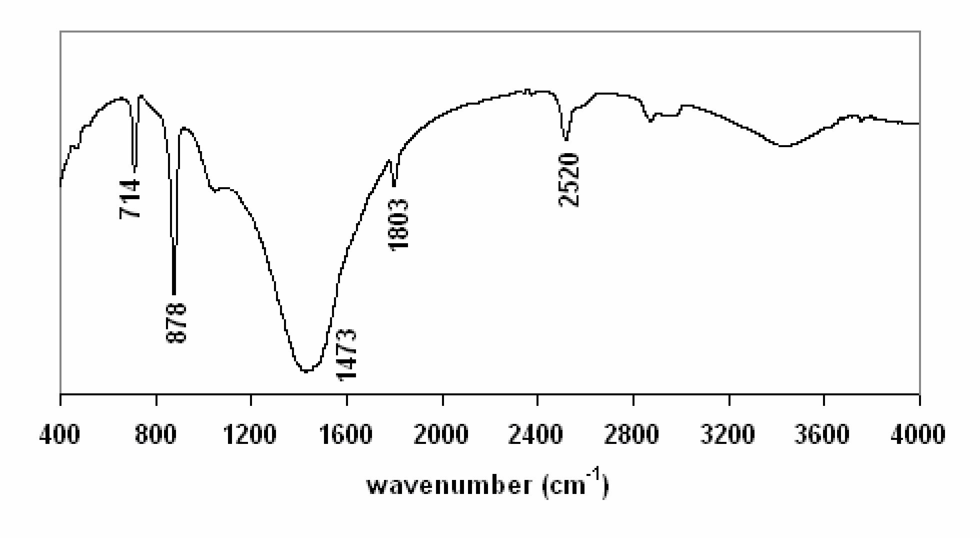


(a)

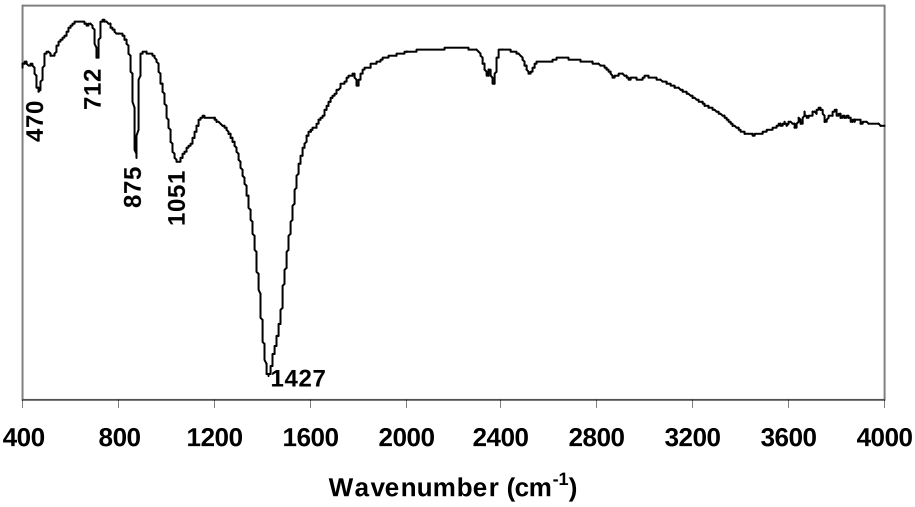


(b)

Figure 3.3. FT-IR spectrum of (a) Marmara and (b) Muğla marbles.



(a)



(b)

Figure 3.4. FT-IR spectrum of (a) white and (b) grey limestones.

3.3. Chemical Compositions of Marbles and Limestones

Chemical compositions of marbles and limestones were determined by Philips XL 30S-FEG Scanning Electron Microscope (SEM) equipped with X-Ray Energy Dispersive System (EDS). In order to determine their chemical compositions, samples were ground to the fineness of less than 53µm and then pressed into pellets. SEM-EDS analyses were performed on these pellets. The results of the analyses are given in Table

3.3. As it is seen in table 3.3, the Marmara marble contains a high percentage of CaO (~97%), and a low percentage of MgO about 2%. It shows that the Marmara marble is composed of mainly CaO and contains low amounts of MgO. Similarly, CaO content in Muğla marble is high. However, they differ from each other in terms of magnesium content. The magnesium found in the composition of marble can be originated from dolomite ($CaMg(CO_3)_2$). On the other hand, white limestone contains higher percentages of SiO_2 and Fe_2O_3 when compared with the chemical compositions of marbles. The grey limestone is composed of low percentages of CaO and high percentages of SiO_2 and Al_2O_3. This shows that the grey limestone contains high amounts of silicates.

Table 3.3. Elemental compositions of marbles and limestones and percentage of weight loss at temperature 900° C.

Sample	**CaO**	**MgO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**Na_2O**	**K_2O**	**W. loss (900 ° C)**
Mar-M	96.7±0.2	2.3±1.6	N.D	N.D	N.D	N.D	N.D	N.D	43.3±0.1
Mu-M	81.6±0.4	10.1±0.7	2.4±0.4	2.2±0.4	0.8±0.8	0.2±0.3	2.2±0.5	0.5±0.3	44.8±0.1
W-L	84.4±2.5	2.8±0.6	5.2±0.6	2.6±0.4	2.4±0.7	0.5±0.3	1.5±0.9	0.6±0.1	38.8±0.1
G-L	58.6±0.8	2.8±0.3	26.5±3.5	6.6±0.0	2.7±0.7	0.5±0.4	1.2±0.6	1.1±0.1	29.6±0.1

N.D: Not detected

3.4. Microstructural Characteristics of Marmara and Muğla Marbles

Microstructural characteristics of the Marmara marble was determined by SEM analyses. According to the results of the analyses, the sizes of the calcite crystals of the marble are in the range of 2 to 3.5mm. (Figure 3.5). Calcite crystals are tightly bounded to each other. In previous studies, similar characteristics of Marmara marble has also been reported (Moens et al. 1989).

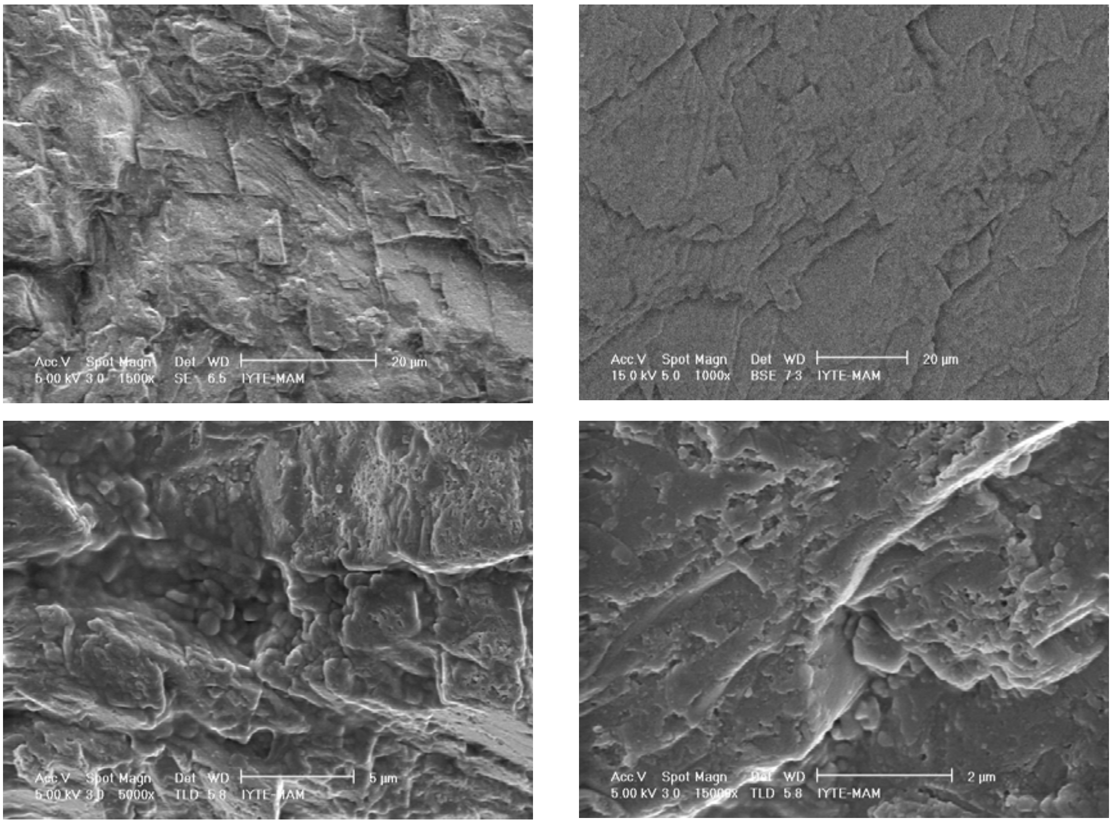


Figure 3.5. SEM pictures of calcite crystals in the Marmara marble.

The mineral sizes of calcite crystals that form the Muğla marble, are smaller when compared to the Marmara marble and vary in the range of 22-800 micrometres (Figure 3.6). Calcite crystals are tightly bounded to each other in the marble matrix. In previous studies, similar characteristics of Muğla marble has also been reported (Yavuz et al. 2002).

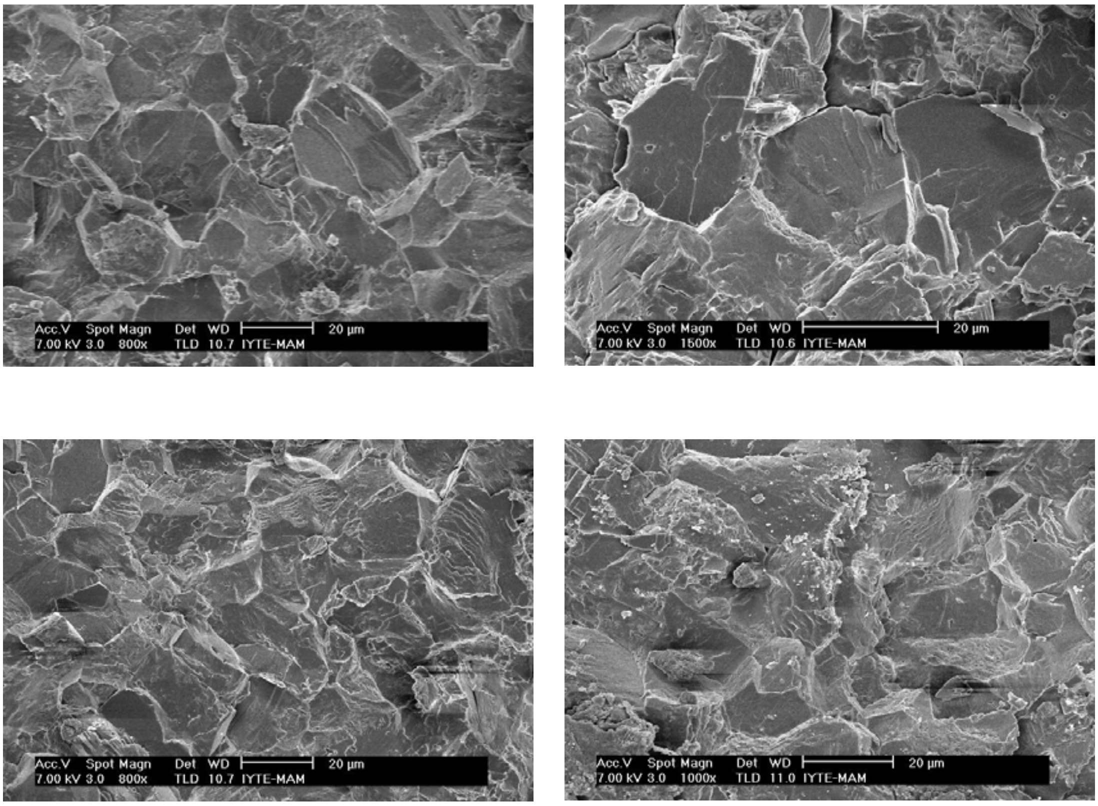


Figure 3.6. SEM pictures of calcite crystals in the Muğla marble.

3.5. Microstructural Characteristics of White and Grey Limestones

The microstructure analyses of white limestone carried by using SEM show that small and large grain size calcite crystals are not homogeneously distributed in the stone matrix (Figure 3.7).

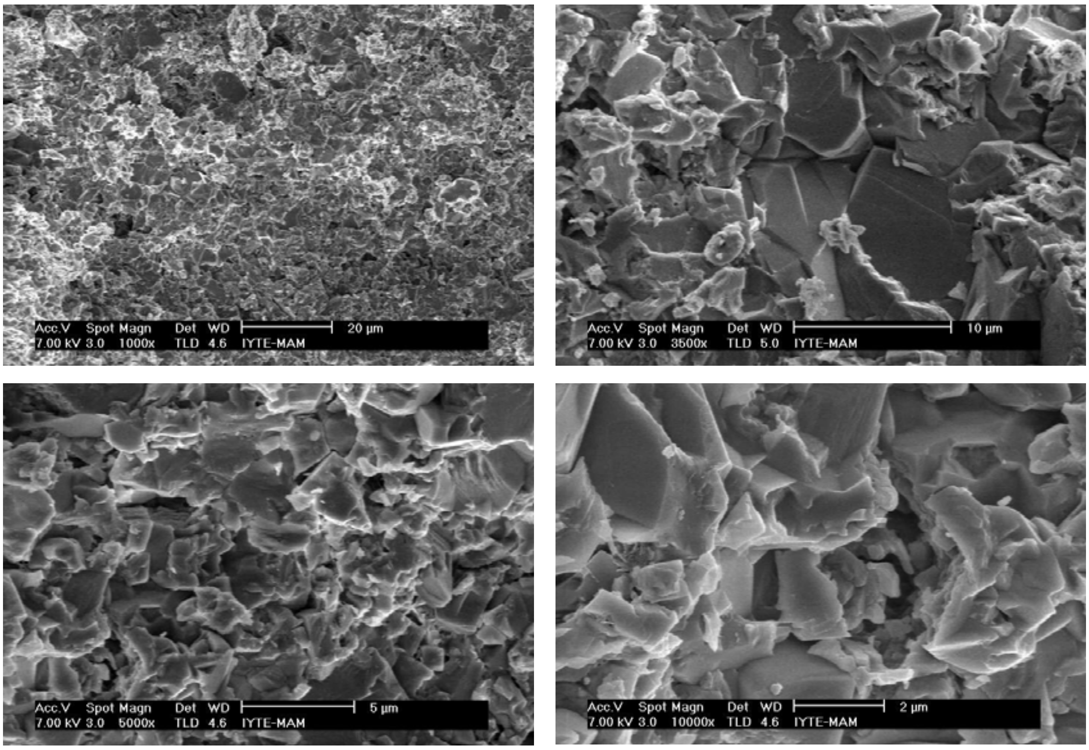


Figure 3.7. SEM pictures of micritic calcite crystals in white limestone.

The SEM analysis of the grey limestone shows that it is composed of small and large grain size calcite crystals (Figure 3.8). Differently from the white limestone, the grey limestone contains high amounts of amorphous silica from diatoms. The SEM-EDS analysis indicates that the limestone contains nearly 30 % of silicon oxide in its composition that is originated by the presence of the high amounts of diatoms. Diatoms are composed of skeletal shells originated from many kinds of unicellular algae (Korunic 1998, Gürel and Yıldız 2006, Fragoulis et al. 2005). Mainly disk, bow and cone shaped diatom frustules are noticed in the SEM pictures (Figures 3.9, 3.10).

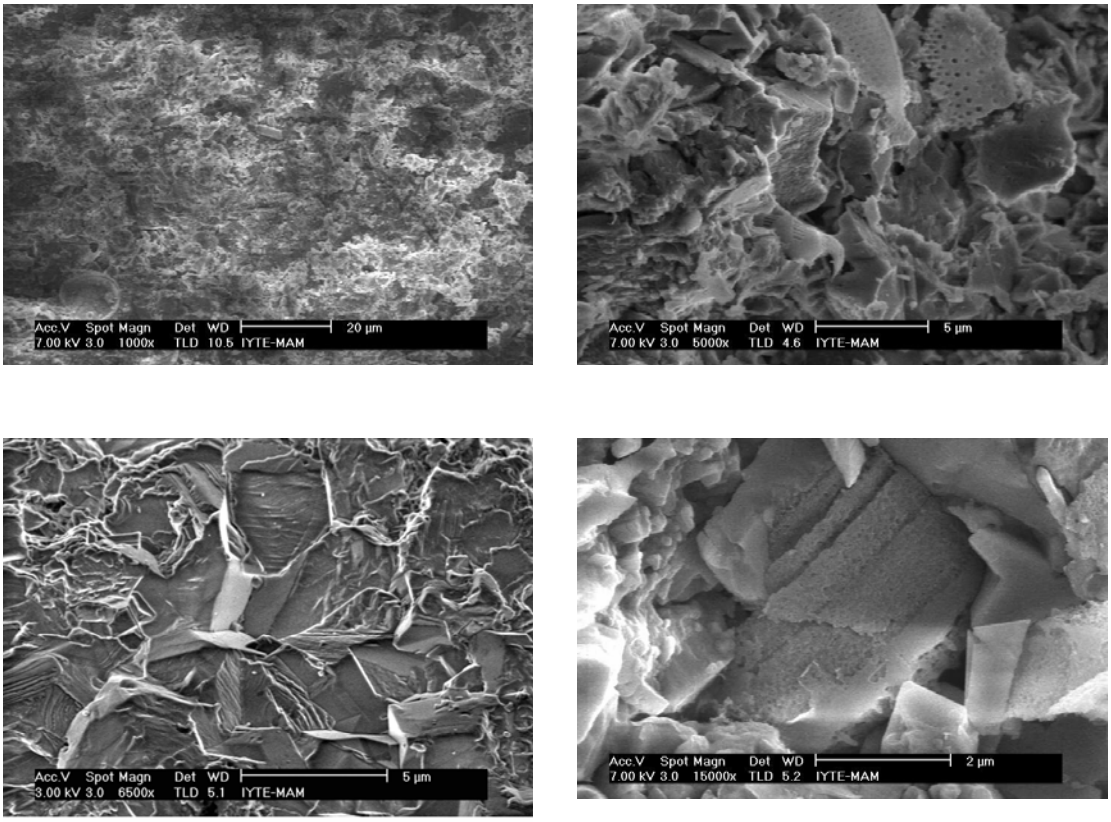


Figure 3.8. SEM pictures of micritic calcite crystals in grey limestone.

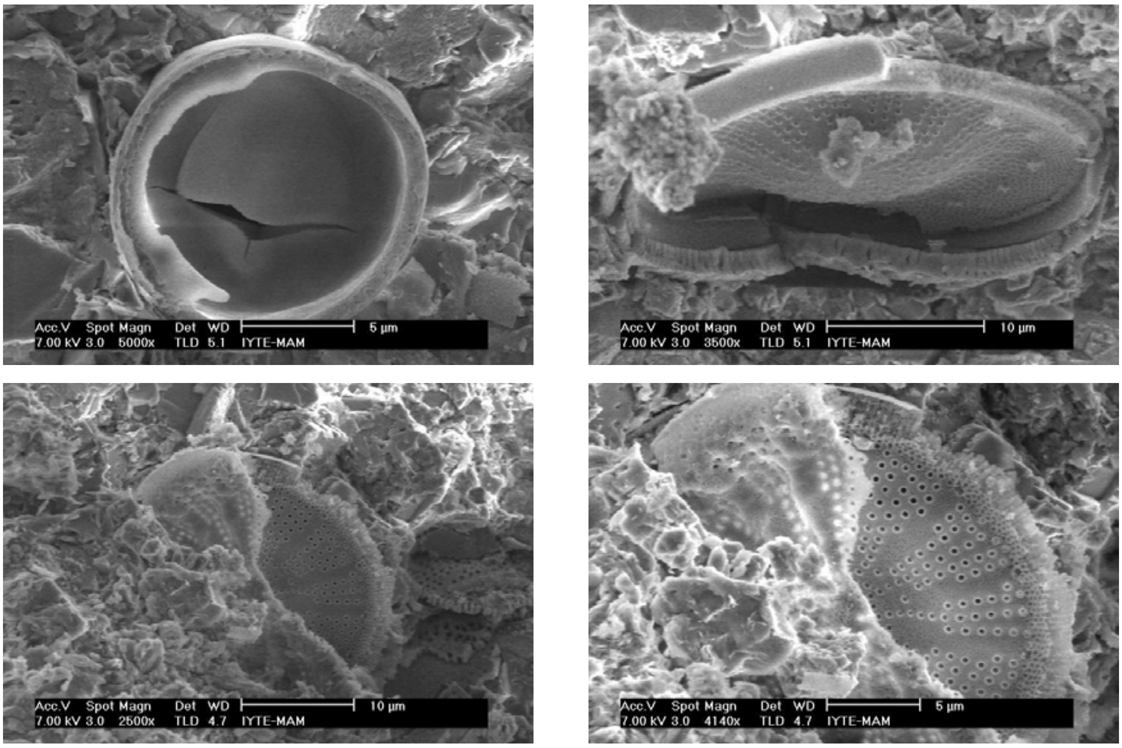
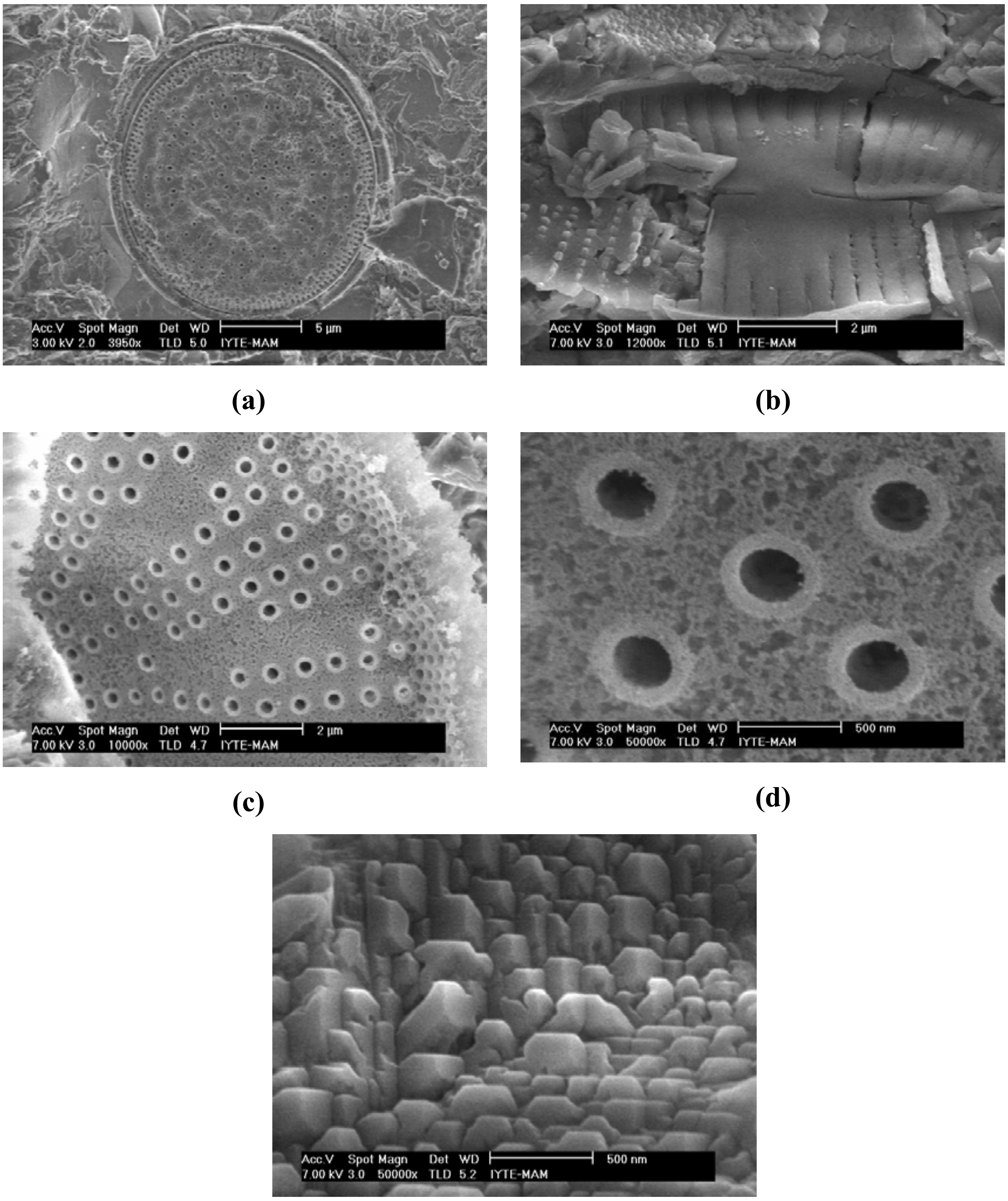


Figure 3.9. SEM images of diatoms embedded in calcite crystals in grey limestone.



(a) **(b)**

(c) **(d)**

(e)

Figure 3.10. SEM images of a (a) disk and (b) bow shaped diatom frustules; (c,d) small holes on their surfaces; (e) precipitated small size of calcite crystals on the surface and the holes of the diatoms.

3.6. Calcination Temperatures of Marbles and Limestones

When calcite crystals, which are the main constituents of marbles and limestones, are heated at a temperature of around 900 ° C, they will transform into calcium oxide through the release of carbon dioxide gas. The calcination process of calcite begins when the partial pressure of CO_2 in the gas above the solid surface is less than the decomposition pressure of the $CaCO_3$ (Reaction 3.1) (Stanmore and Gilot 2005).

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \Delta H = +\ 182.1\ \text{kJ mol}^{-1}$$ **(Reaction 3.1)**

Calcination temperatures of marbles and limestones were determined by the TGA analysis. The TGA analysis of the Marmara marble and white limestone show that their calcinations begin at a temperature of 700 ° C and end at 800 ° C. Between the range of temperatures of 700-800 ° C, the percentage of weight loss due to the release of carbon dioxide gas was around 40% (Table 3.4, Figure 3.11). This loss in weight refers that, the samples of the stones contain calcium carbonate over 90 %. However, 30% weight loss due to driving of carbon dioxide was observed in the grey limestone . This results indicate that the grey limestone contains nearly 70 % of calcite (Table 3.4). On the TGA graphs of marbles and limestones, none weight loss were observed due to the dehydroxylation of clay minerals between 400-600 ºC, which indicates that they don't contain clay minerals.

Table 3.4. Percentage of weight loss observed in the marbles and limestones between 700-800 ° C by the TGA analysis.

Sample	**% Weight loss**
Mar-M	44.01
Mu-M	39.6
W-L	38.8
G-L	29.61

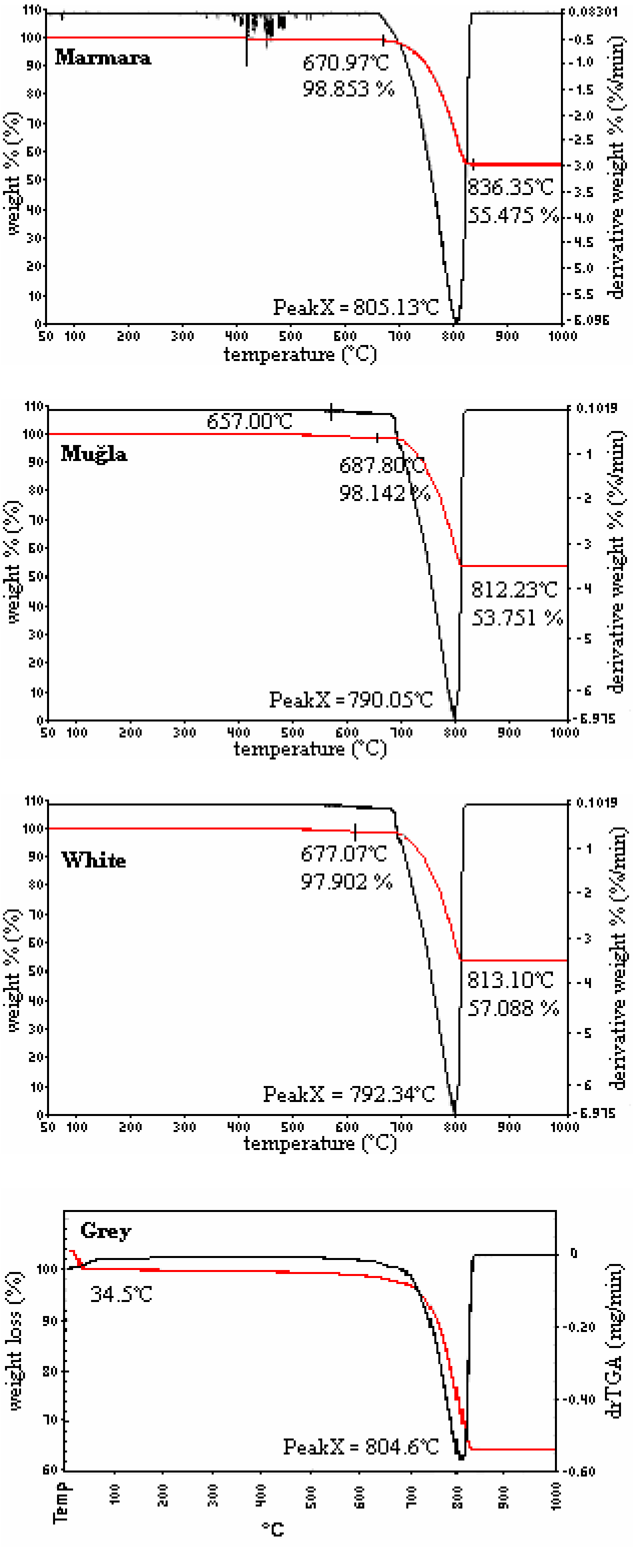


Figure 3.11. TGA graphs of marbles and limestones.

3.7. Mineralogical Characteristics of Calcined Marbles and Limestones

Considering the calcination temperatures determined by TGA analyses, the samples were calcined at 850 ° C temperature during 12 hours. The calcined samples were then cooled in a desiccator in dry conditions. The mineralogic characteristics of dry samples were determined by the XRD analysis.

After the calcination process, basic peak of $CaCO_3$ (29. 2 2Θ) was not observed in XRD patterns. It shows that, calcite crystals are completely transformed into CaO in 12 hours and in a temperature of 850 ° C .

In the XRD diffraction patterns of Marmara, Muğla marbles and white limestone samples, basic peaks of CaO with values of about 32.3, 37.5 and 53.9 2Θ have been observed (Table3.5 and Figures 3.12, 3.13). On the other hand, basic peak of magnesium oxide (at 42.9 2Θ) has been detected as well as calcium oxide peaks in Muğla marble.

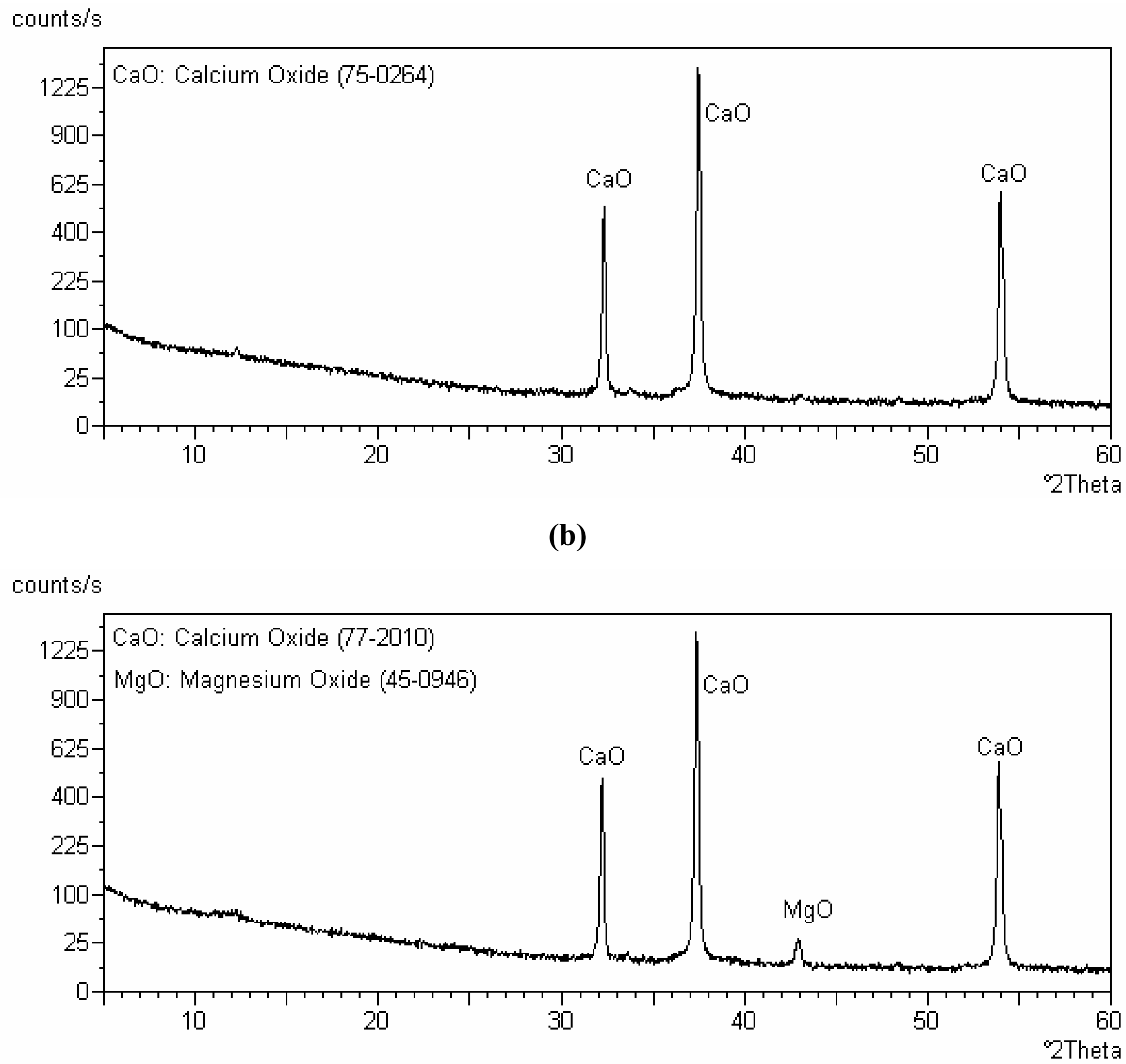
XRD diffraction patterns of grey limestone samples differ from the other samples. Dicalcium silicate (Ca_2SiO_4) peaks with the values of 32.5, 33.11, 39.8 and 41.3 2Θ have been observed as well as CaO peaks (Figure3.13). This formation indicates that, diatoms (amorphous silicates) in the grey limestone have reacted with the calcium oxide and formed calcium silicates (Reaction 3.2)

$$2CaO + SiO_2 \rightarrow 2\,CaO\,.\,SiO_2 \qquad \textbf{(Reaction 3.2)}$$

This result shows that the production of the hydraulic lime at a relatively low calcination temperature (850ºC) is possible. This results may also explain the finding of the use of hydraulic limes in a 15th century Ottoman bath mortars (Böke et al. 2007, Çizer 2004).

Table 3.5. Minerals determined by the XRD analysis after calcination of marbles and limestones.

Sample	Calcium Oxide (CaO)	Magnesium Oxide (MgO)	Calcium Silicate ($2CaO.SiO_2$)
Ma-M	+++	-	-
Mu-M	+++	+	-
W-L	+++	-	-
G-L	+++	-	++

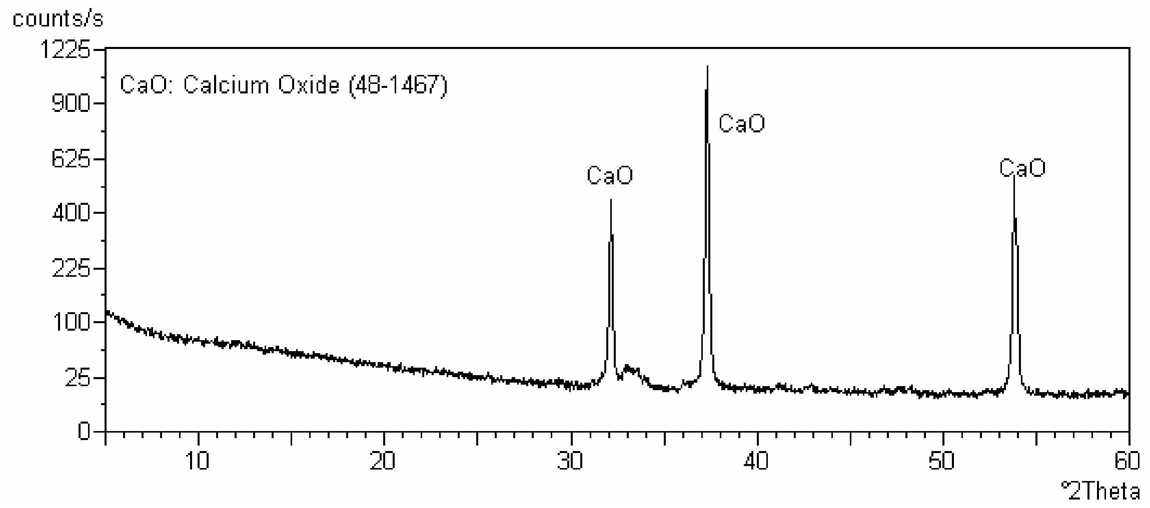


(a)

(b)

Figure 3.12. XRD patterns of calcined (a) Marmara and (b) Muğla marbles.

(a)



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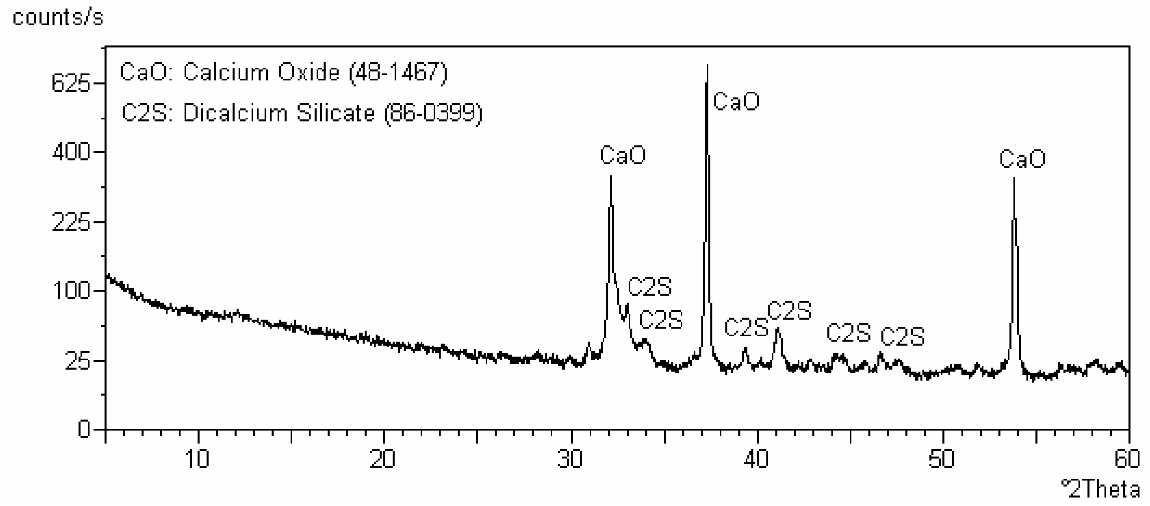


Figure 3.13. XRD patterns of calcined (a) white and (b) grey limestones.

3.8. Microstructural Characteristics of Calcined Marmara and Muğla Marbles

The microstructural characteristics of the calcined Marmara and Muğla marble have been determined by SEM analysis. Porous structures on calcite crystals were observed due to the release of carbon dioxide gas after calcination processes (Figures 3.14, 3.15). The diameters of pores are ranged between 5 to 10 microns (Figures 3.14, 3.15).

The molar volume of calcite is 36.9 cm^3 mol^{-1}. After the calcination process of calcite, the molar volume of quicklime will be 16.9 cm^3 mol^{-1} volume (Stanmore and Gilot 2005).

Previous studies showed that high calcination temperatures cause the denser and the more perfect crystal lattice. Calcite crystals have rhombohedral structure and the crystal lattice is imperfection. At low calcination temperatures, more vacancies and defects in the calcite crystal structure are formed. At these temperatures, crystal structures are loose and their sizes are small. With the rise of temperature, the crystals of CaO grow and change to cubic structure (Huisheng et al. 2002).

In this study, heating Marmara and Muğla marbles in low temperatures caused the formation of imperfect crystals. In the SEM-EDX analysis of the Marmara marble, only calcium and oxygen peaks have been observed. It indicates that calcite crystals have been completely transformed into the calcium oxide (Figure 3.14). On the other hand, magnesium peaks have been shown in the Muğla marble as well as calcium peaks, which are originated from calcinations of magnesium carbonate.

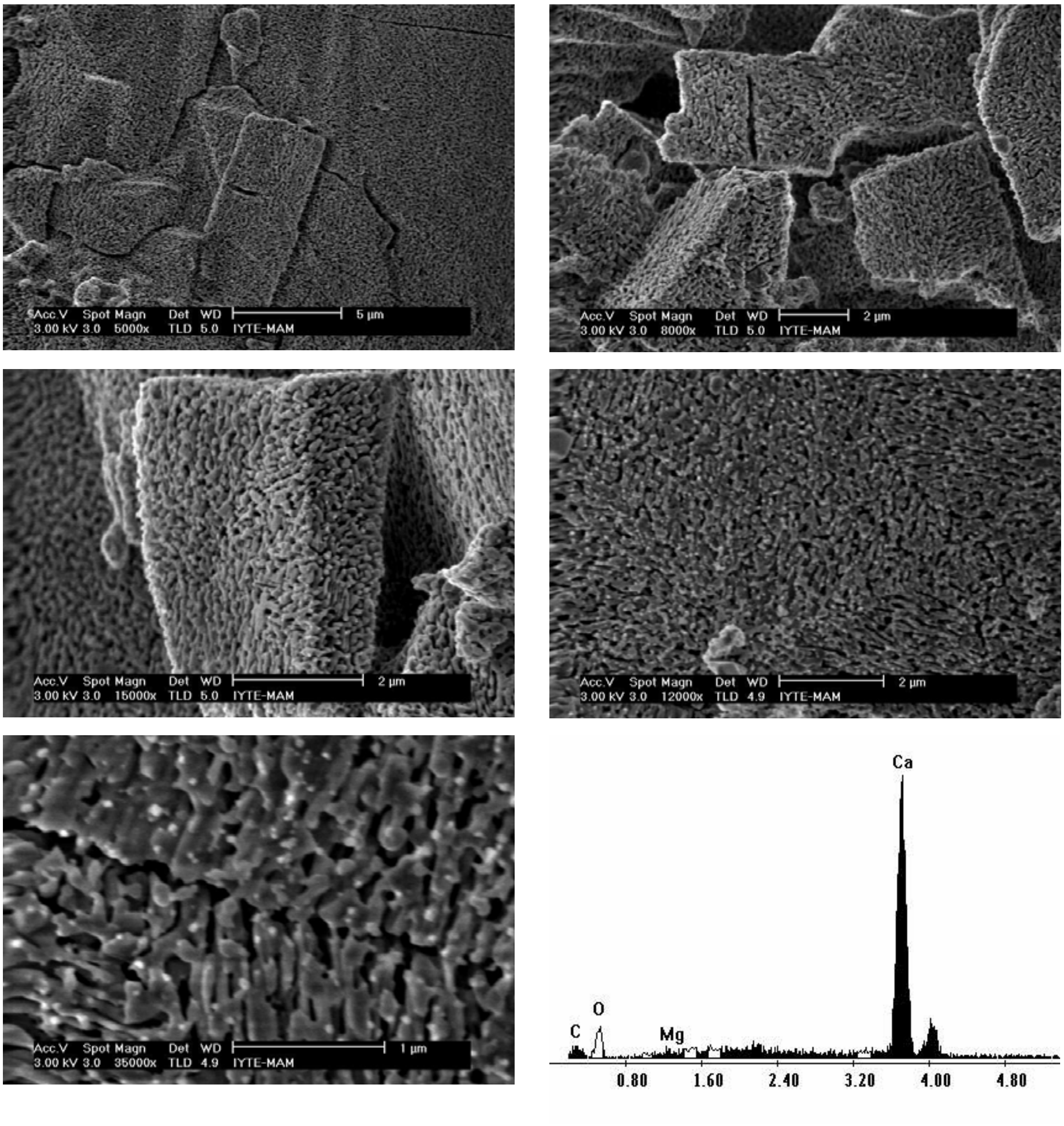


Figure 3.14. Secondary electron images and EDS spectrum of calcium oxide crystals of calcined Marmara marble.

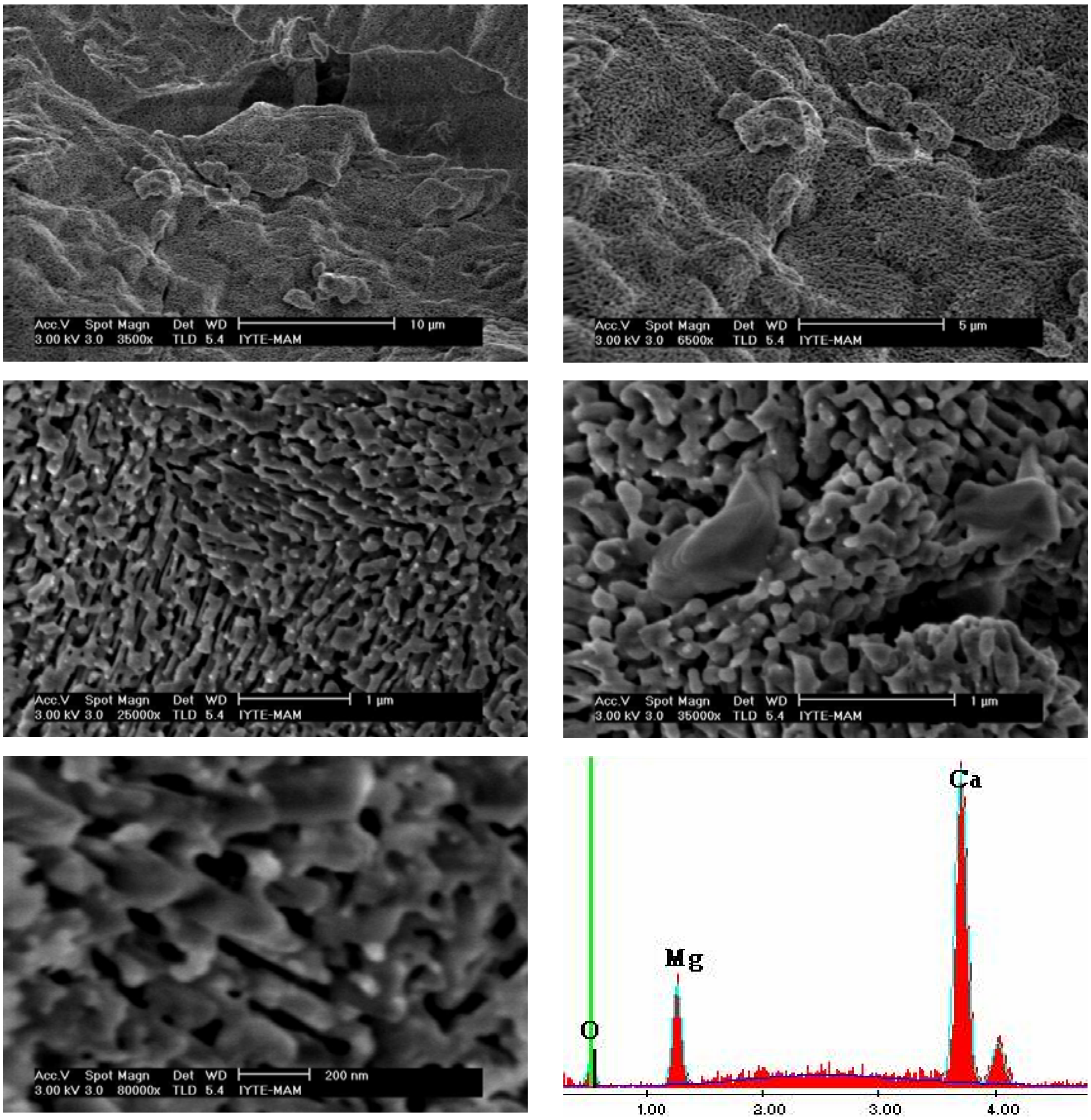


Figure 3.15. Secondary electron images and EDS spectrum of calcium oxide crystals of calcined Muğla marble.

3.9. Microstructural Characteristics of Calcined White and Grey Limestones

The SEM images show that the white limestone consists of small individual CaO crystals after the calcination process. CaO grains were varied in diameter from <0.05 micron to 0.8 micron. The individual CaO crystals are partly bonded to other grains and partly surrounded by voids. Smaller calcium oxide crystals with voids increases their surface area. It leads to calcium oxide crystals to be more reactive with water (Huisheng et al. 2002, Stanmore and Gilot 2005).

Previous works show that limestones are composed of over 90% calcite and contains from 3 to 35% open porosity (Huisheng et al. 2002, Stanmore and Gilot 2005). Pores are generally large with few micropores. Hence, the surface area of limestones range from 1 to 10 m^2g^{-1}. When the calcination occurs, the porosity of the calcium oxide is greater than 0.6 than that of calcite crystals (Huisheng et al. 2002, Stanmore and Gilot 2005).

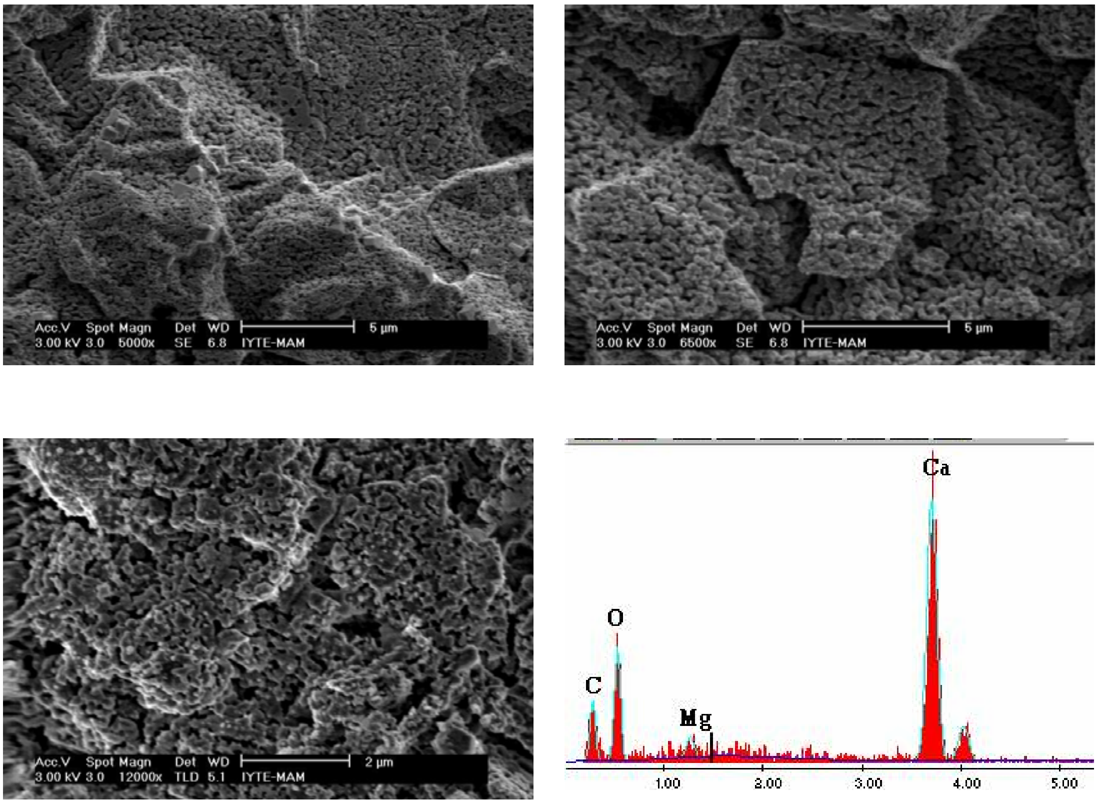


Figure 3.16. Secondary electron images and EDS spectrum of the calcium oxide crystals of calcined white limestones.

The microstructure analysis of the grey limestone shows that small and large grain size of calcite crystals with diatoms are distributed inhomogeneously in the stone (Figure 3.17). After the limestone was heated to 850 ºC in a laboratory furnace, calcium oxide and calcium silicate peaks (C_2S) were identified by the XRD analysis (Figure 3.17). The SEM analysis presented that the quicklime formed at this temperature has a porous structure due to the carbon dioxide driven from the calcite minerals (Figure 3.18). The observation of mainly calcium and silicon peaks in the EDS spectrum of the diatoms shows that the diatoms are converted to C_2S by reaction with quicklime (Figure 3.18) (Callebaut et al. 2001, Gualtieri et al. 2006, Varas et al. 2005).

A high contact surface area of precipitated calcite crystals on the surfaces and the pores of the diatoms (Figure 3.18) and the amorphous character of the diatoms themselves may be the main reasons for the formation of C_2S at this low temperature.

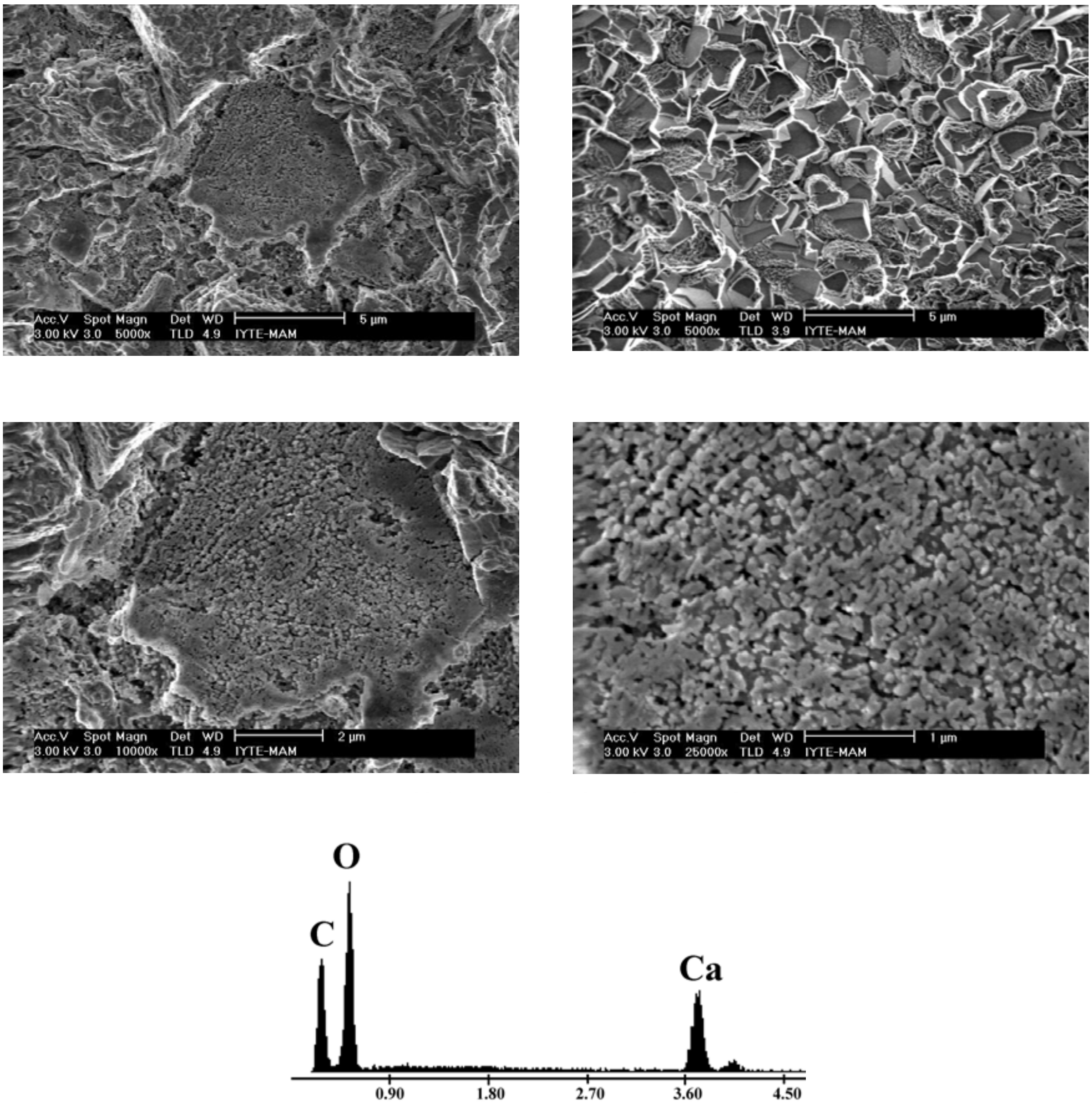


Figure 3.17. Secondary electron images and the EDS spectrum of calcium oxide crystals of calcined grey limestone.

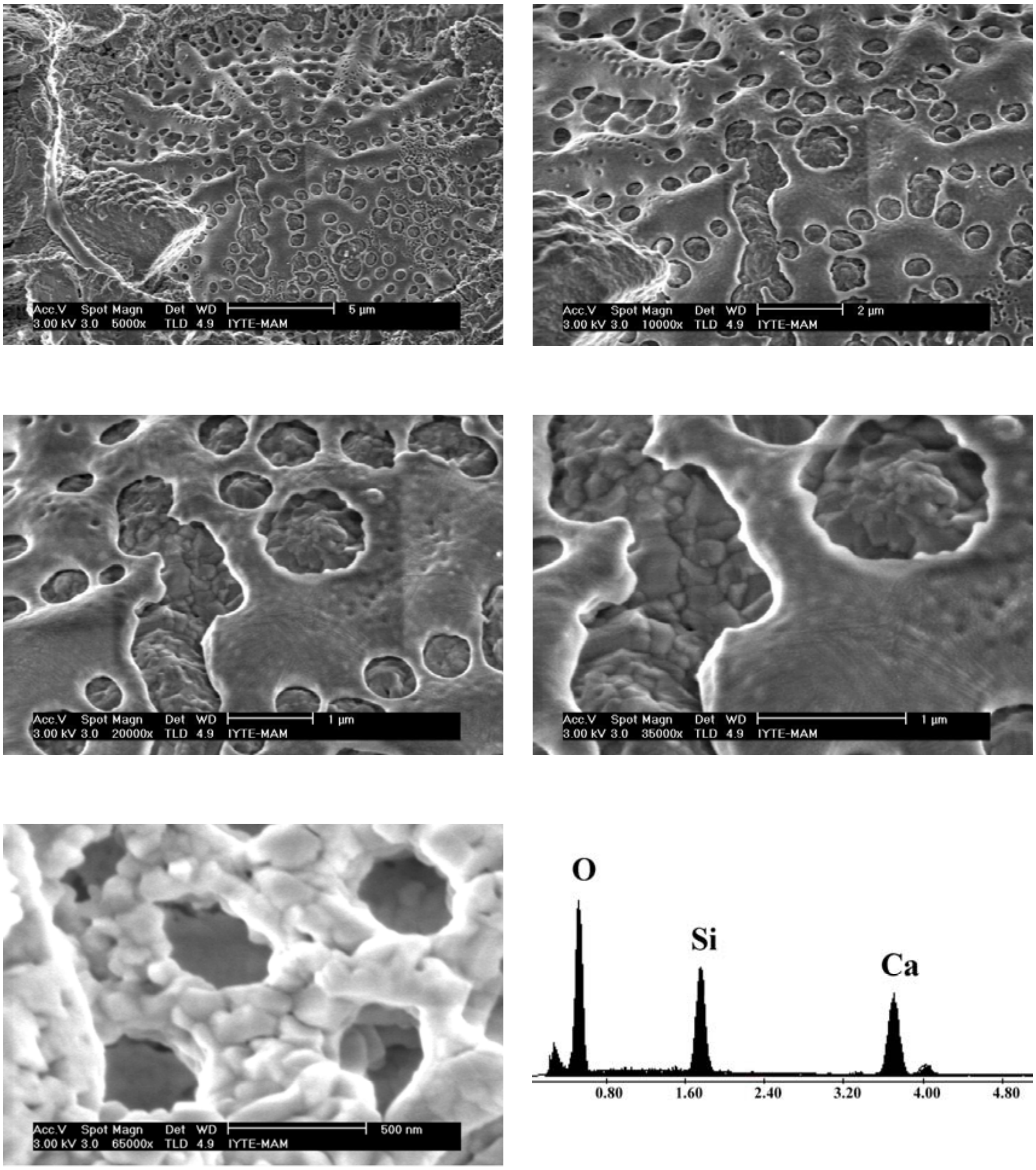


Figure 3.18. Secondary electron images and the EDS spectrum of calcium silicate formed by the reaction of diatoms and calcium oxide during the calcination of the grey limestone.

3.10. Mineralogical Characteristics of Limes Produced from Slaking of Calcined Marbles and Limestones

The calcined marbles and limestones were slaked with distilled water. When calcium oxide reacts with water, calcium hydroxide is formed (Reaction 3.3).

$$CaO + H_2O \rightarrow Ca(OH)_2 + Heat \qquad \textbf{(Reaction 3.3)}$$

After the slaking process, samples were dried and their mineralogical compositions were determined by the XRD analysis. The XRD patterns are shown in Figures 3.19, 3.20 and the observed minerals are given in Table 3.6. In the XRD patterns of the Marmara marble and white limestone, the main peaks of the portlandite crystals were observed at d values of 4.895, 2.619, 1.917, and 1.790 corresponding to 2 theta angles: 18.110, 34.215, 47.386 and 50.965. Magnesium hydroxide was identified as well as portlandite minerals in the Muğla marble.

In the XRD patterns of the grey limestone, calcium hydroxide (portlandite) and dicalcium silicate were indicated (Figure 3.20 b). This may suggest that the formation of calcium hydroxide is more favorable than the formation of calcium silicate hydrate.

Table 3.6. Minerals identified by the XRD analysis after the hydration of calcined marbles and limestones.

Samples	**Lime ($Ca(OH)_3$)**	**Brucite ($Mg(OH)_2$)**	**Coesite SiO_2**	**Calcium silicate (Ca_2SiO_4)**
Marmara	+++	-	-	-
Mugla	+++	+	-	-
White	+++	-	+	-
Grey	+++	-	-	++

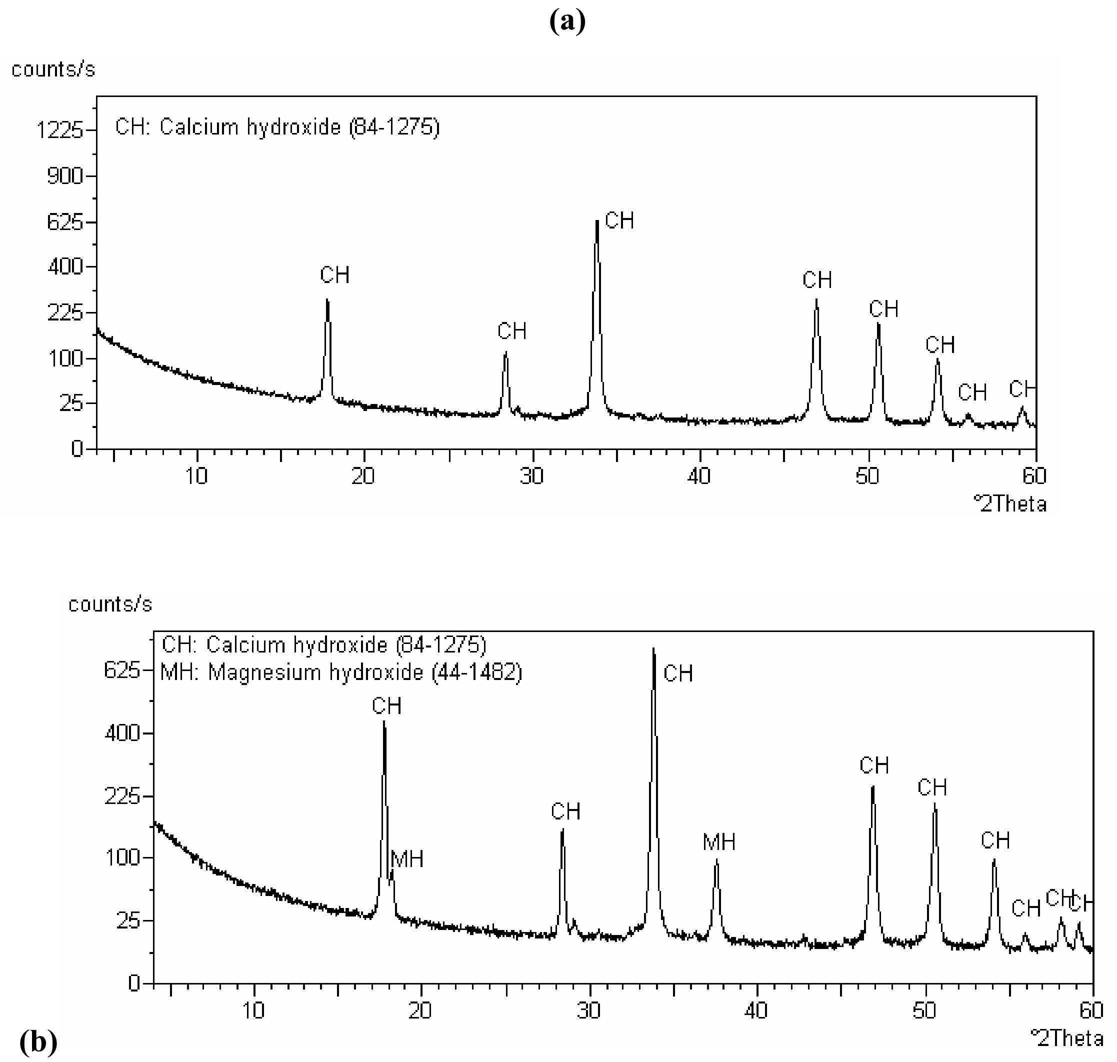
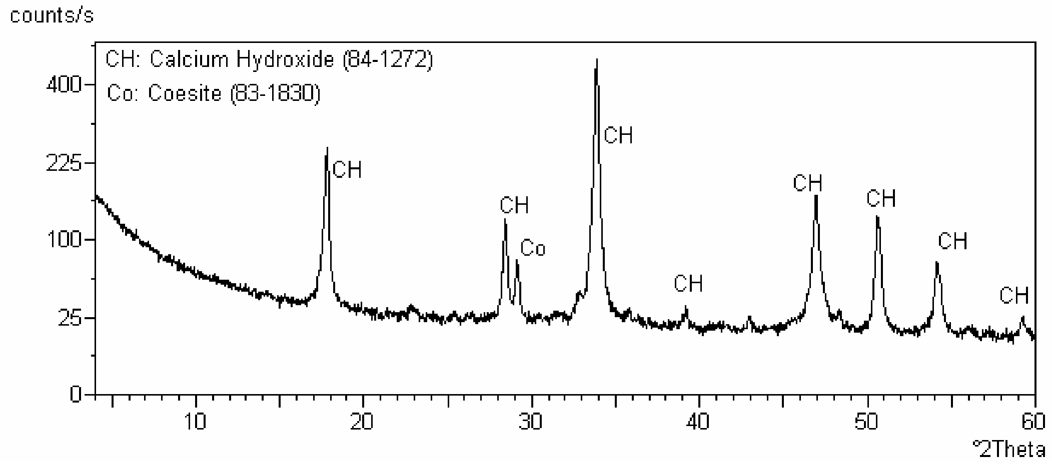
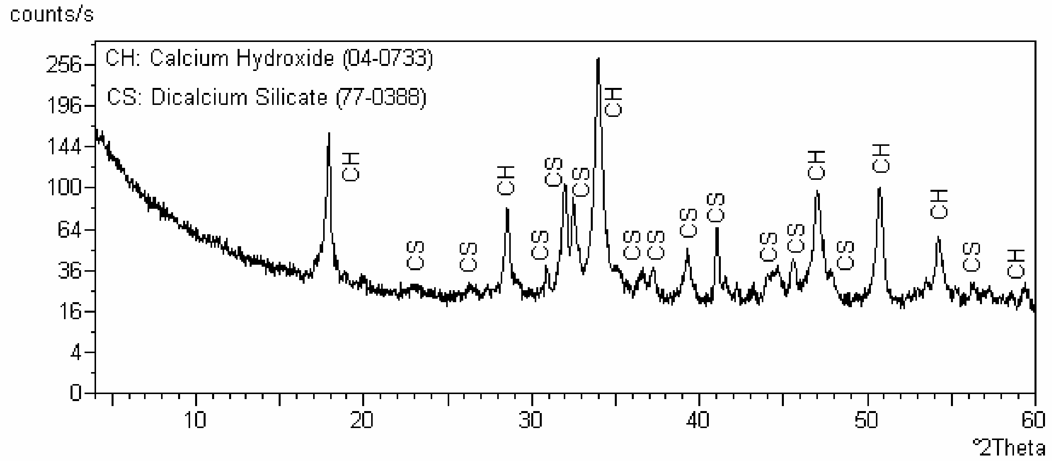


Figure 3.19. XRD patterns of slaked (a) Marmara and (b) Muğla marbles.



(a)



(b)

Figure 3.20. XRD patterns of slaked (a) white and (b) grey limestones.

3.11. Microstructural Characteristics of Limes Produced from Slaking of Calcined Marmara and Muğla Marbles

The heating temperature of calcium carbonate mainly affects the microstructure of CaO. The difference in the microstructure of CaO heated at various temperatures results in its different hydration activity. The hydration activity decreases with the increase of the calcination temperature (Huisheng et al. 2002, Moropoulou et al. 2001).

In this study, the hydration activities of limes produced from marbles should be high due to the low calcination temperature (850 °C).

In the slaked Marmara and Muğla marbles calcium hydroxide crystals form a network with grains of irregular shape and average size in the sub-micrometer range. The formation of sub-micron size of calcium hydroxide crystals may show high hydration activities of quicklime produced from marbles.

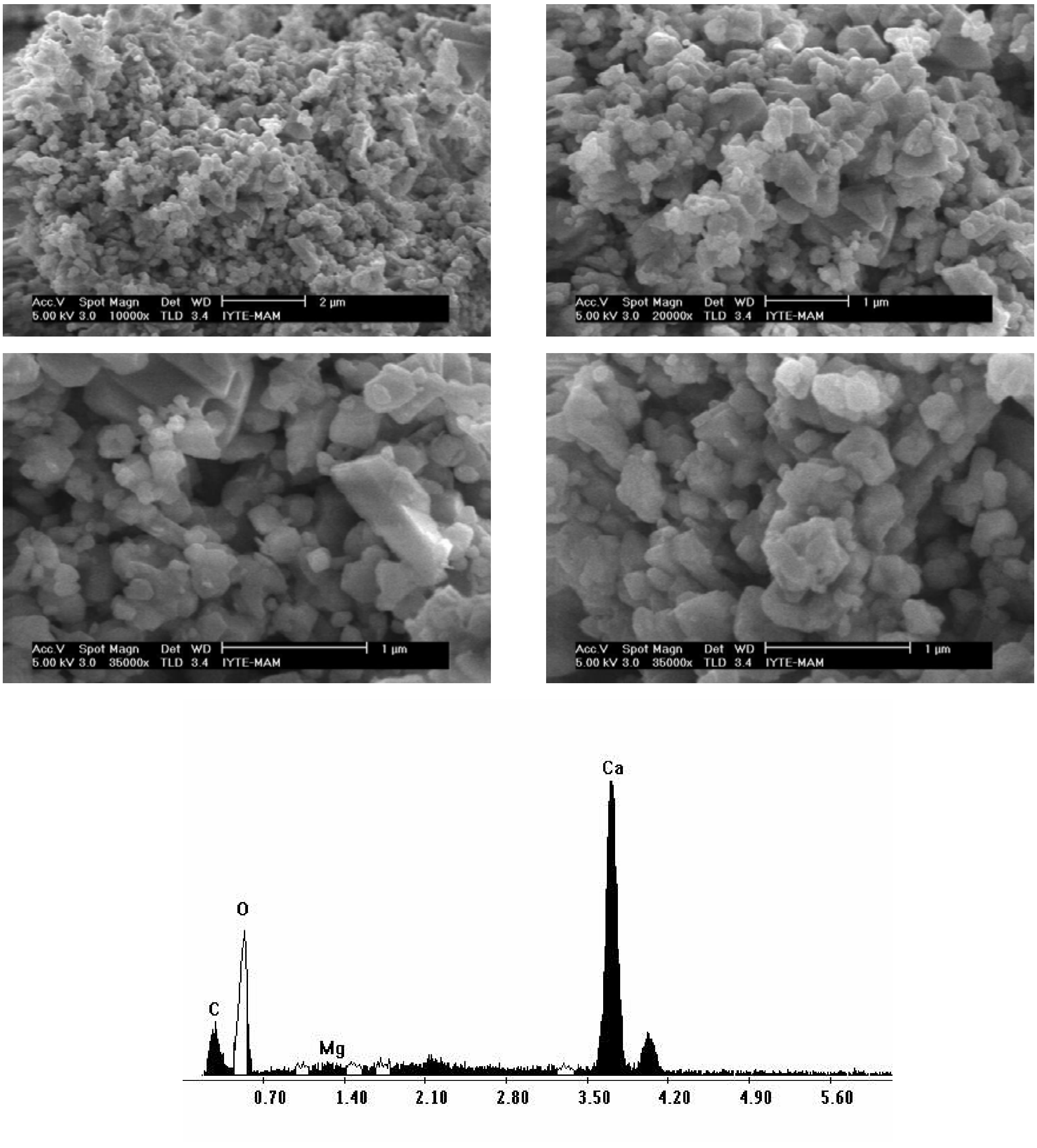


Figure 3.21. Secondary electron images and the EDS spectrum of calcium hydroxide formed by slaking of calcined Marmara marble.

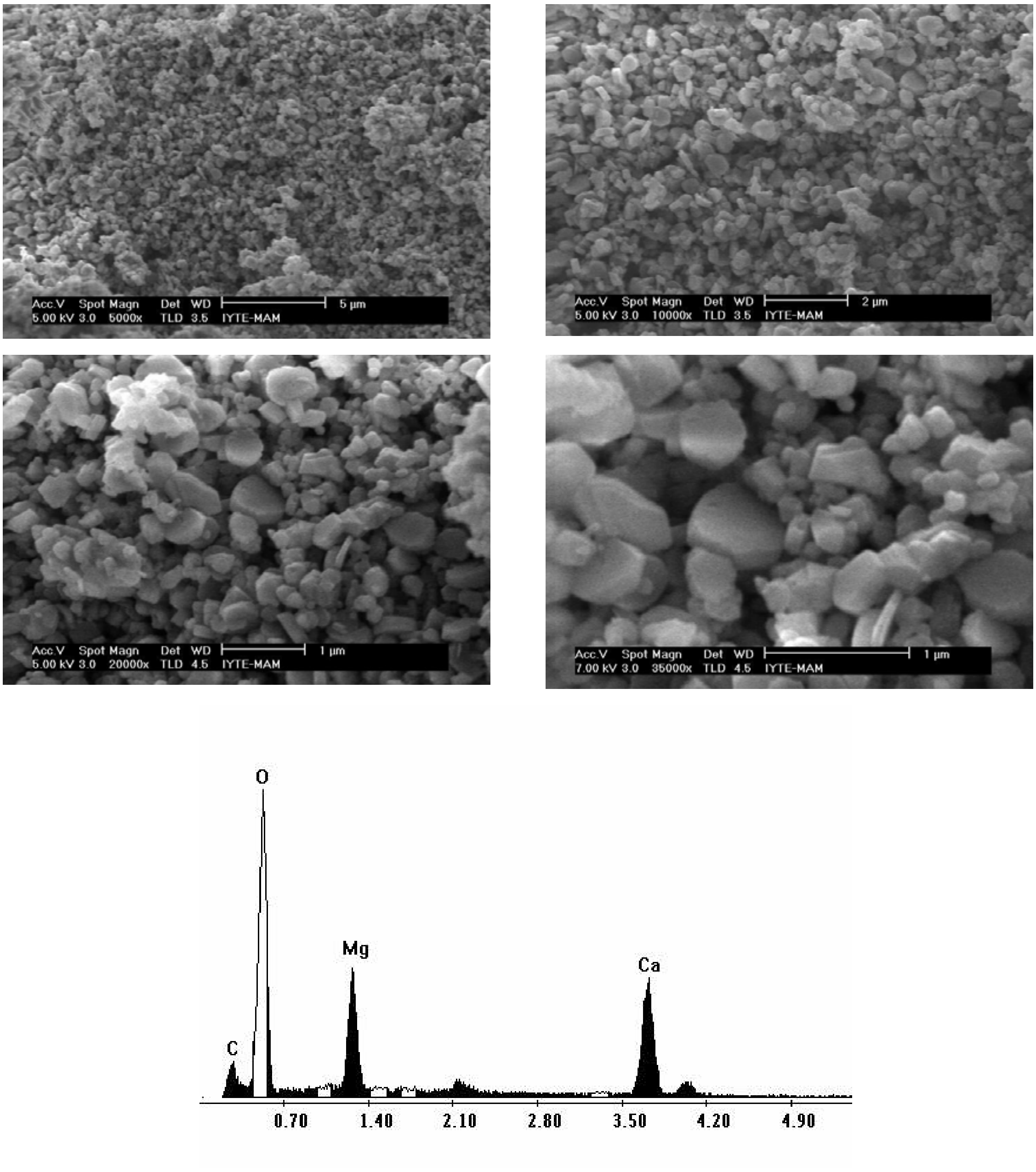


Figure 3.22. Secondary electron images and the EDS spectrum of calcium hydroxide crystals formed by slaking of the calcined Muğla marble.

3.12. Microstructural Characteristics of Limes Produced from Slaking of Calcined White and Grey Limestones

The calcium hydroxide crystals which are formed by slaking of heated white and grey limestones differ from the crystals of Marmara and Muğla marbles. Limes which are formed by grey and white limestones have an amorphous appearance, whereas limes produced from Marmara and Muğla marbles have a microcrystalline structure. (Figures 3.23, 3.24). On scanned electron micrographs, formed limes appear as a cluster of very fine particles having less than 1 micrometer diameter.

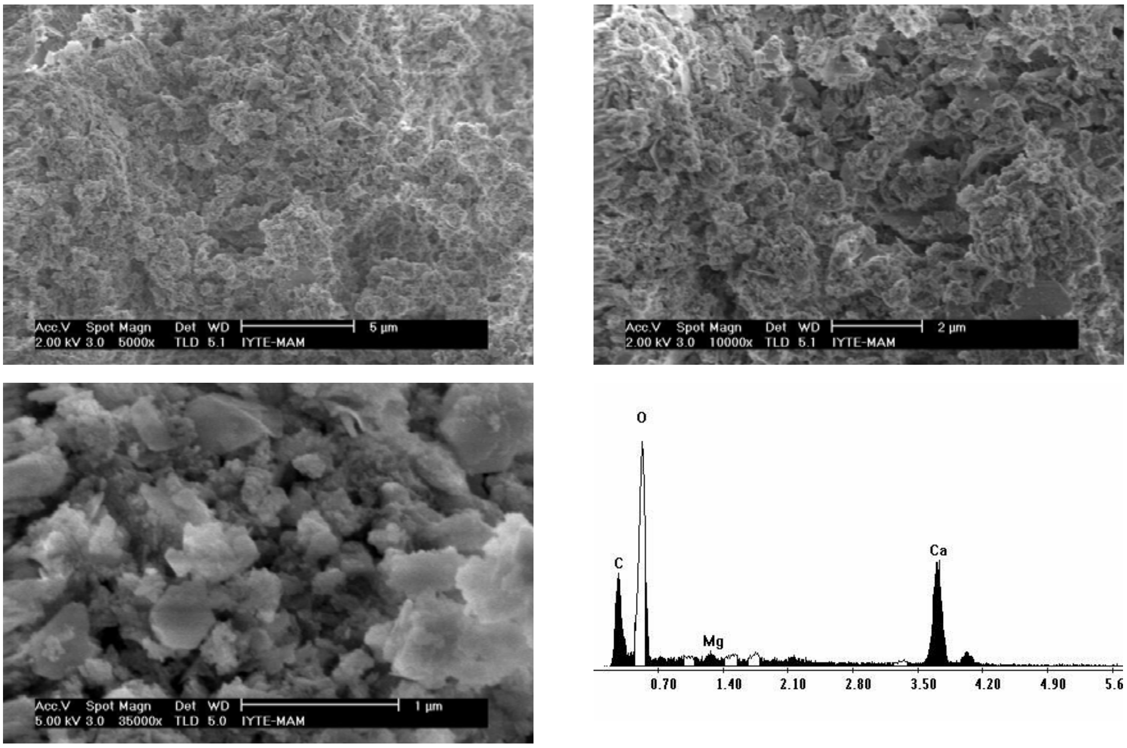


Figure 3.23. Secondary electron images and the EDS spectrum of calcium hydroxide crystals formed by the slaking of calcined white limestone.

Differently from the white limestone, on SEM pictures of grey limestone weathered textured of diatomite due to the formation of calcium silicate, were observed as well as very fine calcium hydroxide crystals (Figure 3.24).

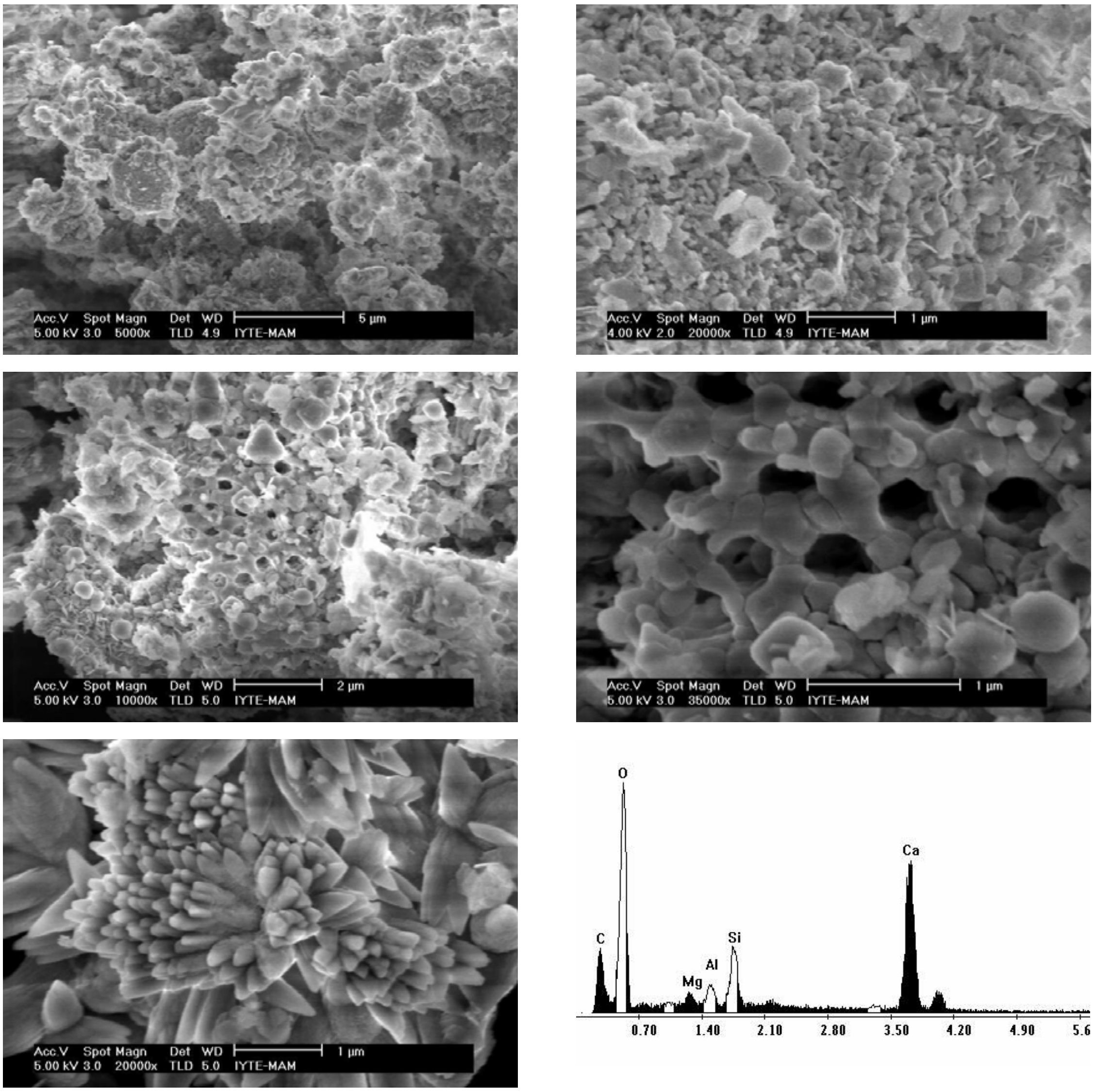


Figure 3.24. Secondary electron images and the EDS spectrum of calcium hydroxide and calcium silicate crystals formed by the slaking of calcined grey limestone.

3.13. Mineralogical Composition of Carbonated Limes Produced from Calcined Marbles and Limestones

The carbonation of lime in the air is done by the reaction of carbon dioxide. The carbonation reaction is exothermic (Reaction 3.4).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O + 74\ KJ \qquad \textbf{(Reaction 3.4)}$$

The rate of the carbonation depends on the CO_2 concentration and pressure, moisture content, temperature, relative humidity and thickness of specimen (Silva et.al. 2006).

During the carbonation, calcium hydroxide reacts with the carbon dioxide and forms calcite crystals. There are several stages in the carbonation process of the lime (Arandigoyen et al. 2005). They are;

a) CO_2 diffuses through the lime being influenced by the microstructure and by the water content
b) The carbon dioxide is dissolved in the water
c) The chemical equilibrium of CO_2 occurs and
d) The precipitation of calcite occurs

After the process, the volume is increased by 11.8% due to carbonation of calcium hydroxide (Dario et al. 2005).

In this study calcined marbles and limestones (quicklimes) were hydrated with distilled water in the glass beaker until lime putty was produced. The lime putty was then spread out on glass slides and carbonated for one month in the laboratory. During carbonation, the lime was wetted with distilled water. After one month, the samples were dried in an oven at 40 °C for 24 hours. Mineralogical compositions of the carbonated lime were determined by using a Philips X-pert X-ray diffraction (XRD) and a Spectrum BX II FTIR spectrometer (Perkin Elmer). After the carbonation of lime, only calcium carbonate peaks were observed in the XRD patterns of the Marmara marble, and white limestones (Table3.7, Figures 3.25, 3.26). This shows that limes produced from calcined Marmara marble and white limestone have been completely carbonated (Figures 3.25, 3.26). However, an incomplete carbonation reaction in the lime produced from the Muğla marble has been observed after a month. This may explain the higher thickness of the lime putty on the glass compared to the lime of Marmara marble.

After the carbonation of lime produced from the grey limestone, mainly calcium carbonate peaks and a basic peak of calcium silicate in low intensity have been observed in the XRD patterns (Figure 3.25). The disappearance of calcium silicate peaks (C_2S) in the XRD patterns of lime was explained by the formation of calcium silicate hydrate (CSH) with water. The expected main XRD peaks of CSH were not observed in the carbonated lime. This was probably due to the amorphous character of CSH or its principal peaks overlap with calcite (Luxan 1996).

Table 3.7. Minerals identified by XRD analysis after carbonation.

Samples	**Calcite (CaCO3)**	**Lime ($Ca(OH)_3$)**	**Brucite ($Mg(OH)_2$)**	**Calcium silicate (Ca_2SiO_4)**
Marmara	+++	-	-	-
Mugla	+++	+	+	-
White	+++	-	-	-
Grey	+++	-	-	+

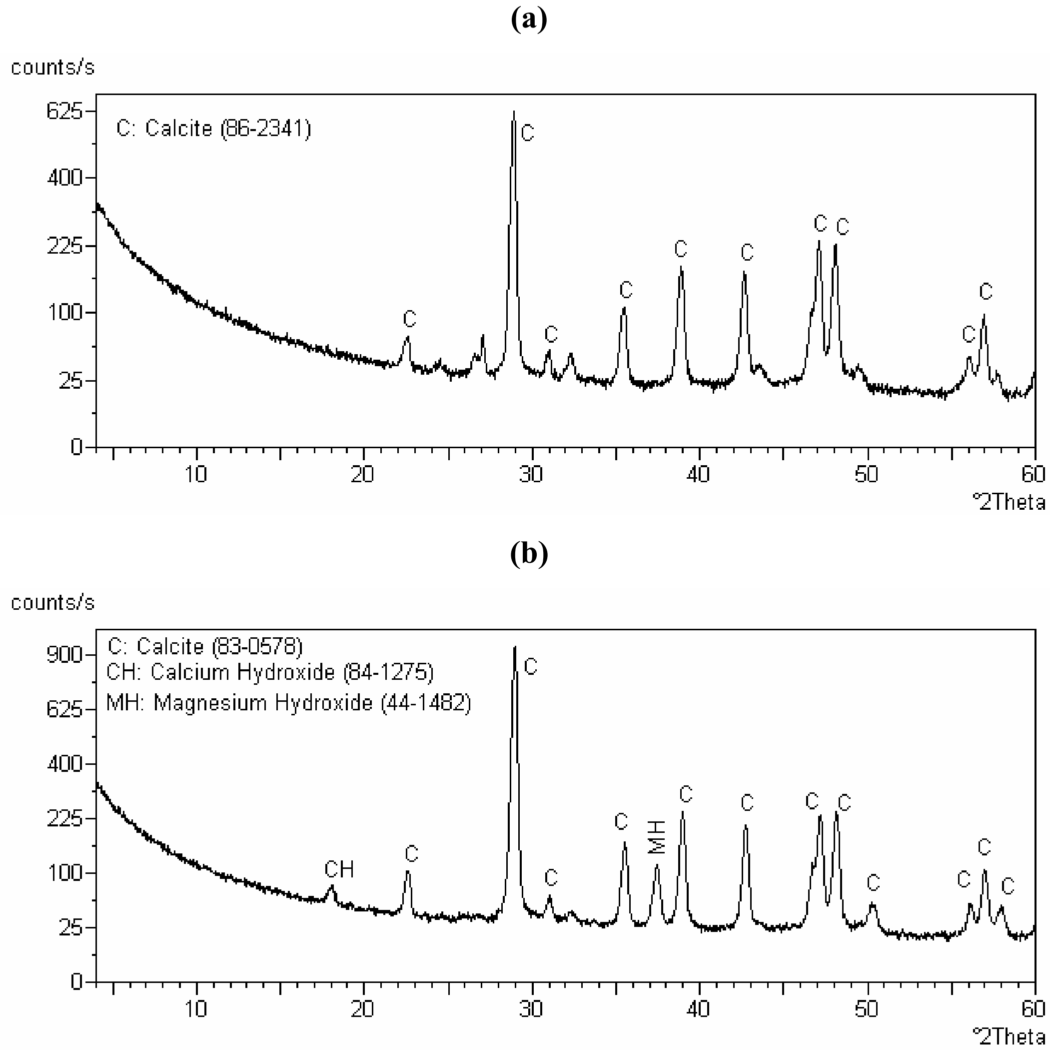


Figure 3.25. XRD patterns of carbonated (a) Marmara and (b) Muğla limes.

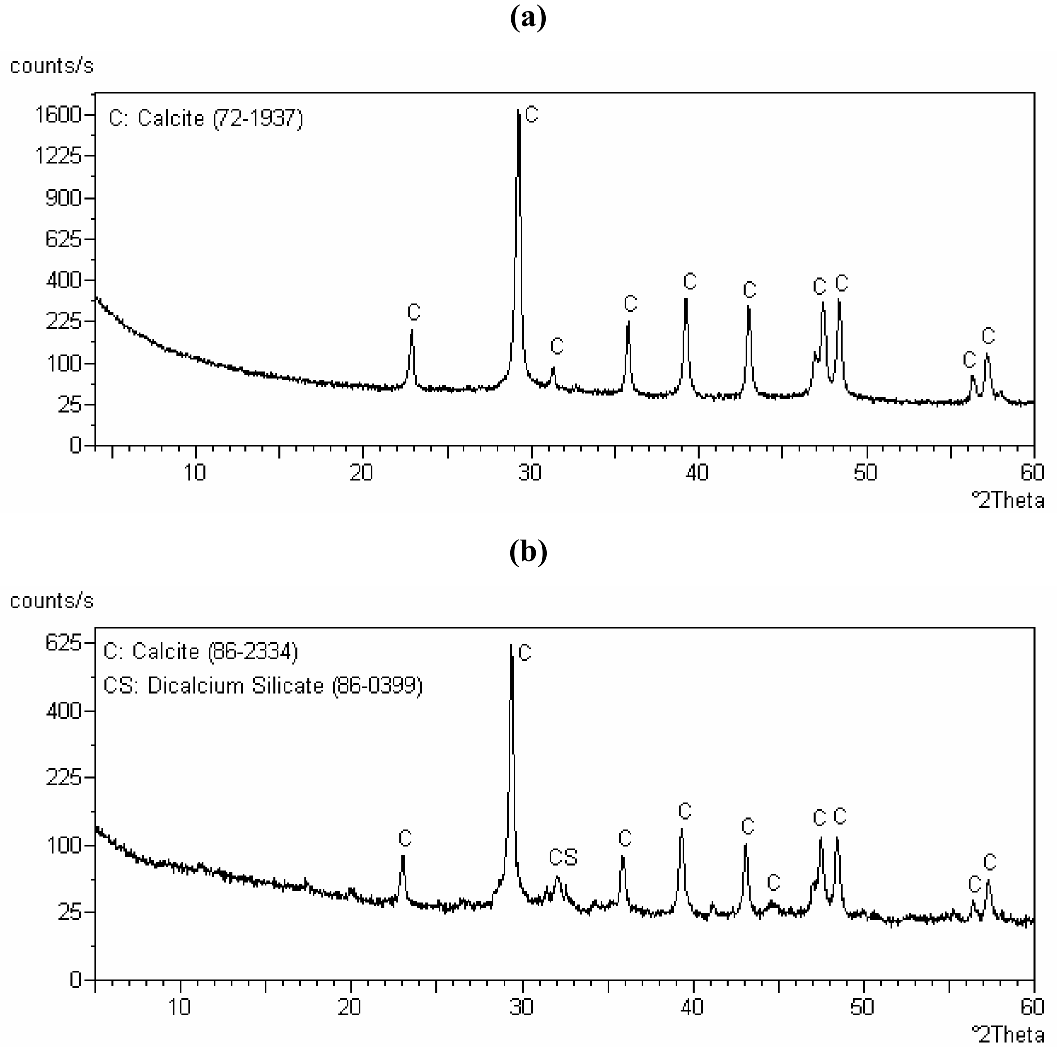


Figure 3.26. XRD patterns of carbonated limes produced from (a) white and (b) grey limestones.

3.14. Microstructure of Carbonated Lime Produced from Marmara and Muğla Marbles

SEM-EDS analysis indicated that carbonated limes produced from Marmara and Muğla marbles were composed of micritic calcite crystals (Figures 3.27, 3.28). Crystals are nearly between 2-5 μm in size and they are well developed crystalline structures.

When carbonation of lime is completed, calcium hydroxide crystals transforms into a much denser calcite crystal structure. Pore size distribution shifts towards smaller pores. Volume of the calcium hydroxide increase when it transforms into calcite (Arandigoyen et al. 2005). The volume increases by 11.8% due to carbonation of calcium hydroxide. However, excess water present in the lime causes the shrinkage of the lime due to the evaporation. The evaporation of the excess water in the lime leads also to the porous structure (Arandigoyen et al. 2005).

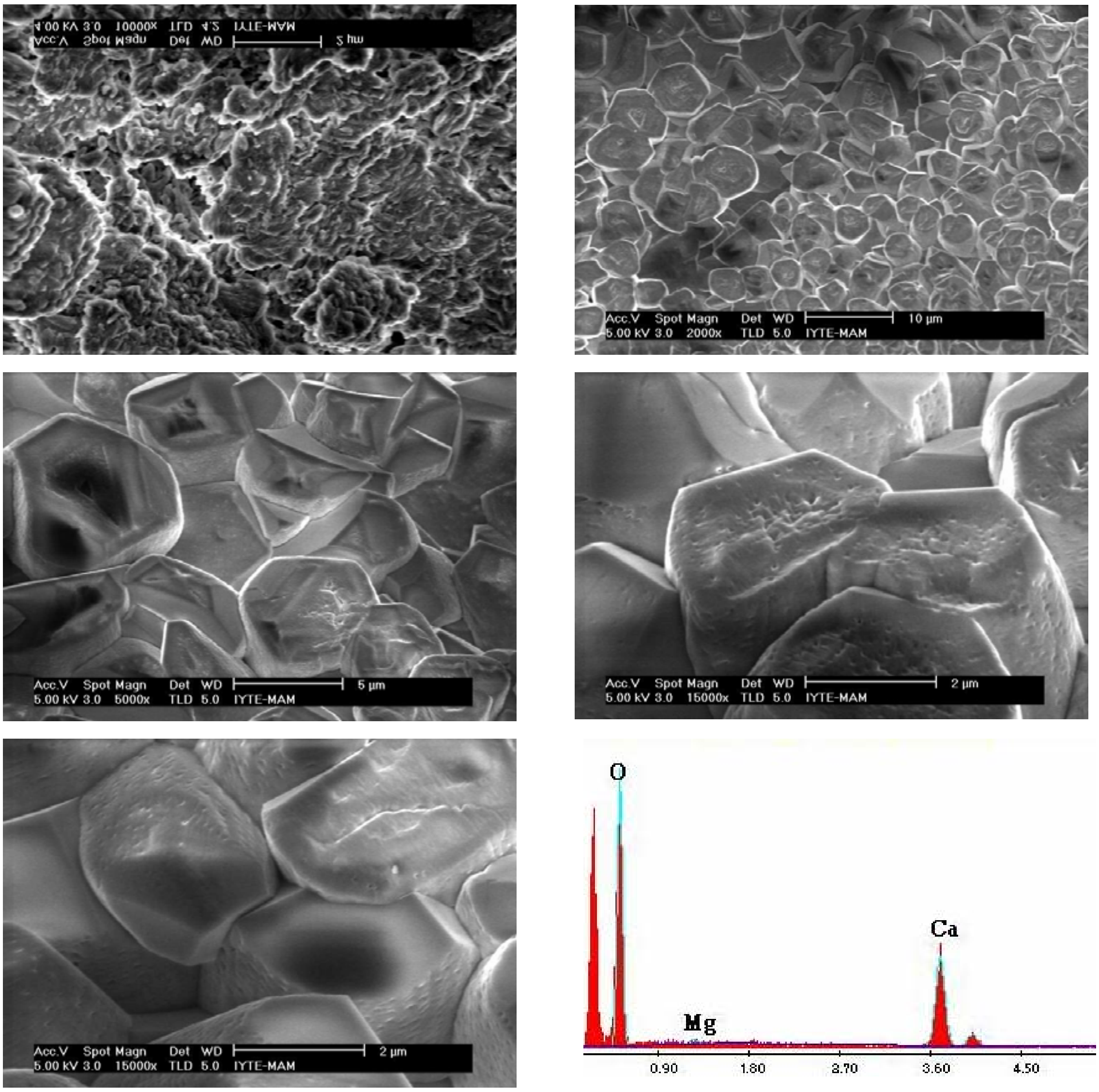


Figure 3.27. Secondary electron images and EDS spectrum of carbonated lime produced from Marmara marble.

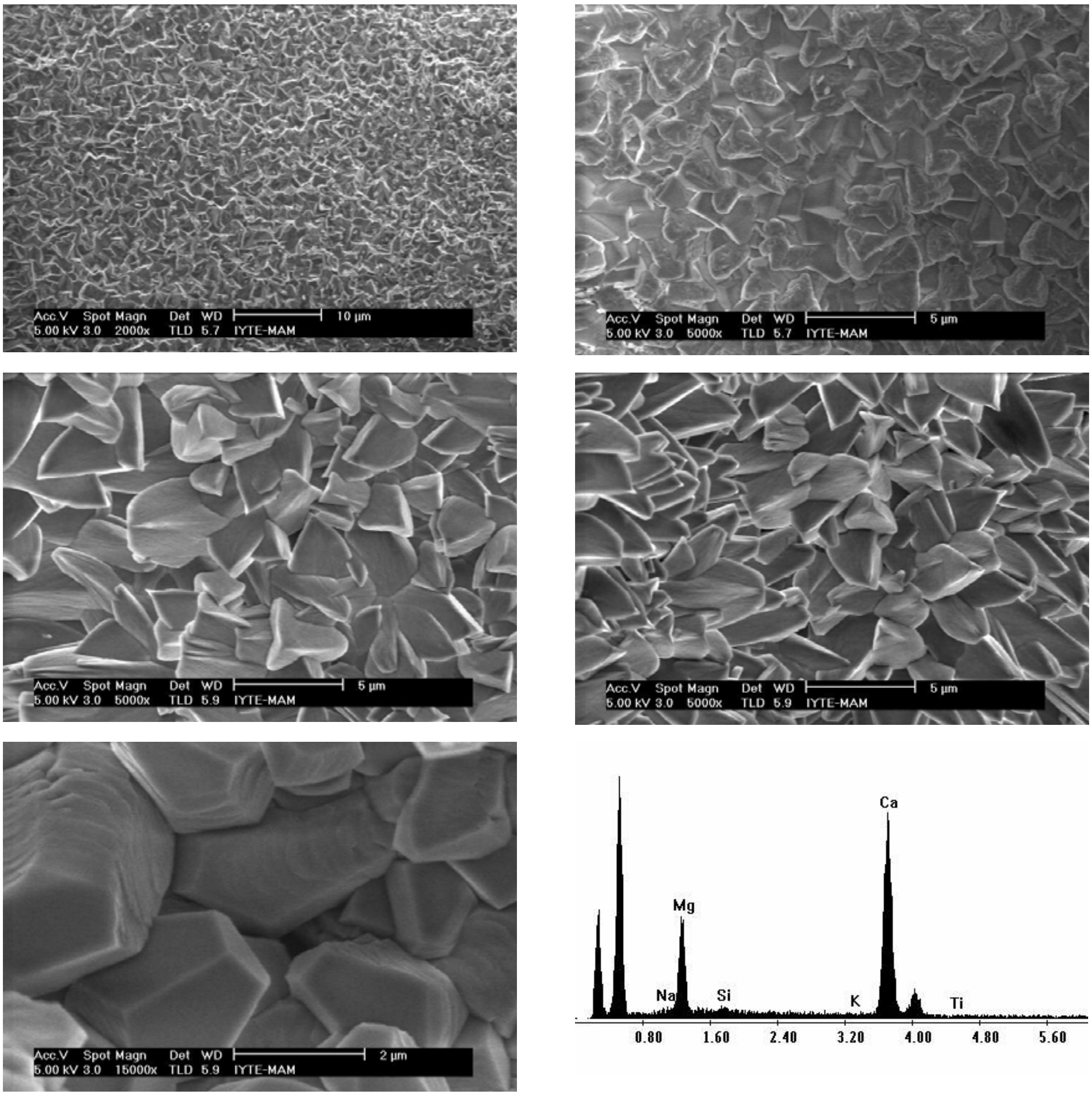


Figure 3.28. Secondary electron images and EDS spectrum of calcite crystals containing magnesium in carbonated lime produced from Muğla marble.

3.15. Microstructure of Carbonated Lime Produced from White and Grey Limestone

SEM-EDS analysis indicated that carbonated lime produced from white limestone was composed of micritic calcite crystals (Figure 3.29). Crystals are nearly 4 μm in size and they were well packed together (Figure 3.29).

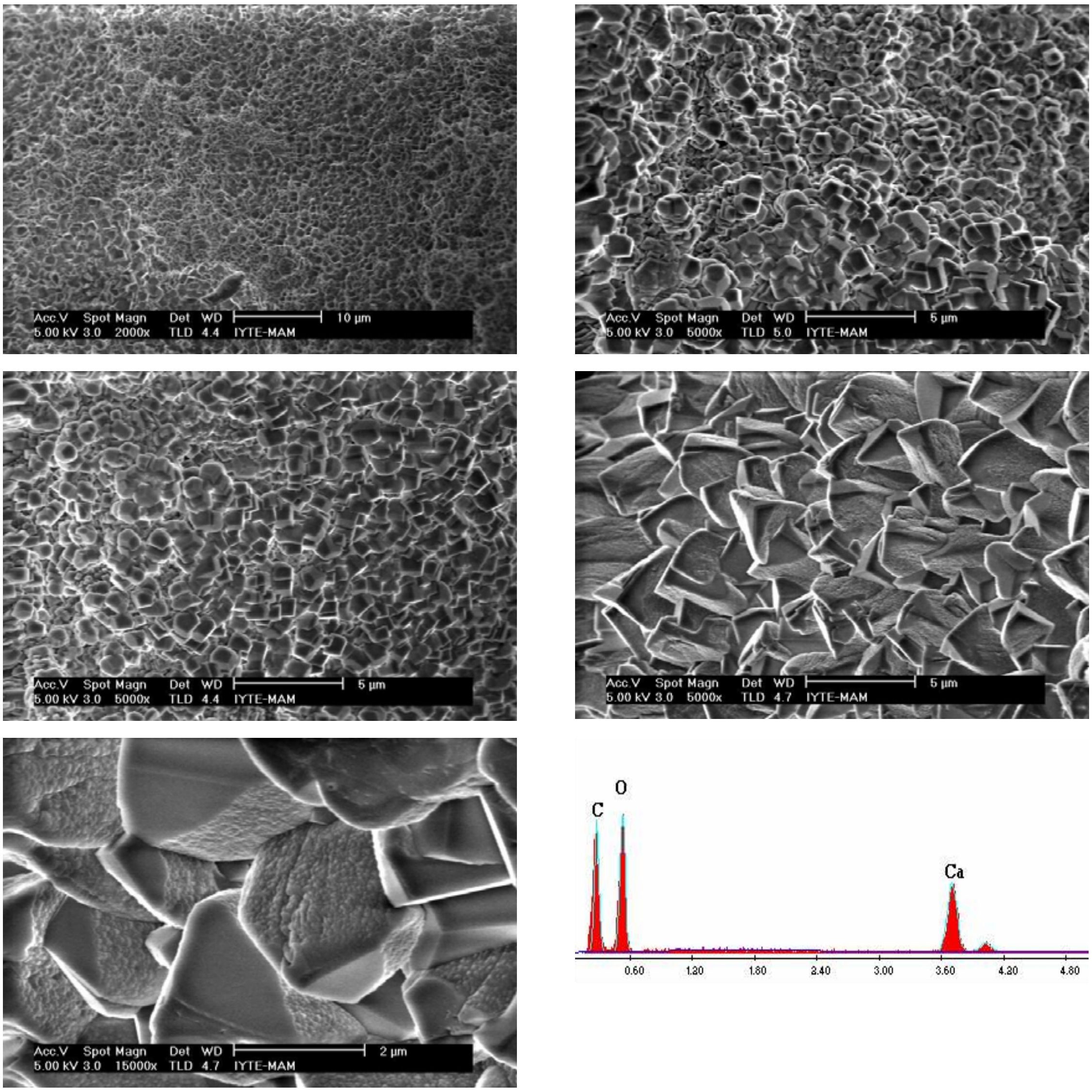


Figure 3.29. Secondary electron images and EDS spectrum of calcite crystals in carbonated lime produced from white limestone.

SEM-EDS analysis indicated that carbonated lime produced from grey limestone was composed of micritic calcite crystals connected with fibrous network rich in silicon oxide (Figure 3.30). Diatoms in the carbonated lime were weathered due to the formation of amorphous needle like calcium silicate hydrate formation (Figure 3.31).

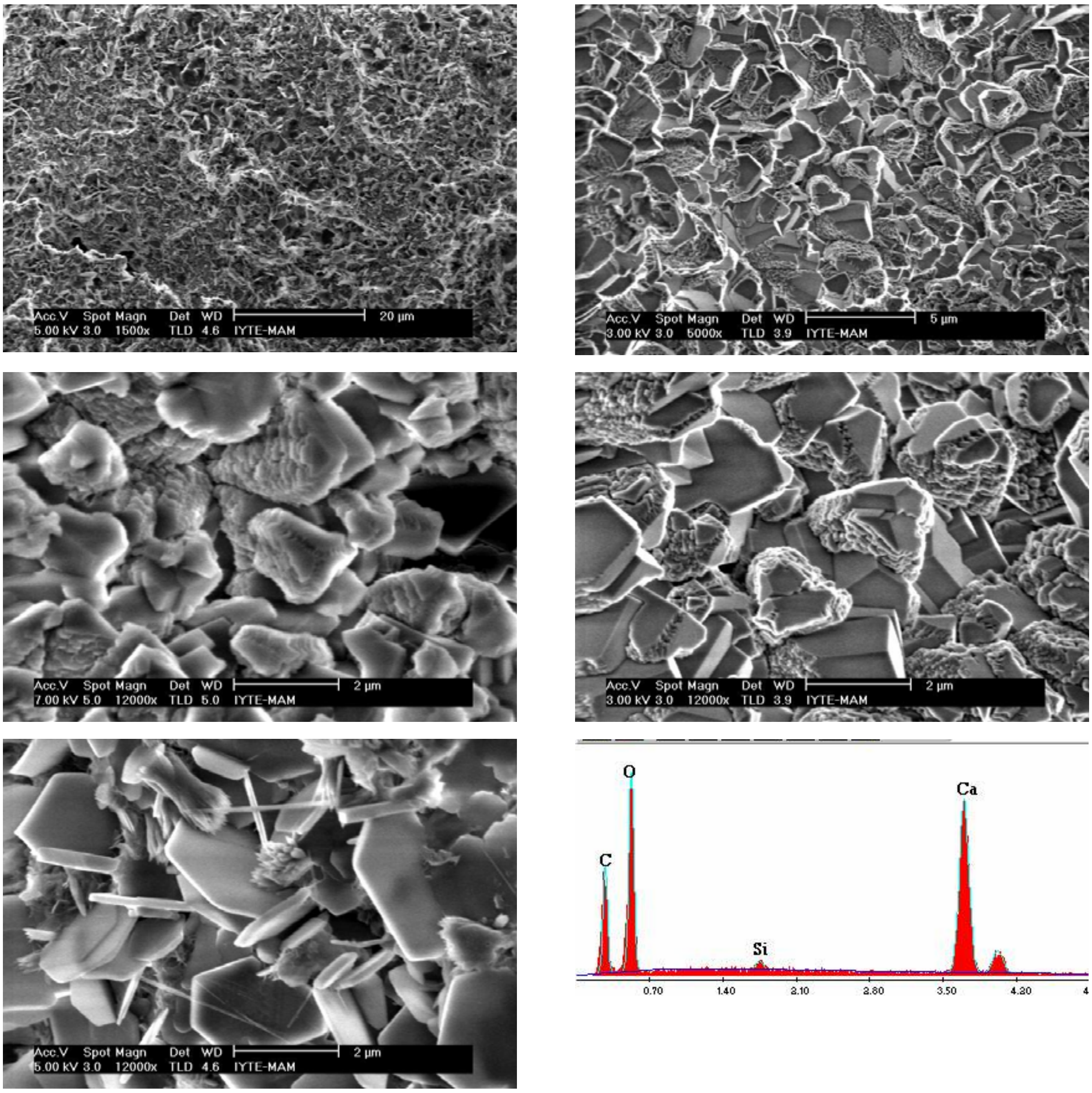


Figure 3.30. Secondary electron images and EDS spectrum of calcite crystals in carbonated lime produced from grey limestone.

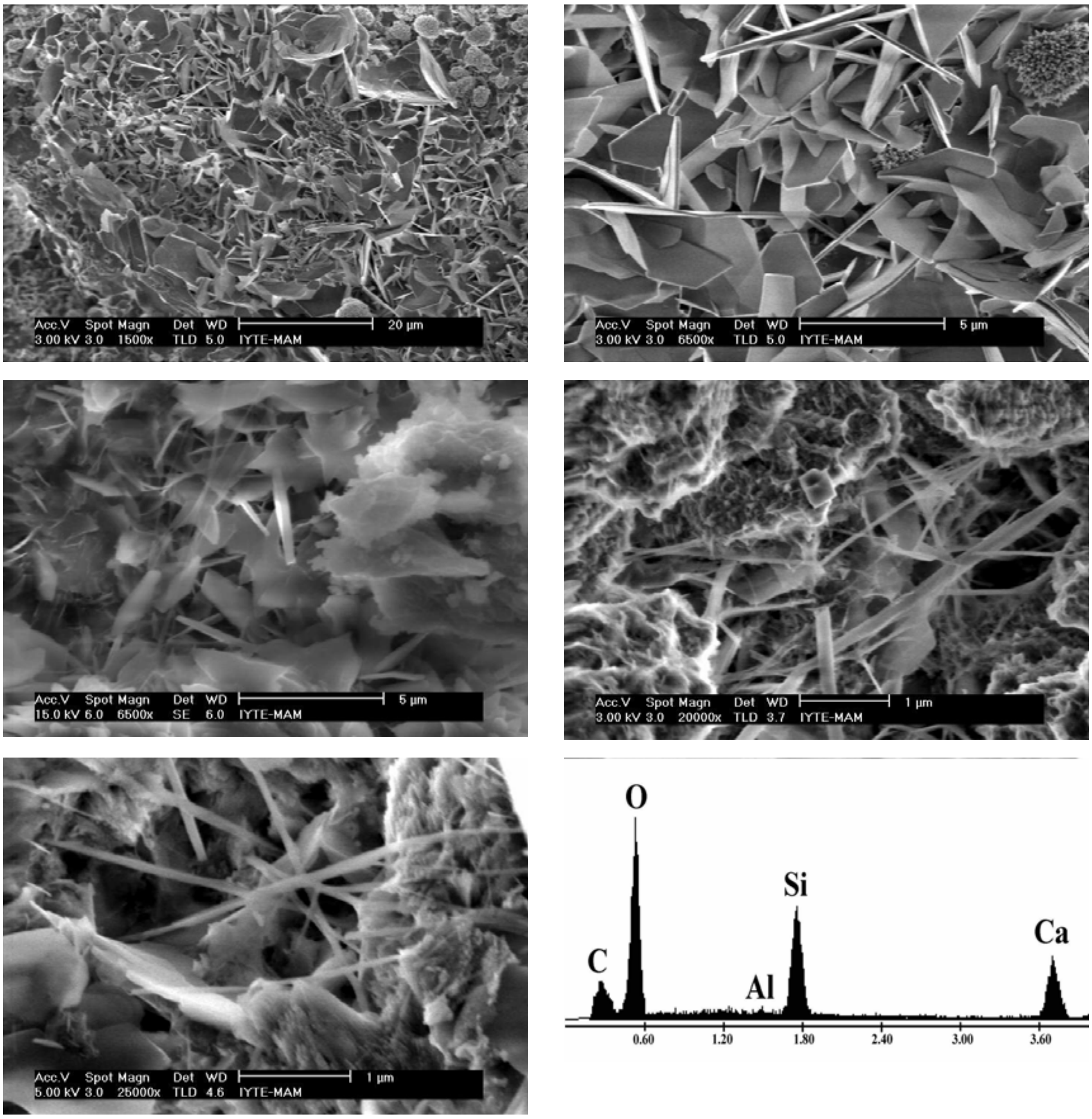


Figure 3.31. Secondary electron images and EDS spectrum needle like calcium silicate hydrate formation in carbonated lime produced from grey limestone.

3.16. Hydraulicity of the Carbonated Limes

Hydraulic properties of lime can be determined by calculating hydraulic (HI) and cementation (CI) indices according to Boynton formula (Reactions 3.5, 3.6). The higher indices values indicate the more hydraulic character of lime (Table 3.8).

$$\mathrm{HI} = \frac{\%\mathrm{Al_2O_3} + \%\,\mathrm{Fe_2O_3} + \%\,\mathrm{SiO_2}}{\%\mathrm{CaO} + \%\mathrm{MgO}} \qquad \textbf{(Equation 3.1)}$$

$$\mathrm{CI} = \frac{2.8\ \%\,\mathrm{SiO_2} + 1.1\,\%\mathrm{Al_2O_3} + 0.7\,\%\,\mathrm{Fe_2O_3}}{\%\mathrm{CaO} + 1.4\,\%\mathrm{MgO}} \qquad \textbf{(Equation 3.2)}$$

The cementation and hydraulicity indices values of lime are given in Table 3.9. According to the cementation and hydraulic indices values, lime produced from grey limestone limes can be classified as highly hydraulic lime. On the other hand, limes produced from Marmara and Muğla marble are not hydraulic (Table 3.9). Because their hydraulic and cementation indices are less than 0.1 and 0.3. The lime produced from white limestone can be accepted as weakly hydraulic.

Table 3.8. Classification of limes according to cementation and hydraulicity indices.

Lime	Hydraulic Index	Cementation Index
Weakly hydraulic	0.1 – 0.2	0.3 -0.5
Moderately hydraulic	0.2-0.4	0.5-0.7
Highly hydraulic	<0.4	0.7 -1.1

Table 3.9. Cementation and hydraulicity indices of carbonated limes.

Sample	Hydraulic Index	Cementation Index
Mar-M	0.00	0.00
Mu-M	0.06	0.11
W-L	0.12	0.22
G-L	0.58	1.35

Hydraulicity of lime can also be evaluated by thermal analysis (TGA). For this purpose, percentages of weight losses at 200-600°C and at temperatures over 600°C were determined on carbonated limes. Weight loss at temperatures of 200-600°C was mainly due to loss of chemically bound water of hydraulic products, such as calcium silicate hydrates and calcium aluminate hydrates (Bakolas et al. 1995). Weight loss at temperatures over 600°C was due to carbon dioxide released during the decomposition of carbonates (Bakolas et al. 1995). It has been reported that if the ratio of CO_2/H_2O is between 1 and 10 in a given mortar, it can be accepted as a hydraulic lime mortar (Moropoulou et al. 2000, Moropoulou et al. 2001).

Table 3.10. The weight losses between 200°C and 600°C and weight losses over 600°C of carbonated limes.

Sample	**200-600 °C (H_2O)**	**>600 °C (CO_2)**	**CO_2/H_2O**
Mar-M	0.67	46	68.7
Mu-M	5.1	38.63	7.6
W-L	6.2	38.55	6.2
G-L	6.4	25.6	4

Table 3.9 shows that, limes excepting Marmara marble have hydraulic properties. Muğla marble does not contain silica and aluminum that are needed for formation of hydraulic lime. Therefore, lime produced from Muğla marble is not expected to be hydraulic. Weight loss in carbonated lime observed at 200-600 °C temperature can be explained by lime that is not carbonated. Observing non-carbonated lime in XRD patterns of lime produced from Muğla marble support this idea. Similarly, white limestone does not contain sufficient silica and alumina. Therefore, the hydraulic properties of the lime produced from white limestone can be explained by non-carbonated lime.

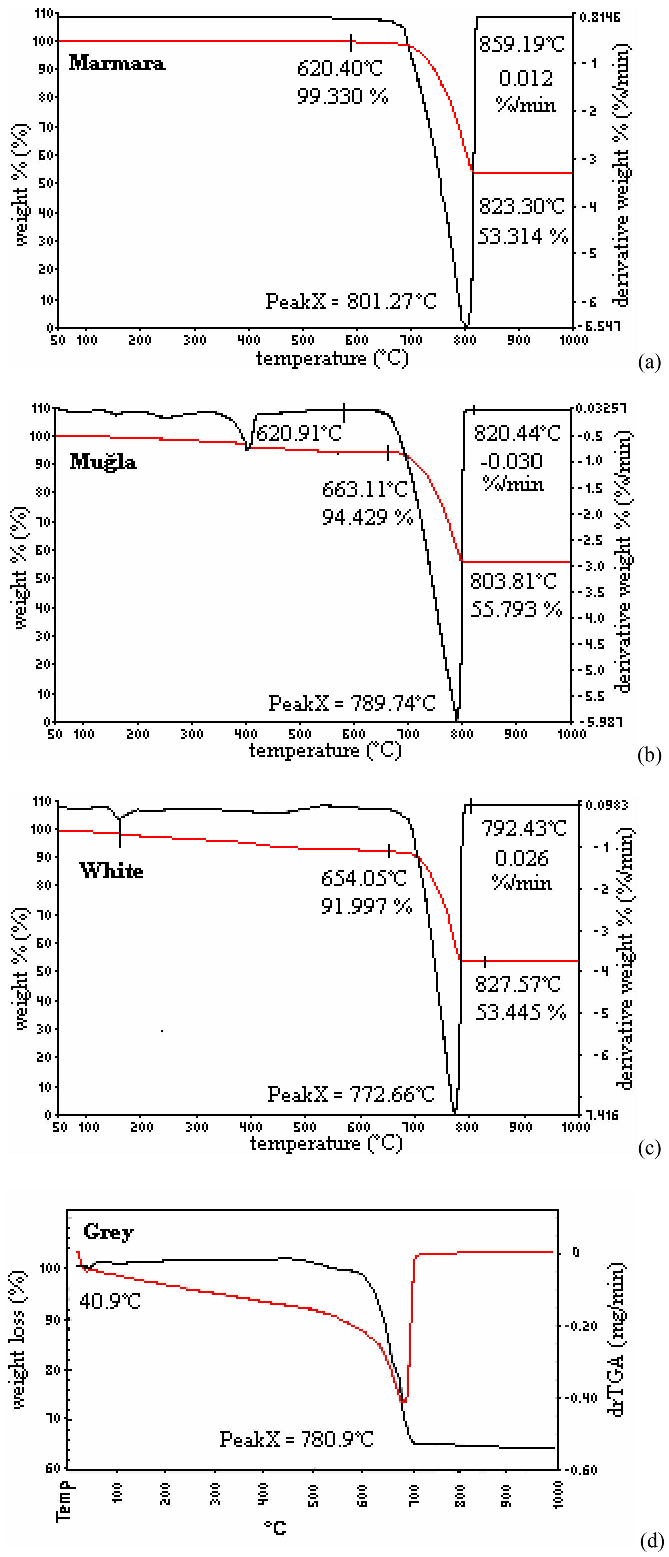


Figure 3.32. TGA graphs of carbonated limes produced from (a) Marmara, (b) Muğla marbles and (c) white and (d) grey limestones.

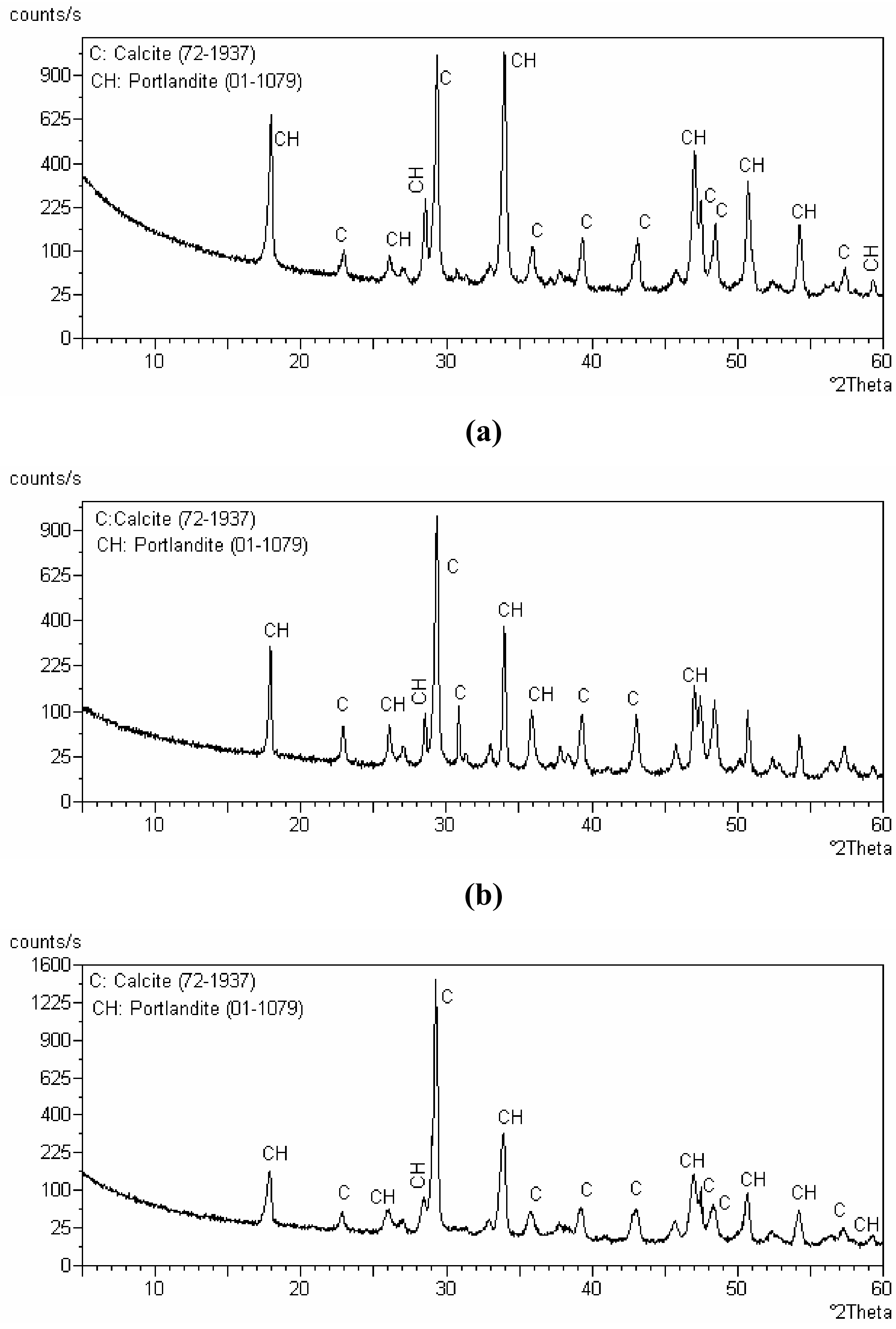
3.17. Mineralogical Compositions of Lime Mortars after One Year Carbonation

Mechanical properties of mortars (4.5x5 cm), which were prepared by mixing marble aggregates and mortars produced from limestones, were tested after 3, 6, and 12 months. Mineralogical compositions of samples broken in these tests were determined by XRD analysis. The minerals determined by these analysis were shown in Figures 3.33, 3.34, 3.35, 3.36 and Table 3.11.

As is shown in XRD analysis, calcium hydroxide peaks have become less intense after 3 months. It shows that, carbonation is enhanced by time. (Table 3.11). However, there are no calcium silicate peaks in mortars prepared by lime produced from grey limestone. It refers that, during the carbonation process calcium silicate has transformed into amorphous calcium silicate hydrate by the reaction of moisture in the air.

Table 3.11. Ratios of intense peak of $CaCO_3$ (29.4 2Θ) to $Ca(OH)_2$ (34.0 2Θ) after 3, 6 and 12 months carbonation.

Samples	**$CaCO_3$ / $Ca(OH)_2$**			
	Initial	**3 Months**	**6 Months**	**12 Months**
Marmara	0	0.86	4.08	2.97
Mugla	0	1.54	5.41	2.72
White	0	0.98	3.09	19.93
Grey	0	4.76	9.31	31.6

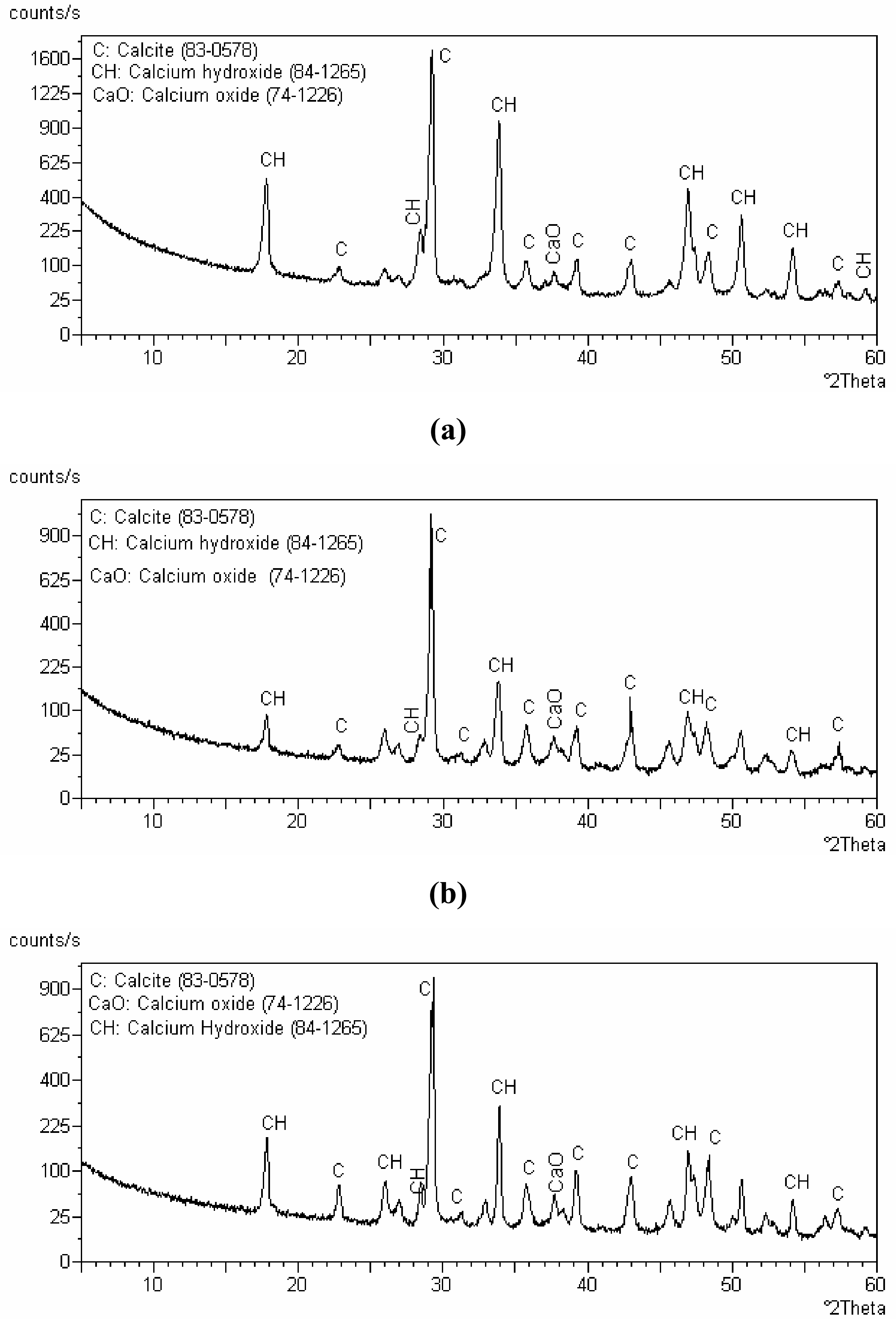


(a)

(b)

(c)

Figure 3.33. XRD patterns of mortars produced from Marmara lime after (a) theree, (b) six and (c) twelve months carbonation.



(a)

(b)

(c)

Figure 3.34. XRD patterns of mortars produced from Muğla lime after (a) theree, (b) six and (c) twelve months carbonation.

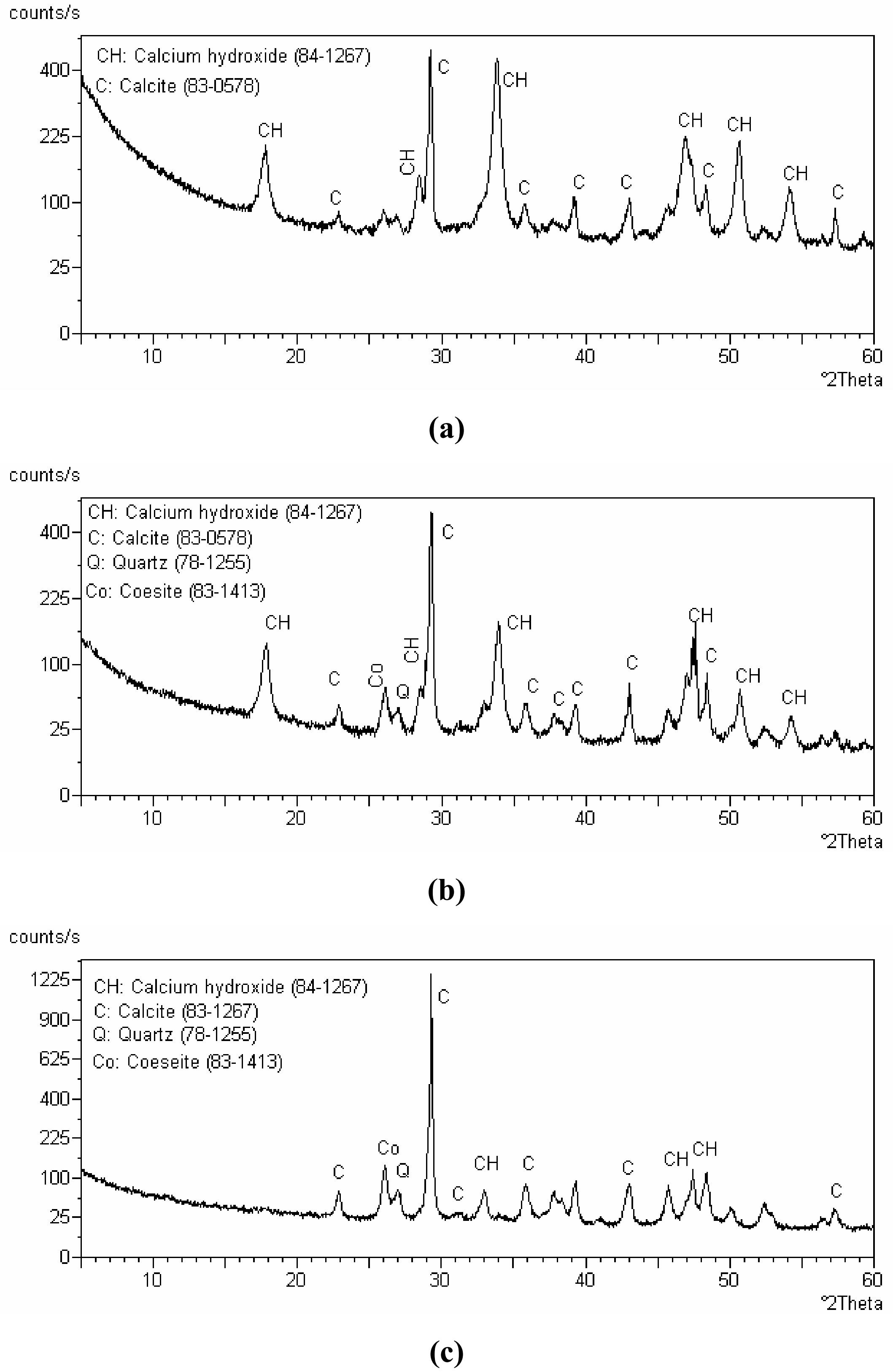


Figure 3.35. XRD patterns of mortars produced from white lime after (a) theree, (b) six and (c) twelve months carbonation.

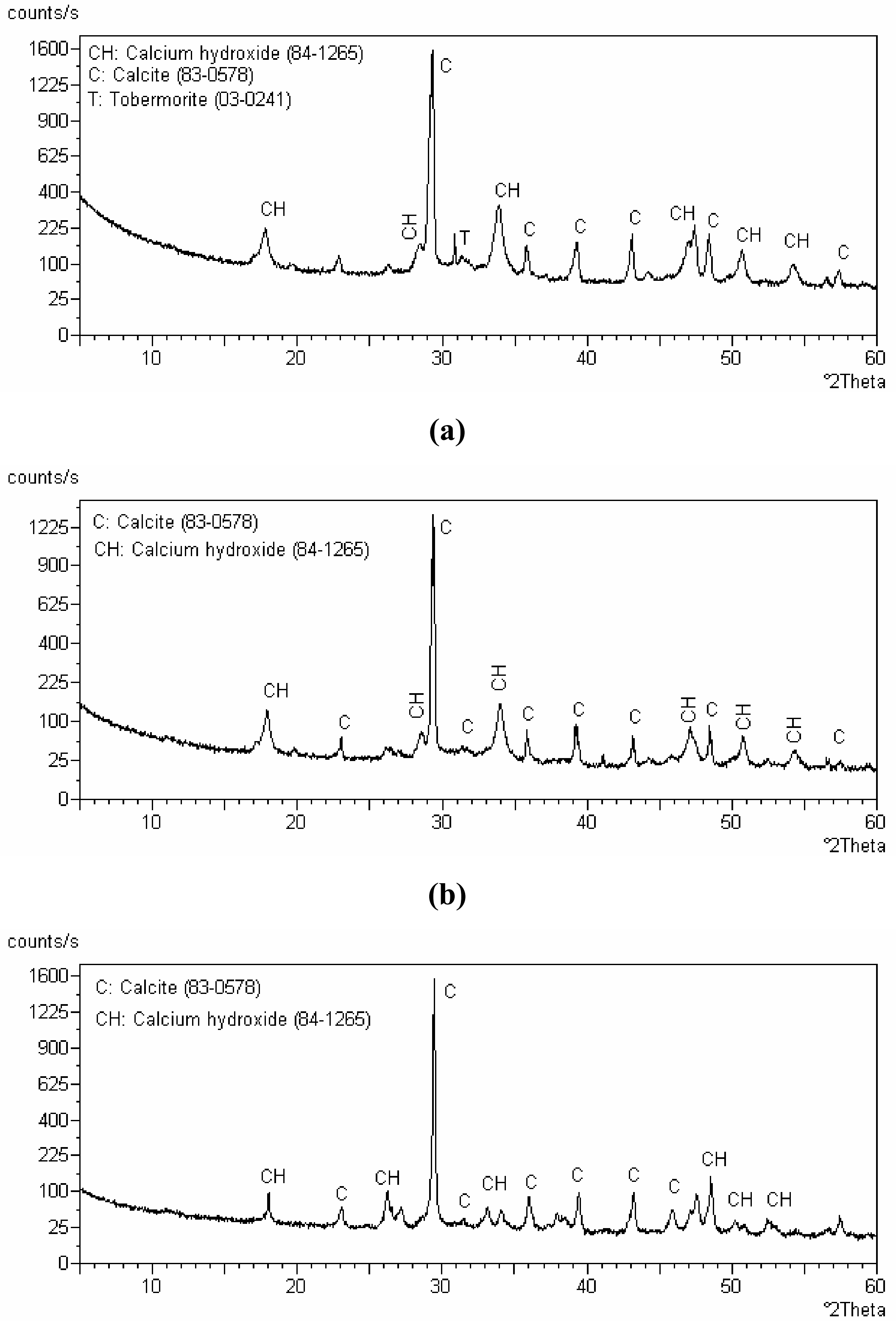


Figure 3.36. XRD patterns of mortars produced from grey lime after (a) three, (b) six and (c) twelve months carbonation.

3.18. Uniaxial Compressive Strengths and Modulus of Elasticities of Test Mortars

Uniaxial compressive strengths and modulus of elasticities of mortars were determined after 3, 6, and 12 months of carbonation in the laboratory conditions. Compressive strength tests were carried out with AG-I Shimadzu under a uniaxial pressure of 15 KN.

Figure 3.37. Uniaxial compressive strengths and modulus of elasticities of test mortars.

According to the test results, mortar produced from grey limestone had the highest compressive strength values of 3.70 MPa., after 3 months carbonation process while the mortar produced from white limestone had the lowest values of 0.70 MPa. The Muğla and Marmara marbles had the values of 1.02 MPa. and 1.17 MPa. The second test was performed after 6 months carbonation process. When compared to the first tests results, a remarkable increase in the values of the limes produced from grey and white limestone have been observed due to increase in waiting period. The value of the lime produced from grey limestone was 5.83MPa. and the value of lime produced from white limestone was 1.55 MPa. However, the limes produced from Muğla and Marmara marbles had approximate values. Similarly, according to the last tests results, after 12 months carbonation period, the strongest lime that resist highest compression forces was the one produced from grey limestone which had the value of 6.62 MPa. The lime produced from white limestone had the secondary highest value of 2.17 MPa. It is shown that, there is a significant increase in the compressive strengths values of the lime produced from grey limestone due to the highly hydraulic properties of the lime since hydraulic limes harden in time. Similarly, a considerable increase has been observed in the values of the lime produced from white limestone which is weakly hydraulic. On the other hand, limes produced from Muğla and Marmara marbles which are non-hydraulic limes, had lower values of 1.44 MPa. and 1.46 MPa.

In order to understand the elastic behaviour of the mortars against the applied forces, modulus of elasticitiy of the mortars were calculated after 3, 6 and 12 months carbonation processes. According to the results, the lime produced from grey limestone have the highest modulus of elasticity values of 218.08 MPa., 277.59 MPa., 302.61 MPa. The values of lime produced from white limestone were 23.44 MPa., 129.14 MPa., 98.77 MPa. The lime of Marmara marble had the values of 42.03 MPa., 97.00 MPa., 74.89 MPa. and the lime of Muğla marble had the values of 47.86 MPa., 69.63 MPa., 73.79 MPa.

Table 3.12. Compressive strength values of the samples.

Sample	Compressive Strength (MPa.) after 3 months	Compressive Strength (MPa.) after 6 months	Compressive Strength (MPa.) after 12 months
grey	3.7	5.8	6.6
white	0.7	1.6	2.2
marmara	1.2	1.7	1.5
muğla	1.0	1.3	1.4

Table 3.13. Modulus of elasticity values of the samples.

Sample	Modulus of Elasticity (MPa.) after 3 months	Modulus of Elasticity (MPa.) after 6 months	Modulus of Elasticity (MPa.) after 12 months
grey	218.1	277.6	302.6
white	23.4	129.1	98.8
marmara	42.0	97.0	74.9
muğla	47.9	69.6	73.8

CHAPTER 4

CONCLUSION

In this study, characteristics of lime produced from some marbles and limestones were investigated in order to compare their effects as binders on the lime mortars. For this purpose, limestones that contain low and high amounts of diatoms and marbles quarried from the city of Muğla and the Marmara Island were selected as stone samples.

The Marmara marble and white limestone are composed mainly of calcite crystals, whereas Muğla marble contains low amounts of dolomite crystals as well as calcite crystals. Furthermore, white limestone contains low amounts of SiO_2 and Fe_2O_3 differently from the Muğla and Marmara marbles. On the other hand, the grey limestone is mainly composed of $CaCO_3$, SiO_2 and Al_2O_3.

The sizes of the calcite crystals of the Marmara marble, which are tightly bounded to each other since the stone sample has a low porosity, are in the range of 2.2 to 3.6 mm. On the other hand, the Muğla marble has smaller calcite crystals that vary in the range of 22-800 micrometres. The white and grey limestones show small and large grain size calcite crystals that are distributed inhomogeneously in the stones.

The calcination temperature of the stones is around 800 °C. The calcined white limestone, Marmara and Muğla marble are mainly composed of calcium oxide. However, Muğla marble consists higher amounts of magnesium oxide that is derived from dolomite in its composition. On the other hand, calcinated grey limestone contains calcium silicate (Ca_2SiO_4) as well as calcium oxide (CaO). Formation of calcium silicate (Ca_2SiO_4) indicates that production of hydraulic lime at a relatively low calcination temperature is possible.

The slaked Marmara marble and white limestone are composed of portlandite crystals. However, the slaked Muğla marble contains magnesium oxide as well as portlandite in its composition. Owing to the formation of calcium silicate, the diatomites have weathered textures. Moreover, the calcium hydroxide crystals that are formed by slaking of the Marmara and the Muğla marbles have microcrystalline structure, while the grey and the white limestone have amorphous appearance.

The carbonated white limestone and the Marmara marble are composed of mainly calcium carbonate. However, lime produced from the grey limestone consist of calcium silicate hydrate as well as calcium carbonate. The carbonated lime produced from the grey limestone is composed of micritic calcite crystals connected with fibrous network rich in silicon oxide.

Carbonated limes produced from the Marmara and the Muğla marbles are composed of micritic calcite crystals that form well developed crystalline structures and vary in size between 2-5 µm. On the other hand, the calcite crystals of lime produced from the white limestone are nearly 4 µm in size and well packed together.

According to the cementation and hydraulic indices values, lime produced from grey limestone can be classified as highly hydraulic lime whereas the lime produced from white limestone can be accepted as weakly hydraulic. On the other hand, limes produced from Marmara and Muğla marble are not hydraulic.

According to the mechanical test results, the lime produced from grey limestone had relatively high compressive strength values compared to the others. It means that, hydraulic lime mortars have higher mechanical strength than non-hydraulic lime mortars.

This study has shown that, producing hydraulic limes at relatively low temperatures by using limestones containing diatoms is possible. Considering this result, it can be concluded that hydraulic lime could be produced by the calcining of limestone containing diatoms in historic kilns.

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