ARCHAEOMETRICAL STUDY ON MARBLE FORGERY

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

GÜNEŞ SONGÜL

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
ARCHAEOMETRY

JULY 2012

Approval of the thesis:

ARCHAEOMETRICAL STUDY ON MARBLE FORGERY

Submitted by **GÜNEŞ SONGÜL** in partial fulfillment of the requirements for the degree of **Master of Science in Archaeometry Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen ________________
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Ümit Atalay ________________
Head of Department, **Archaeometry**

Prof. Dr. Asuman Günal Türkmenoğlu ________________
Supervisor, **Geological Engineering Department, METU**

Prof. Dr. Şahinde Demirci ________________
Co-Supervisor, **Chemistry Department, METU**

Examining Committee Members:

Prof. Dr. Ay Melek Özer ________________
Physics Department, METU

Prof. Dr. Asuman Günal Türkmenoğlu ________________
Geological Engineering Department, METU

Assoc. Prof. Dr. Enver Bulur ________________
Physics Department, METU

Asst. Prof. Dr. Zeynep Kalaylıoğlu ________________
Statistics Department, METU

Asst. Prof. Dr. Çiğdem Atakuman ________________
Settlement Archaeology, METU

Date: 17.07.2012

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced materials and results that are not original to this work.

Name, Last Name : Güneş Songül

Signature :

ABSTRACT

ARCHAEOMETRICAL STUDY ON MARBLE FORGERY

Songül, Güneş
M.Sc., Graduate Program of Archaeometry
Supervisor : Prof. Dr. Asuman Günal Türkmenoğlu
Co-Supervisor: Prof. Dr. Şahinde Demirci

July 2012, 57 Pages

This thesis focuses on the detection of marble sculpture forgery made of cultured marble. Cultured marble is a mixture of marble dust, polyester and accelerators. Thus chemical analysis of cultured marble would give declined levels of calcium when compared to authentic sculptures. Since sample removal is a problem when dealing with archaeological heritage, the instrument used was portable X-Ray Fluorescence device which provides in situ analysis of the samples. Device has been used to analyze six authentic and four forgery sculptures. Seven of the sculptures were provided by Anatolian Civilizations Museum and three of them were provided by a sculpture workshop, Akşit Sanat. In the assessment of the results the software SPSS has been used. The results support the idea of lower levels of calcium in forgeries. Also cobalt and lead elements show distributional differences between authentic sculptures and forgeries. Further studies with a larger sample size is needed. However, the technique proves to be useful in distinguishing cultured marble sculptures from authentic marble sculptures.

Keywods: Marble Sculptures, Forgery, Cultured Marble

ÖZ

MERMER HEYKEL SAHTECİLİĞİ ÜZERİNE ARKEOMETRİK ÇALIŞMA

Songül, Güneş
Yüksek Lisans, Arkeometri Ana Bilim Dalı
Tez Yöneticisi : Prof. Dr. Asuman Günal Türkmenoğlu
Ortak Tez Yöneticisi: Prof. Dr. Şahinde Demirci

Temmuz 2012, 57 Sayfa

Bu tez, yapay mermer kullanılarak yapılan mermer heykellerin sahteliğinin tespit edilmesi için yapılmış bir çalışmadır. Yapay mermer, mermer tozu, polyester ve hızlandırıcıların karıştırılması ile yapılan bir malzemedir. Bu sebeple yapay mermerin kimyasal analizinin, gerçek mermer heykellerin mermerlerine oranla daha düşük kalsiyum miktarı vermesi beklenmektedir. Arkeolojik eserler söz konusu olduğunda örnek temini bir problem olduğundan araştırma için tahribatsız bir yöntem ve bununla ilgili taşınabilir X-Işınları floresans spektrometresi kullanılmıştır. Altı gerçek ve dört sahte heykel incelenmiştir. Heykellerin yedisi Anadolu Medeniyetleri, üç tanesi ise Akşit Sanat isimli bir heykel atölyesi tarafından sağlanmıştır. Sonuçların değerlendirilmesinde SPSS adlı istatistik programı kullanılmıştır. Sonuçlar sahte heykellerdeki düşük kalsiyum beklentisi ile uyumlu çıkmıştır. Ayrıca kobalt ve kurşun miktarları da gerçek ve sahte heykellerde önemli farklılıklar göstermiştir. Yapılan çalışma bu tekniğin yapay mermer heykellerin gerçek mermer heykellerden ayırt edilmesi konusunda işe yaradığını göstermiştir. Ancak daha fazla heykelin inceleneceği bir çalışmaya ihtiyaç vardır.

Anahtar Kelimeler: Mermer Heykeller, Sahtecilik, Yapay Mermer

To My Family,

ACKNOWLEDGEMENTS

I wish to thank, first and foremost, my supervisor Prof. Dr. Asuman Türkmenoğlu for her support and help throughout the study. Without her guidance and encouragement this thesis would have never been completed.

I am very grateful to my co-advisor Prof. Dr. Şahinde Demirci who supported me not just with her scientific experience and knowledge but also with her guidance through times of crisis.

I share the credit of my work with Mahmut Aydın, who has supported me in every level of the thesis, anytime I needed help. Coming up with the idea for this thesis, he helped me with the permissions and paperworks, he suggested me the samples and he walked me through the analyses. I sincerely thank him for making this thesis possible.

I would also like to thank Latif Özen, Sevdiye Bayram and Tolga Çelik from Anatolian Civilizations Museum for the time and effort they put in to help during my study in the museum.

I am grateful to Şerif Akşit, who had a great role in this study. His precious art and his patience to answer all my questions made this thesis possible.

I cannot find the words to express my gratitude to Evren Y. Geniş who gave me the inspiration and encouragement I needed to go on everytime I got stuck.

Last but not the least, I owe my deepest gratitude to family. My parents, Nalan and Öner Songül for they stood by me and supported me in every way that a person can be supported; Prof. Dr. Nilüfer Koçak for she insightfully guided me through thesis writing with her wisdom; Cansu Ergüç and İdil Koçak for being there for me everytime I felt like giving up. In my heart, all of you earned an M.Sc. degree as me.

TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

CHAPTER 1

INTRODUCTION

When a historical artifact is brought into the museum, an important decision regarding to its authenticity has to be made . The conventional methods of evaluation have been examining its pedigree and history or judging it aesthetically (Ashmole, 1961). Non-professional productions of fake artifacts are mostly eliminated at this step. For those of better production, a detailed visual examination is applied; signs such as surface alterations, depositions and weathering effects are inspected. But in a well designed, professional case both aesthetic and visual examinations can be insufficient. At this point, where the artifact in question causes suspicion beyond limits of visual examination, scientific methods step in to make a more objective evaluation.

In case of historical artifacts, the scientific method chosen to answer the question of authenticity should be of non-destructive nature. There are a few numbers of non-destructive scientific techniques to recognize forgeries of marble structures (Polikreti et al., 2002). One of the most useful techniques involves testing the disputed sculpture with ultra- violet light. However, the results of this method of study have not been scientifically published and thus could not become reliable. Efforts to develop new methodology for solving authenticity problems on marble artifacts also involved performing thermoluminescence measurements (Michael et al., 1997; Michael et al., 1999). However, this technique utilizes powder samples and is disadvantageous since it is destructive for the historical artifacts.

This study contributes authenticating marble structures by means of a non-destructive X-ray Fluorescence Spectroscopy (XRF) which will be useful during doubtful cases of authenticity involving large amounts of money and historical importance.

1.1.Definition of Marble

Marble can be defined in two different ways: scientific and commercial. The scientific (geological) definition of marble is that it is a non-foliated to weakly foliated metamorphic rock derived from limestones and dolomitic limestones (in this case it is dolomarble). Major mineralogical constituents are calcite and dolomite with some minor minerals. Marbles are the products of contact or regional metamorphism of calcareous sediments (Best, 1982). On the contrary, the commercial marble is defined as "a crystalline rock, capable of taking a polish, composed of one or more of the minerals calcite, dolomite, and serpentine" ("Marble 1").

In archaeological literature, the definition of marble mostly overlaps with the commercial meaning which regards rocks composed mainly of limestone, whether crystalline or non-crystalline, that can take a high polish as marble (Herz, 1988) . The word marble is derived from the Greek word marmaros, which means "shining stone", and is also associated with the verb marmairein, which means "to shine" ("Marble 2").

For marble to form, a certain process called metamorphism should occur. Metamorphism is the change of a rock in mineralogical, chemical and structural sense through the effects of temperature and/or pressure, below the surface of the earth that is away from weathering forces (Sen, 2001). The essential condition of metamorphism is the temperature interval in which the process occurs. The temperature that leads to the changes in the parent rock should be above that of sedimentary diagenesis and should be lower than the melting temperature so that the rock should still be in a solid state when undergoing the changes (Ehlers & Blatt, 1982; Williams et. al., 1982).

If the resulting rock contains more than 50% volume of carbonate minerals such as calcite, dolomite and aragonite, it is called marble. In case where the volume of carbonate minerals exceeds 95%, the marble is classified as pure marble as can be seen in Figure 1 (Fettes & Desmons, 2007). The mineral impurities that may be found in marble are brucite, diopside, epidote, feldspars, forsterite, graphite, grossular, humite, periclase, phlogopite, pyrite, quartz, scapolite, serpentine, sphene, spinel, talc, tremolite, vesuvianite and wollastonite (Dietrich & Skinner, 1979).

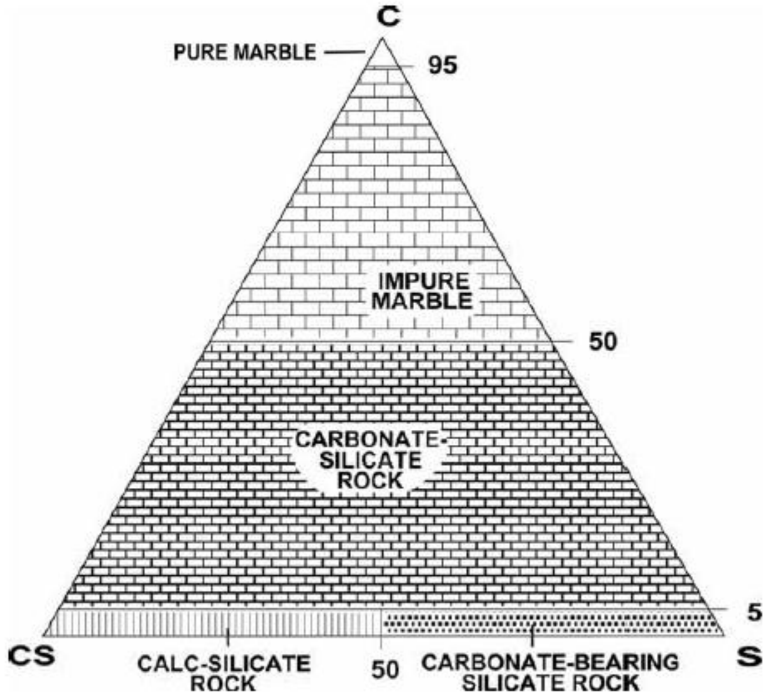


Figure 1 – Subdivision of Carbonate Rocks (Fettes & Desmons, 2007).
C:carbonate ,CS: calc-silicate, S:silicate

The texture and grain size of marble differs with each type. Grain size ranges from very fine to coarse-grained (Dietrich & Skinner, 1979). However, typically, the grains are granoblastic (Figure 2), that is composed of equal sized crystals (Ehlers & Blatt, 1982). *Blasto-* as a prefix refers to a relict fabric, whereas *–blastic* as a suffix refers to solid-state crystallization during metamorphism (Best, 1982). Marble has a texture composed of interlocking grains. This texture can be sutured or saccharoidal (Figures 2 & 3), (Dietrich & Skinner, 1979).

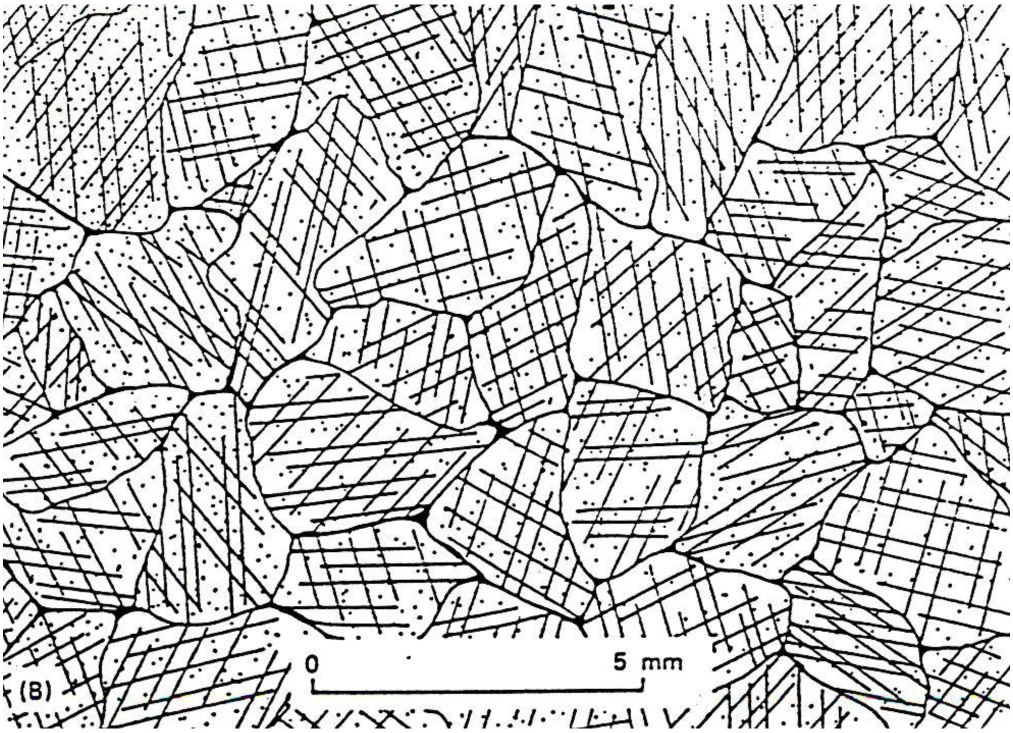


Figure 2 – Granular or Saccharoidal Texture (Dietrich & Skinner, 1979)

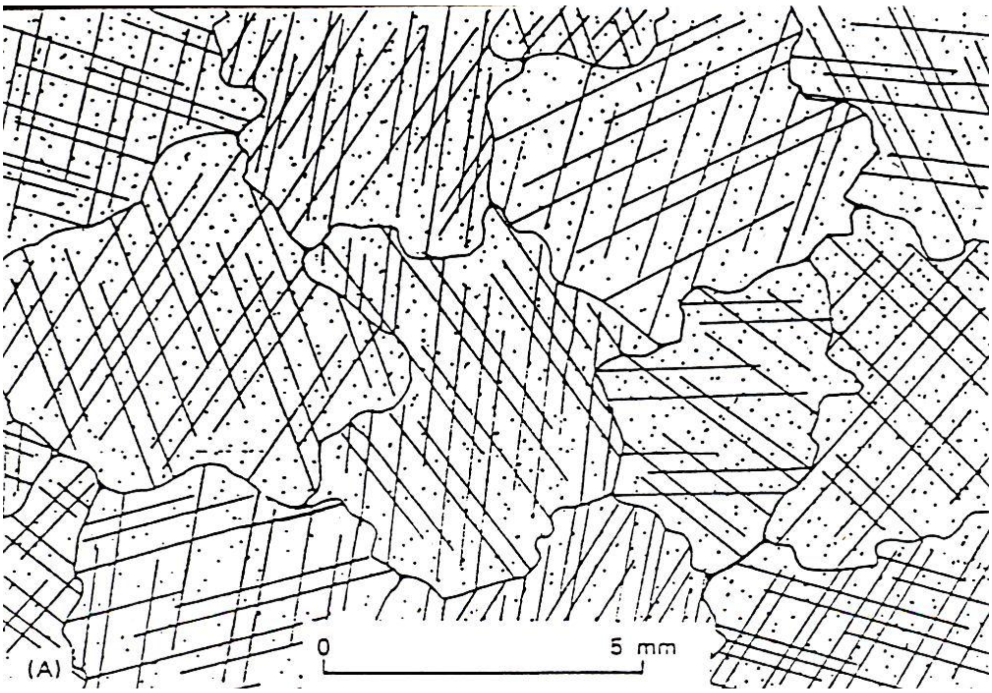


Figure 3 – Sutured Texture (Dietrich & Skinner, 1979)

Marble may be a host to some zinc ore deposits due to metasomatism, like Franklin and Sterling Hill deposits (so called Franklin marble) at New Jersey (USA). In such marbles chemical elements like As, Ba, C, F, Fe, Pb, K, Ti and Zn may occur as trace elements in different mineral structures. For example, at Sterling Hill, calcite is a host mineral for Pb. It is explored that there is a halo of lead in the Franklin marble surrounding ore bodies at these locations (Dunn, 2001).

1.2.Cultured Marble

Cultured marble, also known as artificially produced marble, is a material that gives the appearance of marble at lower cost. The main ingredient of cultured marble is marble dust, which is a byproduct of marble industry (Başer, 2009).

In the production of cultured marble, marble dust is mixed with polyester which works as the binder. As an accelerator for this composite material Cobalt Naphthenate ($CoC_{22}H_{14}O_{4}$), and as a hardener Methyl Ethyl Ketone Peroxide ($C_8H_{18}O_6$) are used (Gürü et. al., 2007). The ratios of the ingredients change depending on the mechanical performance expected from the composite material (Gürü et. al., 2005).

The resulting material is utilized in arts and industry. Lower cost and higher durability makes cultured marble preferable over natural marble in bathroom and kitchen products such as sinks, tubs, counter tops etc. In arts, cultured marble is used in the production of sculptures (Figure 4). Since it allows for molding technique, it is easier to produce than carving out a sculpture from the block of natural marble. It is also seen as a method of recycling waste marble dust (Ecomarble).

Figure 4 – Marble Reproduction of Roman Emperor Marco Aurelio Made of Marble Powder and Polyester (L'artigianato).

1.3.Use of Marble in Artifacts

The first evidence of use of marble is dated to Neolithic age when anthropomorphic figures were carved in Greece, especially in Cyclades (Waelkens et. al., 1988). Marble, being abundant in Greece and its islands, has become a widely used material for production of artifacts (Borghi et. al., 2009). However, these artifacts of early cultures are regarded as collection of already chipped rocks rather than quarrying due to their small sizes (Figure 5) (Waelkens et. al., 1988).

Figure 5 – Marble Figurine of a Woman (Fitton, 1999)

The evidence of first real quarrying, which is defined as removal of large stones from the natural bedrock artificially, is seen in the Eocene limestone beds in Northern Egypt and is dated to the beginnings of Dynastic Period that is 3rd millennium BC (Ulens et. al., 1995). By 1900 B.C. quarrying technology has spread from Egypt to Eastern Mediterranean. However the quarrying technology of Egyptians was fit for softer stones like limestone and sandstone, thus in order to quarry the marble found in Greece, new techniques had to be developed (Palagia, 2006). After the collapse of the Mycenaean civilization, stone use has been suspended for four centuries. Only after 7th Century BC, marble has begun to be quarried and used extensively. By 6th Century B.C. marble becomes a popular material for both architecture and sculpture (Waelkens et. al., 1988). From Hellenistic Periods onwards sculpting continued to be exercised with more or less the same techniques (Palagia, 2006).

1.4. Problem of Authenticity

The importance of distinguishing between authentic artifacts and forgeries is an issue of both historical aspects and monetary concerns. For hundreds of years, copies of original works have been made. The copy in question may be a copy of style, technique or an entire artifact. Yet not all of the copies are labeled as forgeries. For a copy to be considered a forgery the copy has to be presented with a deceptive intention, either by the producer or the seller (Dutton, 2003). When the original work is acknowledged by the copy, this is regarded as an imitation.

The way an artifact is assigned a value is closely related to the cultural norms it is assessed in. One would expect that the value of an artifact comes forth of its aesthetics. This was the case in Medieval era, as Michelangelo's antique looking classical period type of works, which would be considered as forgeries, has been praised for its subject (Fleming, 1975). However from 19th century onwards, the value assigned to an artifact began to be assessed by its authenticity rather than aesthetics. So when van Meergen made paintings with the technique of Vermeer's which could only be differentiated by means of laboratory techniques, despite the aesthetic alikeness, the values offered for the works of two artists was incomparable (Fleming, 1975).

In case of art, as Alfred Lessing says, the value of an artifact depends on the original artistry, whether it brings something new or creative to the history of art ("Forgery").

In case of historical artifacts, the problem arises from the fact that the artifacts are the main tools of writing history. When an artifact is found, it gives clues about the technologies used, level of development and even specific events as they may be depicted on the artifact. So every succesful forgery taken as an original, creates a historical fiction (Haywood, 1987).

The beginnings of reproduction of art and archaeological objects can be traced back to Roman times (Palagia, 2006). But because of the increasing demand for Greek and Roman artifacts which were regarded as sign of intellectuality, 18th and 19th centuries became the peak of forgery (Polikreti, 2007). In the 20th and 21st centuries, possessing an archaeological artifact or an art object, has gone beyond the question of intellectuality and became a serious economical problem. The economical returns on forged items caused the number of forgeries to increase. For the last few decades, thousands of forgeries are thought to have entered the market (Muscarella, 2000).

The increase in forgeries created the need for evaluation of the authenticity of an artifact to assess its value. Until the 1950s the question of whether an artifact was authentic or not was decided on subjective terms by the evaluation of an expert according to the artifact’s appearance (Polikreti, 2007). One such aspect to look at a suspicious sculpture is to examine its history to see historical inconsistencies. Another subjective aspect for evaluation is aesthetic judgment (Ashmole, 1961). But advances in forgery qualities proved such subjective evaluations insufficient. So, more objective and scientific methods for authenticity studies were sought after.

For many types of artifacts such as metal, pottery and painting, techniques for identification of fraud have been developed (Fleming, 1975). But in case of stone artifacts, which include marble, a method that can positively identify the authenticity of the artifact has not been found yet. Moreover, the difficulty of detecting marble forgery lies in the fact that there are various methods of creating a fake sculpture. One can use either modern quarries or antique quarries to acquire the stone needed for the sculpture. If antique stone is needed and is no longer available from the quarry, one can reuse blocks from archaeological sites (Polikreti, 2007). Another method of forgery is molding technique by using marble dust and resins.

1.5. Previous Archaeometrical Studies

Visual examination has been the oldest method of evaluating authenticity of marble artifacts (Ashmole, 1961). With advances in technology, the method shifted from bare eye examinations to microscopic examinations. However, in time other methods have also been applied to marble artifacts which are more petrographical and chemical approaches. A diagram of previous methods applied in detection of marble forgery can be seen in Figure 6.

One of the main problems regarding marble authenticity is the futility of using dating techniques, for the results would yield information about the formation of marble rather than the production of the artifact (Polikreti et. al., 2002). Thus most studies regarding authenticity of marble sculptures focus on the patina on the artifact. Although provenance studies are a field of their own in marble studies, they are also used as determinants of authenticity. Another method of investigating authenticity is thermoluminescence.

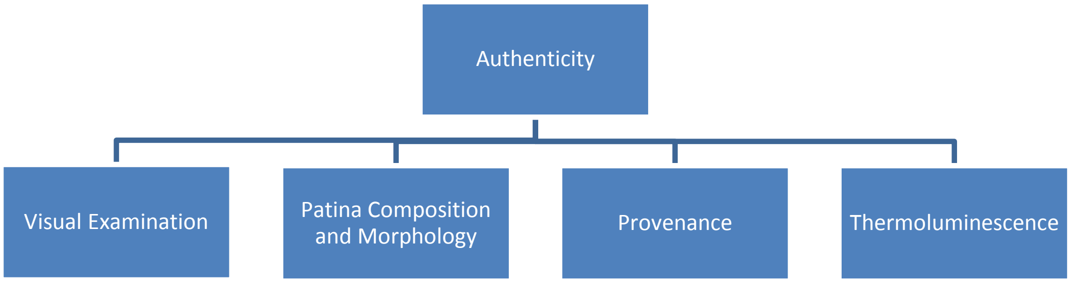


Figure 6 – Previous Archaeometrical Studies Made for Detection of Marble Authenticity

Visual examination of marble artifacts looks for the marks on the artifacts caused either by working tools or by roots of the plants. When the root of a plant gets in contact with the marble artifact, the sap of the root, which is acidic, dissolves the marble and it leaves a mark on the surface in the shape of the root (Polikreti, 2007). The tool marks are made by tools used during the production of the sculpture. Depending on the technique used for shaping marble, distinctive marks can be seen. Tool marks can be an indication of forgery when the age of the technique used and the age of the artifact do not coincide (Ashmole, 1961).

The examination of the weathered surface on the sculpture through various analytical methods gives information about surface alterations and depositions (Margolis & Showers, 1988). Although the findings give clues about the authenticity of the artifact, since weathered layer is dependent on the environmental conditions and the type of the marble used, the information found from the patina is not 100% reliable (Ulens et. al., 1995).

One of the methods used for detecting forgery from the artifact's surface is by using ultraviolet examination. This method assumed different colors would fluoresce depending on whether the artifact is forgery or not, however this method has been abandoned since the colors seen would change not only depending on the authenticity of the artifact but also on the weathering conditions (Margolis & Showers, 1988; Polikreti, 2007).

Margolis and Showers (1988) also examined the patina layer on marble artifacts and concluded that natural weathering layer that is found on ancient artifacts has a character of their own which is formed overtime due to exposure to atmospheric conditions and the chemical and biological conditions of the site it was found in. This layer of weathering progresses inwards through time and in forgeries the artificial patina concentrates on the surface since it does not have time to penetrate into the artifact. However since this method requires removal of a sample in order to perform cross-section analysis, it is not applicable for museum artifacts (Margolis & Showers, 1988).

Provenance studies aim to identify the quarry of the marble. The source of marble is compared to probable quarries known by archaeological data. If the quarry of the marble is irrelevant to historical context, then the object can be labeled as counterfeit. If the sources match, further analysis is required since it is possible to acquire marble from ancient quarries or reuse marble blocks from ancient quarries (Polikreti, 2007). The techniques used for determining provenance include petrographic examinations with microscopes, cathodoluminescence, electron paramagnetic resonance, instrumental neutron activation analyses, stable isotope analysis, electron spin resonance (Herz & Waelkens, 1988; Polikreti, 2007).

Thermoluminescence is another approach used in assessing authenticity of marble. Thermoluminescence is used to compare the sunlight exposure and burial time of the sample. Although the method is not applicable to all artifacts, it can be used with artifacts that were recovered buried or artifacts that were continuously exposed to sunlight (Polikreti et. al., 2002). If the artifact is found buried, the thermoluminescence signals give the time since last exposure to sun. If the artifact is continuously exposed to sunlight, the thermoluminescence signal is evaluated with respect to intensity versus depth, since intensity of signals start to decrease from surface towards the core through time. Thus the measurements give the length of sunlight exposure for the artifact (Polikreti, 2007).

1.6.Aim and Scope of the Study

The advancing consciousness regarding ethical issues about the conservation of historical artifacts and art objects, revises regulations of analysis that can be practiced on these items (Council of Europe, 1992). Many of the scientific methods which can help to disclose the authenticity of a sculpture are prohibited since they require removal of a sample from the artifact. The evaluation of any artifact that is found or brought to the museums should be done by non-destructive methods.

The aim of this study is to test for the applicability of the non-destructive device of portable X-Ray Fluorescence (PXRF) to identify authenticity of a marble artifact. Besides its non-destructive nature, PXRF is also capable of taking in-situ measurements which is an important advantage in the case of archaeological samples. Moreover, since no time is required for sample preparation, the results of the analysis can be accessed in a short while.

As mentioned in section 1.1.4. there are various methods for creating a forgery. Forgeries made by sculpting a marble block are more difficult to detect than forgeries made by casting technique. Nevertheless examples of the latter also turn up in need for an objective evaluation. The scope of this thesis focuses on studying the properties of forgeries made by using cultured marble, in other words by using casting technique.

CHAPTER 2

MATERIALS AND METHODS

2.1. Sample Description

For the aim of this thesis, both authentic marble sculptures and forgeries have been studied. Also, for comparison, a natural sample of Marmara marble has been studied. Six of the samples are authentic marble sculptures, four of them are forgeries made by casting technique and one is the Marmara marble.

All of the authentic samples were provided by the Anatolian Civilizations Museum located at Ankara. The information about these authentic sculptures is taken from the inventorial information cards. Although the information regarding the period of the sculptures has not been specified with some of the sculptures, archaeologists of the museum reported them as belonging the Roman period.

One of the forgery samples, the Zeus was also provided by the Museum. The other forgery samples were provided by sculptor Mr. Şerif Akşit, from Akşit Sanat workshop in Ankara. The Marmara marble is obtained from the Geological Engineering Department of the Middle East Technical University.

The sample size for this study is limited. The device with which the analyses were performed was provided by the museum. Since it was not possible to remove the device from the museum, the samples had to be chosen among the marble sculptures in the museum.

In Figures 7-17 the places of measurements are marked with numbers, which also indicates the order of the measurements.

2.1.1. Authentic Marble Samples

The Statue of a Man (Figure 7) has been retrieved from Keçioren Kızlarpınarı Street by denunciation. It was brought to the museum in 22.06.1983 and registered with inventory number 50.I.83. The statue is assigned to the Roman Period. The dimensions of the statue are 94 cm in height, 42 cm in width and 31 cm in depth. The pedestal it stands on is 8 cm high.

The head of the statue is missing. Left arm of the statue bends over to the back from the elbow. The left arm is also broken from the shoulder to the wrist. There is a shovel whose handle stands adjacent to the man's right arm. The upper part of the body and the feet are naked. The lower part of the body is covered with what seems to be a thick piece of clothing which is held up with the handle of the shovel on the side and with the left hand on the back. Behind the feet depictions of rocks can be seen.

Three measurements were taken from this statue. The first one was taken from the left arm where it is broken on the shoulder. The second measurement was taken from the middle of the blade of the shovel. The third measurement was taken from right side of the chest.

The Statue of a Woman Without Head (Figure 8) has the inventory number 114.50.99. It has a height of 74 cm and its width at the shoulders is 35 cm. Information regarding where and when it was found and which period it belongs to have not been present.

The Statue depicts a woman. Its head has been broken from the neck. She has transparent clothing which does not cover her right breast. Her arms and legs are also broken. There is an unidentified figure on her right shoulder.

Three measurements were taken from this statue. The first one was taken from the place below the neck where the chest begins. The second measurement was taken from the right breast where the marble is chipped off. The third one was taken from below the right breast.

The Sitting Statue (Figure 9) has the inventory number 114.52.99. It has a height of 58 cm and width of 41 cm. Information regarding where and when it was found and which period it belongs to have not been present.

The statue depicts a human sitting on an unidentified object. The upper part of the body is missing. Only the lower part of the human, below the waist, is visible. On the lap of the human there is a four-legged animal lying down which is also partially damaged.

Three measurements were taken from this statue. First measurement was taken from the tip of the clothing above the left foot of the human. The second measurement was taken from the lower part of the right side of the object on which the human is sitting. Third measurement was taken from the hind leg of the animal which is over the left leg of the human.

The Sarcophagus Pieces (Figure 10) has been purchased by the museum from Azmi Yılmaz in Samanpazarı, Ankara. It was brought to the museum in 16.09.1969. The sarcophagus consists of 5 pieces which were registered with the inventory number 118.1.69. The piece analyzed in this study is 118.1.69-D. Its dimensions are 46 cm in height, 42 cm in width.

The studied piece depicts the torso of a human. Other than the scarf around the neck, the human has no other clothing. The arms are broken from the elbows. On the left side there is column which has diagonal lines on the shaft and a Corinth style order. The human is holding something with the left hand.

Three measurements were taken from this statue. The first one was taken from the right cheek of the human. The second measurement was taken from the tip of the scarf on the right side. The third measurement was taken from the flat surface on the left side of the column.

The Acanthus (Figure 11), is a piece from an architectural structure. It was purchased by the museum from Güner Hamamcıoğlu in Hüseyin Gazi, Ankara. It was brought to the museum in 14.11.1989. It was registered with the inventory number 200.I.89. The height of the piece is 67.5 cm and the width is 85 cm.

The facade of the marble is decorated with leaves of acanthus. The decoration is arranged in the form of a Corinth style order. Among the acanthus leaves a flower, which resembles artichoke, rises.

Three measurements were taken from this statue. The first one was taken from the left side of the left iron nail on the top of the sample. The second measurement was taken from the right side of the right nail on the top of the sample. The third measurement was taken from the broken top part of acanthus leaf beneath the artichoke.

The Emperor Statue (Figure 12) was found at the Roman Bath Excavation in Ulus, Ankara. It has the inventory number 85.1.07. The statue is from the Roman Period. The pedestal on which the statue stands is 58 cm in depth and 87,5 cm in width. The total height of the statue is 220 cm and the width of the statue is 80 cm at the shoulders.

The Emperor Statue has been found in five pieces. The pieces were put together by the conservators in the museum's laboratory. The right arm is broken from the shoulder and is missing. Its head is also broken from the neck and it is missing. There is a tree log with nine leaves on it right next to the emperor. The little finger of the left hand is broken and missing. The right arm is broken. The left arm of the statue is holding its hip. The statue has clothing which covers the front of the body as it hangs from the shoulder. The other end of the clothing is wrapped around the ankle.

Three measurements were taken from this statue. The first one was taken from the back of the left lower leg. The second measurement was taken from the left side of the buttocks. The third one was taken from the left biceps.

2.1.2. Forgery Samples

Zeus (Figure 13) is a forgery which was purchased by the museum. However since it turned out to be a forgery, it is not registered in the museums inventory. Information regarding how it is made is unknown.

Three measurements were taken from the Zeus sample. The first one was from the wrist of the right arm. The second measurement was taken from over the knee of the left leg. The third measurement was taken from the middle of the forehead below the hair line.

Eros (Figure 14), Isis (Figure 15) and Bodrum (Figure 16) samples were all made by Şerif Akşit at his workshop, Aksit Sanat. Although these samples were not made for fraudulent purposes, the technique employed for such purposes is the same. The description made by Serif Aksit about how the cultured marble is prepared is in line with the technique described in 1.1.2.

Three measurements were taken from the Eros sample. The first measurement was taken from the left cheek. The second measurement was taken from the forehead. The third one was taken from below the right ear.

Two measurements were taken from the Isis sample. The first one was from the broken shoulder and the second one was from her hip on the back.

Three measurements were taken from the Bodrum sample. The first measurement was taken from the surface with the inscription on it. The second measurement was taken from the surface across the surface with the inscription. The third one was taken from the smaller side where the sample was cut in order to get a slice for the thin section examinations.

In Figure 17, the Marmara Marble sample can be seen. The single measurement taken from the Marmara Marble was from the surface which was cut in order to get a slice for the thin section examinations.

Figure 7 – The Statue of a Man; photographed by Güneş Songül on 08.03.2012

Figure 8 – The Statue of a Woman Without Head; photographed by Güneş Songül on 08.03.2012

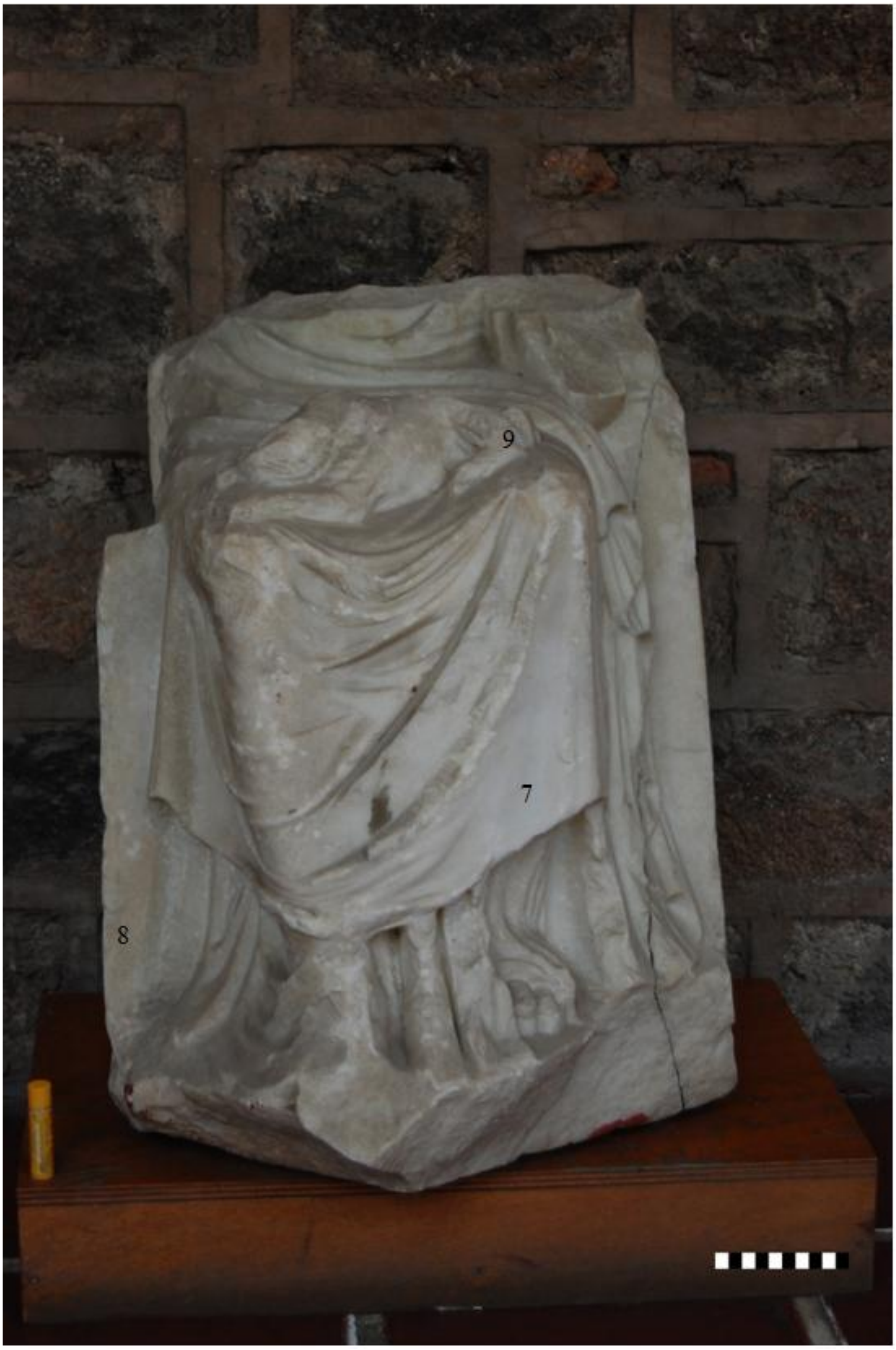


Figure 9 – The Sitting Statue; photographed by Güneş Songül on 08.03.2012

Figure 10 – The Sarcophagus Piece; photographed by Güneş Songül on 08.03.2012

Figure 11 – The Acanthus; photographed by Güneş Songül on 08.03.2012

Figure 12 –The Emperor Statue; photographed by Güneş Songül on 21.02.2012

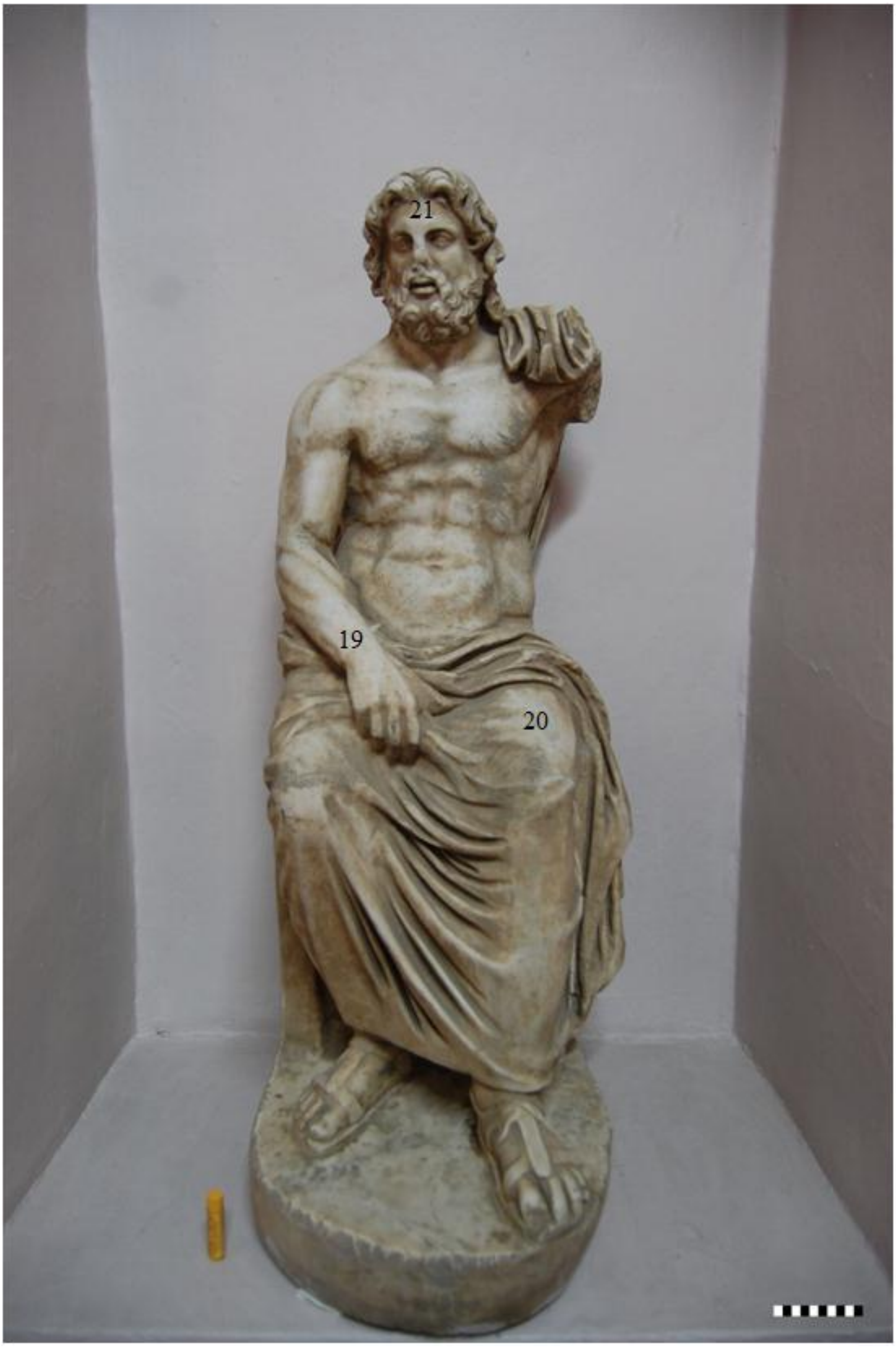


Figure 13 – Zeus; photographed by Güneş Songül on 08.03.2012

Figure 14 – Eros; photographed by Güneş Songül on 21.02.2012

Figure 15 – Isis; photographed by Güneş Songül on 21.02.2012

Figure 16 – Bodrum; photographed by Güneş Songül on 21.06.2012

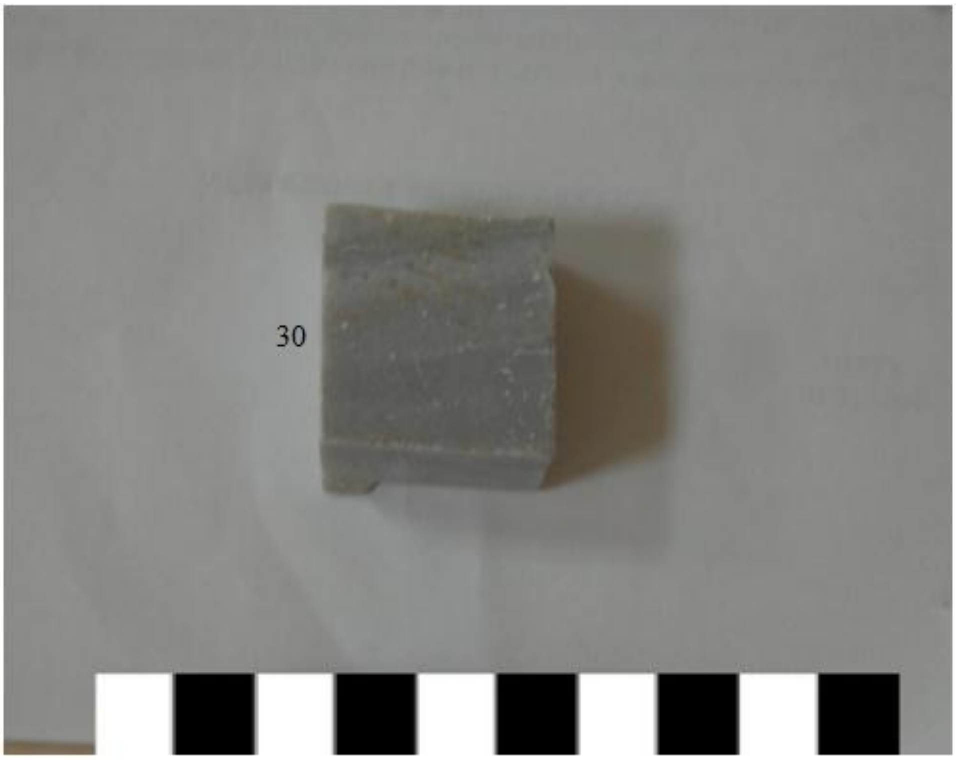


Figure 17 – A Piece of the Marmara Marble; photographed by Güneş Songül on 21.06.2012

2.2.X-Ray Fluorescence Analysis by Portable XRF Instrument

The chemical analyses of the samples were carried out with Innov-X Alpha Series Portable X-Ray Fluorescence instrument owned by the Anatolian Civilizations Museum at Ankara (Figure 18).

Figure 18 – A view of the Portable X-Ray Fluorescence Instrument

The instrument uses an X-ray tube to excite the sample with X-ray photons. The primary X-ray photons excite secondary X-ray photons of the atoms present in the sample (Potts, 2008). The secondary photons are then detected by a Si PIN diode detector.

Portable X-ray fluorescence device does not require any sample preparation. The device is placed on the desired surface for analysis, then kept in contact with the place of analysis until the measurement is completed. The results are reported within seconds after the measurement is completed. Results can be seen in the screen of the device itself, or can be transferred to computers.

The instrument has 6 modes of analysis each detecting different element combinations from magnesium to uranium (Table 1). To make the best fit of elements for marble, soil mode was decided to be used in the analyses. Therefore the atomic number 15, which is related with phosphorus, was the first detected element having the lowest atomic number. The results of soil mode analyses are reported as parts per million (ppm).

Table 1 – Calibration Modes of Innox Alpha

Modes	Filter	Xpress Alloy	Two Beam Mining	Mining	Analytical	Soil
Mg		√	√			
Al		√	√			
Si		√	√			
P	√	√	√			√
S	√	√	√			√
Cl	√		√			√
K	√		√			√
Ca	√		√			√
Ti	√	√	√	√	√	√
V	√	√	√	√	√	√
Cr	√	√	√	√	√	√
Mn	√	√	√	√	√	√
Fe	√	√	√	√	√	√
Co	√	√	√	√	√	√
Ni	√	√	√	√	√	√
Cu	√	√	√	√	√	√
Zn	√	√	√	√	√	√
As	√		√	√		√
Se	√					√
Rb	√					√
Sr	√					√
Zr	√	√	√	√	√	√
Nb		√			√	
Mo	√	√	√	√	√	√
Rh					√	
Pd					√	
Ag	√	√	√	√	√	√

Table 1 (Continued) - Calibration Modes of Innox Alpha

Modes	Filter	Xpress Alloy	Two Beam Mining	Mining	Analytical	Soil
Cd	√		√	√		√
Sn	√	√	√	√	√	√
Sb	√	√	√	√	√	√
Hf		√			√	
Ta		√			√	
W	√	√	√	√	√	√
Re		√			√	
Ir					√	
Pt					√	
Au	√				√	√
Hg	√					√
Pb	√	√	√	√	√	√
Bi	√	√	√	√	√	√
Ac						√
Th	√					
U	√					√

The results of Ca levels are converted into percentages by making use of the Marmara Sample. Marble samples from Marmara have been analyzed by Gürbulak in his thesis and the chemical composition of Marmara marble is measured in percentages (Table 2), (Gürbulak, 2007). The Ca levels of Marmara Sample measured by Portable XRF device is then compared to percentage of Ca measurements measured by atomic absorption spectrometry. The method of converting portable X-Ray Fluorescence readings into percentages is as follows:

Table 2 - Chemical Composition of Marmara Marble from Gürbulak, 2007:

Si	0,72%
Loss on Ignition	43,77%
MgO	0,540%
Fe_2O_3	0,027%
CaO	54,94 %
Total	99,99%

Chemical Calculations:

$CaCO_3$ mol weight = 100,09 gr

For calcite mineral $CaCO_3$: Ca= 40,04%; C=12,00%; O=47,96%

$CaCO_3 \rightarrow CaO + CO_2$

So for calcite mineral CaO= 56,03%; CO_2=43,97%

By using ratios; 100*40,04/56,03= 71,46 thus there is 71,46% of Ca in CaO

The percent of CaO in Marmara marble is 54,94%, so Ca percent in Marmara marble is: 54,94*(71,46%)=39,26%

Since 39,26% will be equal to the portable X-ray fluorescence reading of calcium level of Marmara sample, an equation formed through this ratio can be applied to convert all calcium readings from the other samples to percentages.

The analyses were done on multiple spots of the samples after cleaning of the measurement surfaces carefully by distilled water. Except for the Isis forgery and the Marmara samples, every sample has 3 measurements taken from different spots. The Isis forgery allowed only 2 measurements since the size and shape of the statue did not provide three spots to be analyzed. The Marmara sample is analyzed from a fresh cut surface once.

The device has been standardized with SS316, an Ag standard reference material, three times before the analyses.

2.3.Statistical Analyses

The results of the chemical analysis were evaluated statistically with the software SPSS 16.0 for Windows. Two hypotheses were proposed for this study for the elements of Ca and Co. The repetitive measurements have been computed into one value by taking their means.

Regarding Ca, the expectation is that, because of the polyester amount present in the composite material, the levels of Ca would be lower than that found in authentic marble sculptures and natural marble. Thus the null hypothesis is that the Ca levels would not differ significantly between authentic samples and forgery samples and the alternative hypothesis is that Ca levels would differ significantly between authentic and forgery samples.

Regarding Co, the expectation is that, since Co is almost unproven as a natural impurity found in marble, but is added as an accelerator into marble dust and polyester mix, Co levels would significantly differ between authentic samples and forgery samples.

To test for the difference of Ca levels between forgery samples and authentic samples “2 Independent Samples Nonparametric Test” has been used. This test was chosen because of the limited number of samples available which means that a normal distribution of the data cannot be assumed. With this test the ranks of the samples rather than the numeric values are compared. So, the results indicate whether the values in one group is larger than the other.

For Co levels, statistical analysis could not be used. Since Co was below the limit of detection for the authentic samples group.

2.4.Microscopic Analyses

Thin sections obtained from the forgery Bodrum sample and the natural Marmara marble has been examined to compare textures and grain sizes. The thin section slides were examined in the Geological Engineering Department of Middle East Technical University with an Olympus optical microscope. Samples were examined both with crossed nicols (analyzer in position) and single nicol (analyzer out position) modes by using objectives with 4x and 10x lenses.

2.5.X- Ray Diffraction Analyses

Powder samples obtained from the forgery Bodrum sample and the natural Marmara marble has been examined to look for the minerals present in the samples. For the analyses Rigaku Miniflex II X-Ray Diffraction Spectrometry has been used. System is operated by using a Cu K α radiation using 30 kV and 15 mA with Ni filter. The samples were prepared by grinding and obtaining a powder, then sieving below 170 mesh sieve. Random X-ray powder diffraction spectrums were obtained from these samples.

CHAPTER 3

RESULTS AND DISCUSSION

The results of the analyses have been discussed in five subsections; Results of X-Ray Fluorescence Analyses, Results of Statistical Analyses, Results of Microscopic Analyses, Results of X-Ray Diffraction Analyses and Discussion.

3.1.Results of X-Ray Fluorescence Analyses

The results of chemical analysis are listed below in Table 1.

The sample names have been reduced to one descriptive word to fit the table. The names in Table 1 correspond as follows:

Man for The Statue of a Man

Woman for The Statue of a Woman Without Head

Sitting for The Sitting Statue

Sarcoph. for The Sarcophagus

Acanthus for The Acanthus

Emperor for The Emperor Statue

Zeus for Zeus

Eros for Eros

Isis for Isis

Bodrum for Bodrum

Marmara for Marmara Marble

The second column in Table 1, “No”, indicates the number of measurements taken.

The studied elements are Ca, K, Fe, Ti, Sr, Ni, Cu, Mn, Zn, Pb, Co, S, Rb, Th, Cl, Ag, Au, Hg, As, Mo, Cr, V, Zr, P, Se, Cd, Sn, Sb, W, Bi and U. Among these elements Ca, K, Fe, Ti, Sr, Ni,Cu and Mn were detected in almost all samples. On the other hand, Zn and Pb were detected only in the authentic Marble Samples whereas Co is a distinguishing element for the forgery samples. There is a significant difference in the Ca values of authentic marble and forgery samples so that lower values of Ca concentration indicate the latter type of artifacts (Table 3).

Table 3 – Results of X-Ray Fluorescence Analyses; (in ppm, <LOD: lower than limit of detection)

Name	No	Ca	K	Fe	Ti	Sr	Ni	Cu	Mn
Man	1	1242326	681	294	<LOD	146	57	36	<LOD
Man	2	1222878	713	566	129	129	49	43	<LOD
Man	3	1123728	3030	2274	427	125	38	51	27
Woman	4	1252236	972	1034	203	91	39	42	23
Woman	5	1331844	790	1107	201	94	54	35	<LOD
Woman	6	1087323	794	643	108	97	38	29	18
Sitting	7	1121123	<LOD	786	67	65	28	44	22
Sitting	8	1257508	<LOD	270	32	62	53	344	32
Sitting	9	1140131	<LOD	502	61	61	35	39	22
Sarcoph.	10	1206548	<LOD	503	47	88	46	59	20
Sarcoph.	11	1187935	733	649	61	89	34	121	37
Sarcoph.	12	1176913	794	752	100	103	38	42	22
Acanthus	13	1205196	<LOD	482	66	91	44	61	<LOD
Acanthus	14	1182713	2134	627	<LOD	114	62	39	26
Acanthus	15	1217151	1204	936	159	84	44	42	<LOD
Emperor	16	1148639	978	494	110	75	37	17	24
Emperor	17	1142656	2733	823	107	76	59	13	32
Emperor	18	1116421	5229	1890	356	93	64	11	50
Zeus	19	869835	1410	1120	1343	95	34	37	27
Zeus	20	705639	1519	1262	1439	86	<LOD	43	37
Zeus	21	758270	915	563	1494	89	19	40	28
Eros	22	456220	577	105	33	76	<LOD	<LOD	19
Eros	23	471488	558	145	69	78	<LOD	8	16
Eros	24	409468	289	51	<LOD	69	<LOD	<LOD	23
İsis	25	779560	815	256	191	90	30	13	<LOD
İsis	26	709741	1067	651	1936	91	34	21	18
Bodrum	27	807585	2158	747	227	78	<LOD	26	30
Bodrum	28	826528	1102	67	124	78	22	20	19
Bodrum	29	881864	2932	2058	277	80	23	38	29
Marmara	30	1044298	821	174	<LOD	204	37	27	18

Table 3 (continued) – Results of X-Ray Fluorescence Analyses

Name	No	Zn	Pb	Co	S	Rb	Th	Cl	Ag
Man	1	11	14	<LOD	<LOD	3	23	<LOD	32
Man	2	17	13	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Man	3	34	19	<LOD	<LOD	4	<LOD	<LOD	<LOD
Woman	4	13	8	<LOD	<LOD	3	<LOD	<LOD	<LOD
Woman	5	13	11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Woman	6	13	8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sitting	7	<LOD	21	<LOD	<LOD	<LOD	31	<LOD	<LOD
Sitting	8	<LOD	18	<LOD	<LOD	<LOD	<LOD	<LOD	35
Sitting	9	12	12	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sarcoph.	10	16	11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sarcoph.	11	15	19	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sarcoph.	12	<LOD	9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Acanthus	13	15	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Acanthus	14	18	<LOD	<LOD	9684	<LOD	<LOD	2647	<LOD
Acanthus	15	16	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Emperor	16	17	<LOD	<LOD	8412	<LOD	<LOD	<LOD	<LOD
Emperor	17	12	<LOD	<LOD	6120	3	<LOD	1618	40
Emperor	18	11	8	<LOD	6672	3	18	1693	49
Zeus	19	<LOD	<LOD	76	<LOD	<LOD	22	<LOD	<LOD
Zeus	20	8	<LOD	119	<LOD	<LOD	<LOD	<LOD	<LOD
Zeus	21	<LOD	<LOD	100	<LOD	<LOD	29	<LOD	<LOD
Eros	22	<LOD	<LOD	20	3142	<LOD	<LOD	<LOD	<LOD
Eros	23	<LOD	<LOD	19	3199	<LOD	<LOD	503	<LOD
Eros	24	<LOD	<LOD	22	<LOD	<LOD	<LOD	<LOD	<LOD
İsis	25	<LOD	<LOD	26	<LOD	<LOD	<LOD	<LOD	31
İsis	26	12	<LOD	38	24005	<LOD	<LOD	<LOD	30
Bodrum	27	<LOD	<LOD	23	<LOD	3	<LOD	1645	<LOD
Bodrum	28	<LOD	<LOD	26	<LOD	3	19	1048	<LOD
Bodrum	29	<LOD	<LOD	<LOD	<LOD	<LOD	20	<LOD	<LOD
Marmara	30	10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table 3 (continued) – Results of X-Ray Fluorescence Analyses

Name	No	Au	Hg	As	Mo	Cr	V	Zr	P
Man	1	<LOD	<LOD	<LOD	7	<LOD	<LOD	<LOD	<LOD
Man	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Man	3	<LOD	11	8	<LOD	<LOD	8	<LOD	<LOD
Woman	4	<LOD	10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Woman	5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Woman	6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sitting	7	<LOD	<LOD	<LOD	14	<LOD	<LOD	<LOD	<LOD
Sitting	8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sitting	9	<LOD	11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sarcoph.	10	34	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sarcoph.	11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sarcoph.	12	<LOD	<LOD	<LOD	10	<LOD	<LOD	<LOD	<LOD
Acanthus	13	<LOD	<LOD	6	<LOD	<LOD	<LOD	<LOD	<LOD
Acanthus	14	<LOD	11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Acanthus	15	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Emperor	16	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Emperor	17	3	<LOD	5	<LOD	<LOD	<LOD	<LOD	<LOD
Emperor	18	3	9	<LOD	<LOD	11	<LOD	<LOD	<LOD
Zeus	19	3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Zeus	20	<LOD	<LOD	<LOD	<LOD	<LOD	8	4	<LOD
Zeus	21	<LOD	<LOD	4	6	<LOD	<LOD	<LOD	<LOD
Eros	22	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Eros	23	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Eros	24	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
İsis	25	3	<LOD	<LOD	<LOD	10	<LOD	<LOD	<LOD
İsis	26	<LOD	<LOD	<LOD	<LOD	22	<LOD	<LOD	<LOD
Bodrum	27	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Bodrum	28	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Bodrum	29	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Marmara	30	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table 3 (continued) – Results of X-Ray Fluorescence Analyses

Name	No	Se	Cd	Sn	Sb	W	Bi	U
Man	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Man	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Man	3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Woman	4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Woman	5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Woman	6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sitting	7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sitting	8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sitting	9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sarcoph.	10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sarcoph.	11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sarcoph.	12	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Acanthus	13	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Acanthus	14	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Acanthus	15	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Emperor	16	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Emperor	17	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Emperor	18	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Zeus	19	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Zeus	20	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Zeus	21	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Eros	22	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Eros	23	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Eros	24	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
İsis	25	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
İsis	26	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Bodrum	27	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Bodrum	28	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Bodrum	29	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Marmara	30	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

The results of the calcium levels acquired from the portable X-ray fluorescence are converted to percentages below.

As mentioned in the Chapter 2 Materials and Methods, this conversion is made by using the chemical composition of the Marmara marble as reported in Gürbulak's thesis (Gürbulak, 2007). The first step for conversion was to calculate the conversion ratio by making use of the equation of the Marmara sample. Percent side of the equation has been calculated in section 2.2. as 39.26%. Then an equation is set in the following way:

39.26% equals to 1044298

So the conversion ratio is: 39.26/1044298 = 0.0000376

Then each calcium reading is multiplied with 0.0000376 to acquire the percent of calcium such as:

1242326*0.0000376 = 46.71% of Ca for first measurement of Man

In table 4, the results of the calculations that convert PXRF readings into percentages can be seen.

Table 4 – Conversion of Ca Levels Measured by PXRF to Percentages

Sample	Ca in PXRF readings	Ca in percentages
Man	1242326	46.71%
Man	1222878	45.98%
Man	1123728	42.25%
Woman	1252236	47.08%
Woman	1331844	50.08%
Woman	1087323	40.88%
Sitting	1121123	42.15 %
Sitting	1257508	47.28 %
Sitting	1140131	42.87%
Sarcoph.	1206548	45.36%
Sarcoph.	1187935	44.67%
Sarcoph.	1176913	44.25%
Acanthus	1205196	45.32%
Acanthus	1182713	44.47%
Acanthus	1217151	45.76%
Emperor	1148639	43.19%
Emperor	1142656	42.96%
Emperor	1116421	41.98%
Zeus	869835	32.70%
Zeus	705639	26.53%
Zeus	758270	28.51%
Eros	456220	17.15%
Eros	471488	17.71%
Eros	409468	15.40%
Isis	779560	29.31%
Isis	709741	26.69%
Bodrum	807585	30.36%
Bodrum	826528	31.08%
Bodrum	881864	33.16%
Marmara	1044298	39.26%

3.2.Results of Statistical Analyses

The results of the 2 independent samples nonparametric test can be seen in Table 5. For the nonparametric test, Mann-Whitney U test has been used. In the upper box, the comparison of the ranks for 6 authentic samples and 4 forgery samples can be seen. In the lower box the statistical evaluation of the results can be seen. Since the number of samples was too small, “descriptives” table has not been included in the results.

Mann-Whitney

Ranks

	Forgery	N	Mean Rank	Sum of Ranks
Ca	Authentic	6	7,50	45,00
	Forgery	4	2,50	10,00
	Total	10		

Test Statistics[b]

	Ca
Mann-Whitney U	,000
Wilcoxon W	10,000
Z	-2,558
Asymp. Sig. (2-tailed)	,011
Exact Sig. [2*(1-tailed Sig.)]	,010[a]

a. Not corrected for ties.

b. Grouping Variable: Forgery

Table 5 – Results of the 2 Independent Samples Nonparametric Test

3.3.Results of Microscopic Analyses

In order to see the mineralogical and textural differences between a natural Marmara marble sample and a forgery sample obtained from Akşit Sanat workshop, thin section investigations were carried out by means of an Olympus optical microscopy. As can be seen in the Figures 19-21, natural marble sample exhibits granoblastic/ equigranular / interlocking texture of calcite dominant rock composition. Few flakes of muscovite crystals are present and they may exhibit some foliation (slightly orientation), although not as characteristic feature of the marble. Coarse and fine grain sized calcite crystals are unevenly distributed.

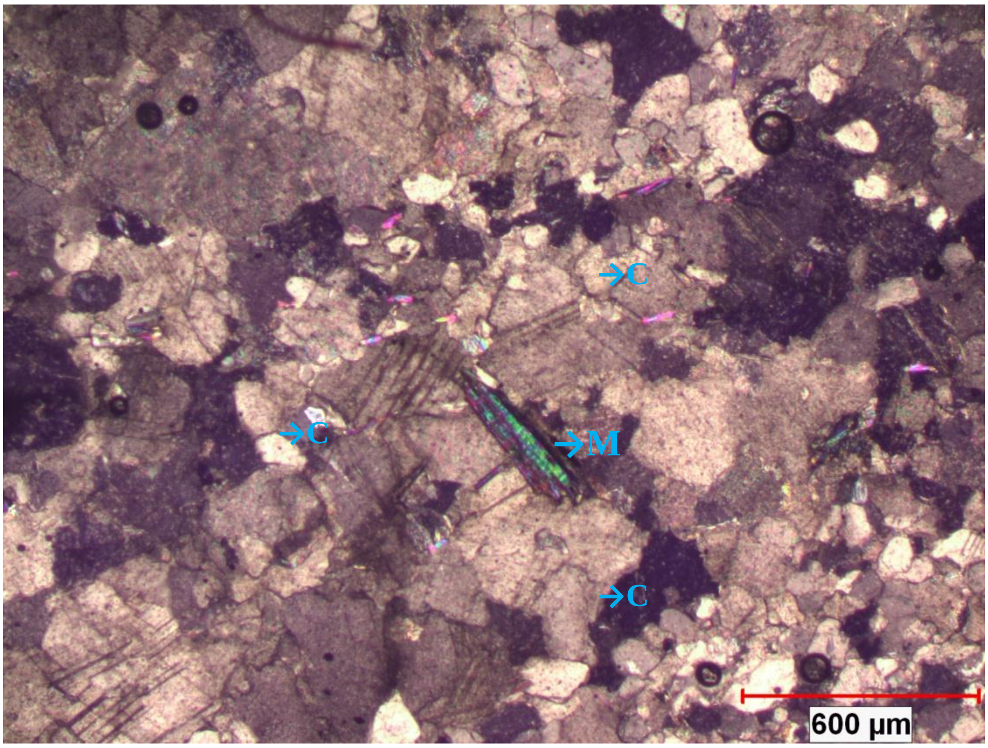


Figure 19 – Thin Section Photomicrograph of Marmara Marble. Coarse and fine grained calcite is the essential mineral, whereas few grains of muscovite mica (M) as seen in the middle of the Figure are seen as distributed among the calcite grains (C) . (Crossed nicols, 4x)

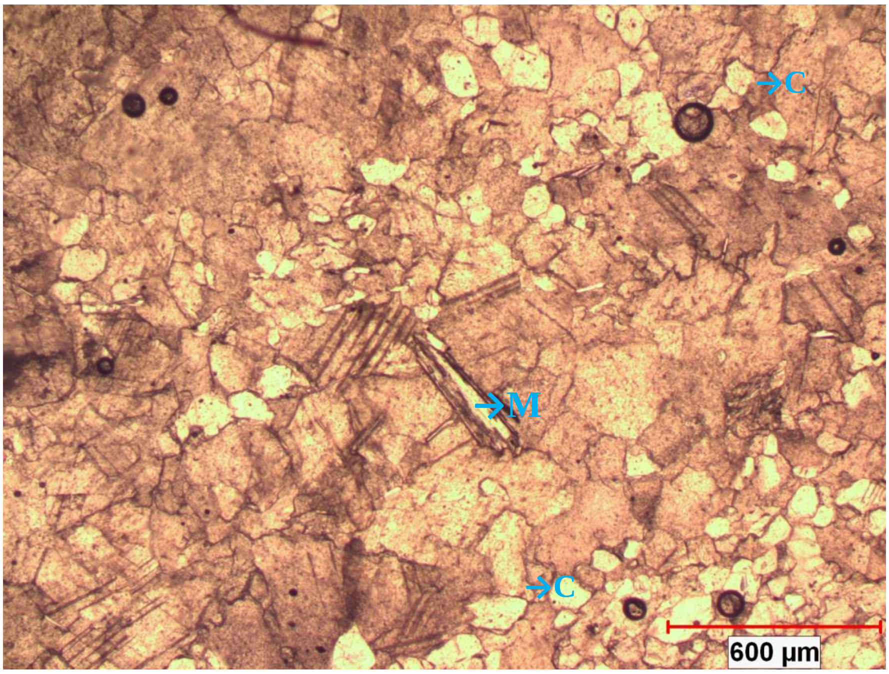


Figure 20 – Same as Figure 19 with Analyzer-Out Position. Muscovite mica (M), Calcite (C).

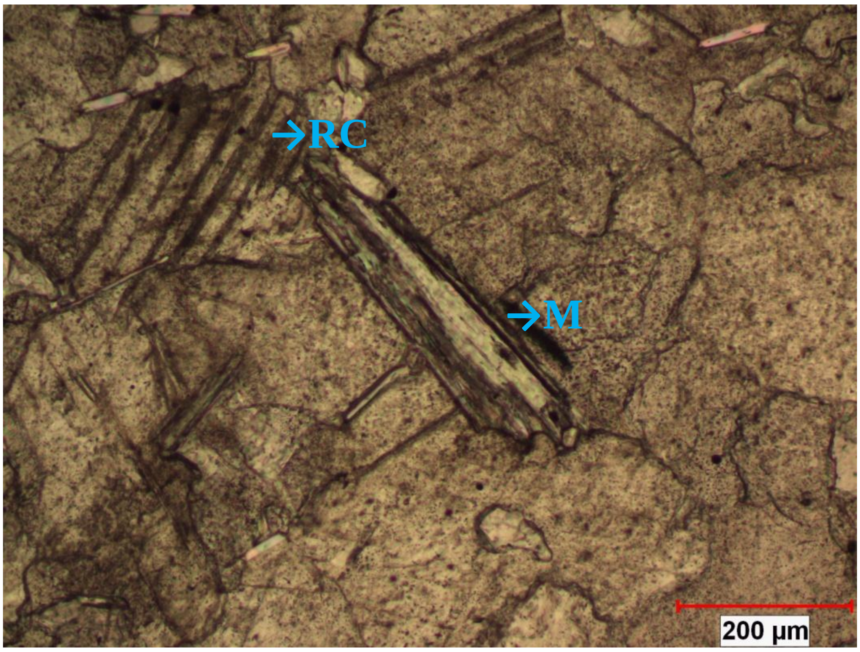


Figure 21 – A photomicrograph of Marmara Marble. Showing in close view the foliated morphology of muscovite crystal (M) and equigranular/ interlocking calcite grains. Rhombohedral cleavage of some calcite crystals (RC) are also observed (single nicol, magnification 10x).

Forgery samples, on the other hand, shows completely different texture where angular and broken calcite crystals of various sizes are unevenly distributed within the artificial polyester binding material (Figures 22-24).

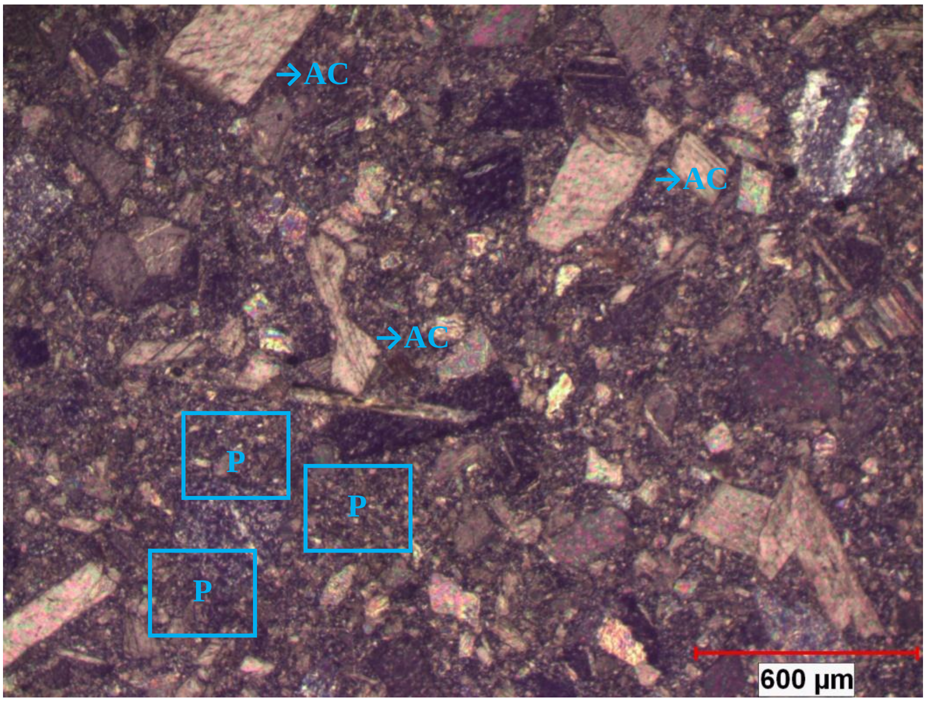


Figure 22 – Thin Section Photomicrograph of Forgery Bodrum Sample. Angular grains of calcite (AC) are distributed within the polyester (P) as the binding material (crossed nicols, magnification 4x)

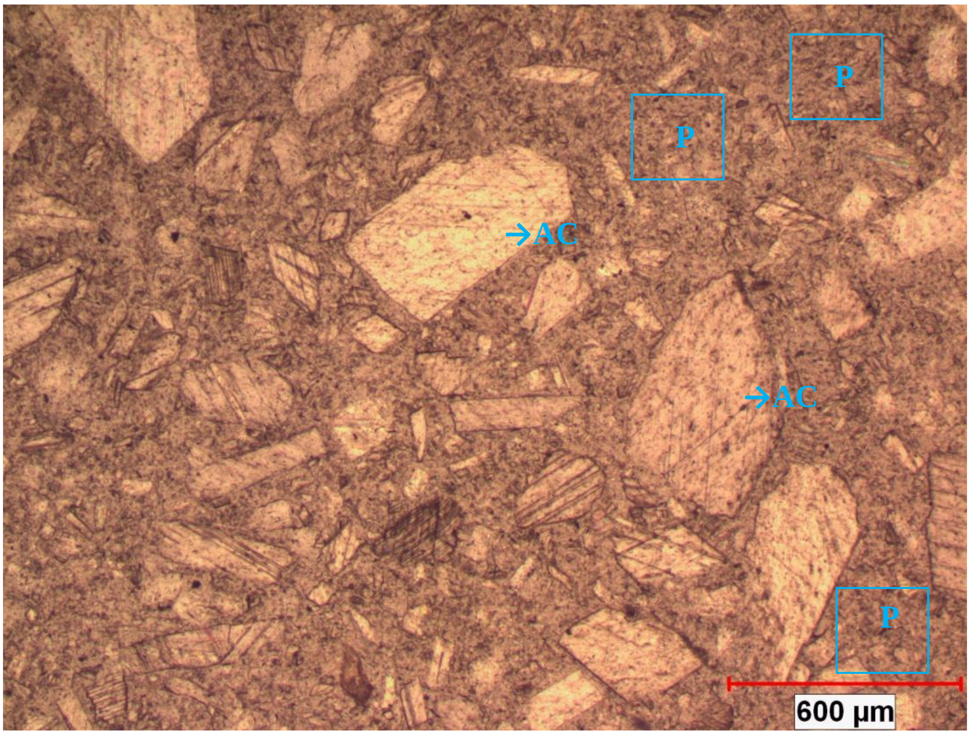


Figure 23 – Same as Figure 22 with Analyzer-Out Position. The calcite crystals (AC) floating in the polyester (P) binding material are clearly observable.

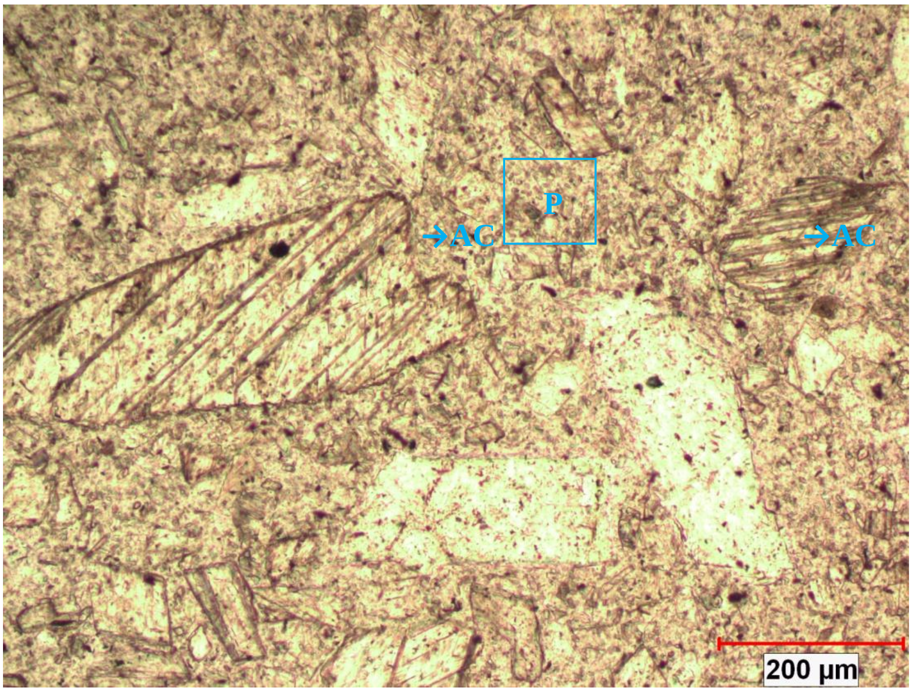
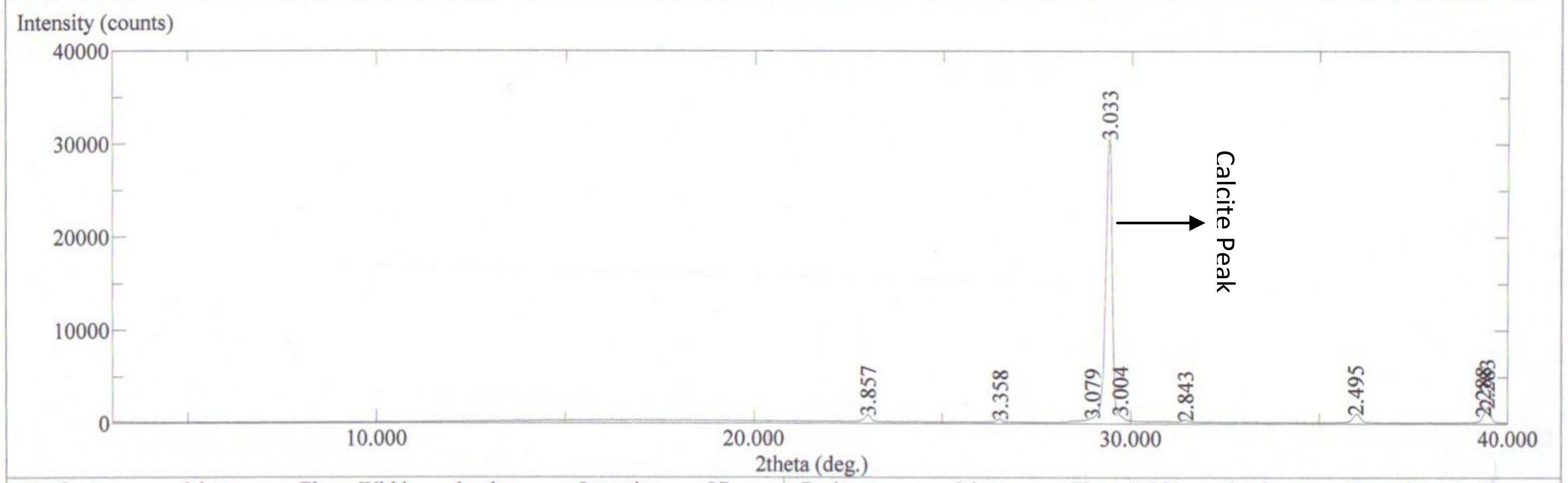


Figure 24 – A photomicrograph of Bodrum Sample. Showing in close view floating calcite grains (AC) in the polyester matrix (P) (single nicol, magnification 10x).

3.4.Results of X-Ray Diffraction Analyses

In order to identify the minerals present in the Bodrum and Marmara samples, X-ray diffraction analyses have been performed. The result for the Bodrum sample which can be seen in Figure 25, gives a peak at 3.033 which is a peak used for identification of calcite mineral. The result for the Marmara sample, which can be seen in Figure 26, gives two peaks at 3.025 and 2.886, calcite and dolomite peaks respectively.

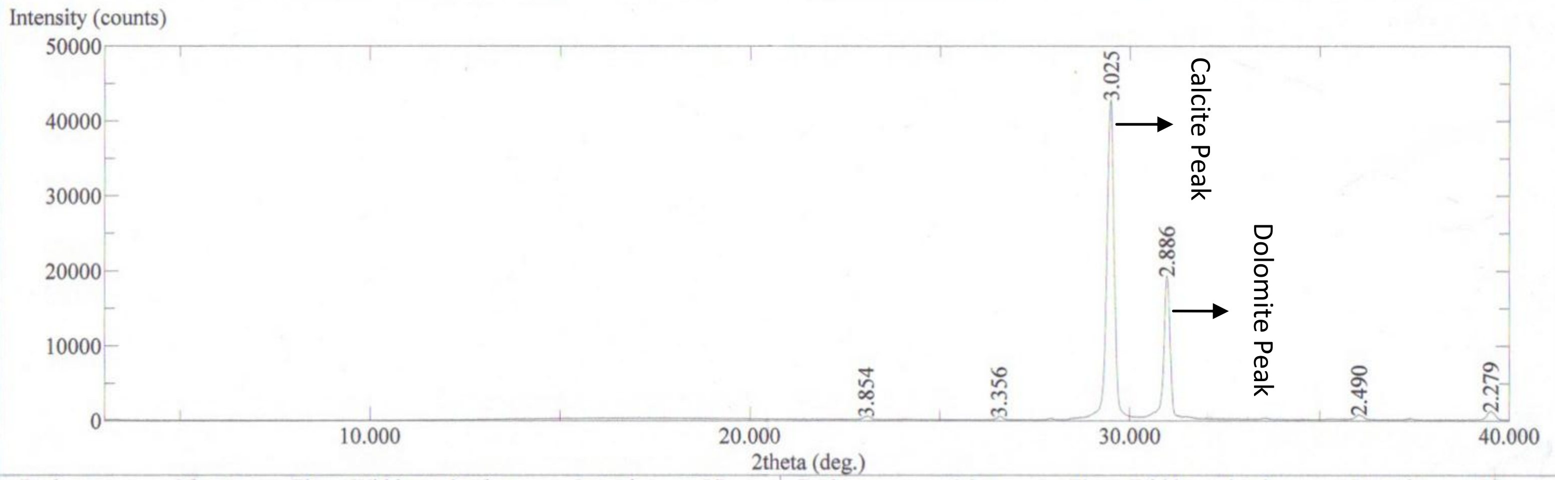
Peak Search



Peak no.	2theta	Flex Width	d-value	Intensity	I/Io
1	23.040	0.141	3.8570	937	4
2	26.520	*****	3.3582	527	2
3	28.980	0.071	3.0785	673	3
4	29.420	0.165	3.0335	30592	100
5	29.720	0.047	3.0035	956	4
6	31.440	*****	2.8430	454	2
7	35.960	0.047	2.4954	1078	4
8	39.340	0.047	2.2884	915	3
9	39.440	0.094	2.2828	1774	6

Figure 25 – Result of XRD Analysis on Bodrum Sample

Peak Search



Peak no.	2theta	Flex Width	d-value	Intensity	I/Io	Peak no.	2theta	Flex Width	d-value	Intensity	I/Io
1	23.060	0.071	3.8537	615	2						
2	26.540	0.118	3.3558	618	2						
3	29.500	0.212	3.0254	42825	100						
4	30.960	0.141	2.8860	19399	46						
5	36.040	*****	2.4900	858	3						
6	39.500	0.118	2.2795	1340	4						

Figure 26 – Result of XRD Analysis on Marmara Sample

3.5.Discussion

The aim of this study is to test for the applicability of the non-destructive device of portable X-Ray Fluorescence (PXRF) to identify authenticity of a marble artifact. To test for this method, a total of eleven samples that include authentic sculptures, forgeries and a natural marble piece have been analyzed. To serve the scope of this thesis, in the study only forgeries made with casting technique by using marble dust and polyester mixtures has been used.

The X-ray fluorescence results show that Ca, Fe and Sr have been detected in all samples. Ca is the main element in the composition of all samples. K, Ti, Sr, Ni, Cu and Mn have been detected in most samples both authentic and forgery. Pb is detected only in the authentic samples, but has not been detected in the Acanthus although it is also an authentic sample. Co has been detected only in the forgery samples. P, Se, Cd, Sb, Sn, W, Bi and U levels are lower than the limit of detection, in all of the samples. Zn, Rb, Th, Cl, Ag, Au, As, Mo, Cr, V and Zr has been detected in some measurements in both authentic and forgery samples. Hg has been detected only in a few measurements of the authentic samples. A table of detected elements with regard to their occurance quantities can be seen (Table 6). S has been detected in all measurements of Emperor, in one measurement of Acanthus, and two measurements of Eros and one measurement of Isis. The values are considerably high when compared to other elements detected, except for Ca. This might have been due to diffusion of sulfur having ions from the environment during burial conditions for authentic samples.

Table 6 – Elements Detected in Authentic and Forgery Samples

Samples	Authentic	Forgery
In all samples	Ca, Fe, Sr, Ni, Cu	Ca, K, Fe, Sr, Co
>50% of the samples	K, Ti, Mn, Zn, Pb	Ti, Ni, Cu, Mn,
<50% of the samples	S, Rb, Th, Cl, Ag, Au, Hg, As, Mo, Cr, V	Zn, Pb, S, Rb, Th, Cl, Ag, Au, As, Mo, Cr, V, Zr
<LOD in all samples	Co, Zr, P, Se, Cd, Sn, Sb, W, Bi, U	Pb, Hg, P, Se, Cd, Sn, Sb, W, Bi, U

Because of the inconsistency of the elemental concentrations within the repeated measurements and among the samples, elements other than Ca, Co and Pb have not been considered as statistically significant indicators.

Ca readings show variance among authentic, forgery and natural samples. Although a variance was expected between forgery samples and the rest of the samples, a difference between the calicum levels of Marmara sample and authentic samples was not expected since authentic samples were made of natural marble like Marmara marble itself. The Ca values of Marmara marble was lower than Ca levels of authentic samples. The X-ray diffraction analyses show that Marmara marble gave peaks at 2.886 and 3.025, which means that it also includes dolomite as well as calcite. Thus the existence of Mg in Marmara sample might be the reason for relatively low level of Ca when compared with authentic samples.

The difference between forgery samples and the other samples, has been expected because of the compositional differences between cultured marble and natural marble. Although the number of samples was limited, 2 independent samples nonparametric test of Mann-Whitney U test which is designed for small sample sizes has been applied to test whether this difference in Ca levels were significant or not. As can be seen in Table 5, not only is the difference of Ca levels evident when they are converted to rank points with respect to their groups but also they are statistically significant with a p value of .010.

Co was detected in all forgery samples. As supported by the literature, since Co was added to the marble dust and polyester mixture, it was expected to find Co in the forgery samples. In authentic samples and Marmara sample the lack of Co is expected as Co is not a natural impurity of marble.

Pb is detected only in authentic sculptures analyzed in the museum (Man, Woman, Sitting, Sarcophagus, Emperor) except for the Acanthus sample (Figure 11) for an unknown reason. Average lead value of the samples is 9.5 ppm. Marmara marble which is used as reference does not contain any lead like the forgery samples. The existence of lead may come from presence of zinc deposits found in marble (Dunn, 2010).

The microscopic examination shows the compositional and textural differences between natural marble and cultured marble clearly. The Marmara marble, being natural marble, shows interlocking calcite crystals with muscovite as impurity. The Bodrum sample on the other hand presents calcite crystals distributed in a matrix of polyester. The crystals are floating within the matrix and the interlocking texture observed in natural marble cannot be observed in the Bodrum Sample. Also the shape of calcite crystals is different in natural marble and cultured marble. In the Bodrum sample, the calcite crystals have angular shape as a result of fragmentation during the process of dust production. Unfortunately, thin sections of authentic marble sculptures could not be studied because of the destructive nature of the thin-section preparation.

CHAPTER 4

CONCLUSION

At the end of this study, the following conclusions are obtained:

1- The results indicate that analyses made with portable X-ray fluorescence device is capable of distinguishing authentic sculptures from forgeries made of cultured marble through Ca and Co concentrations.

2- Although this study is efficient for detecting forgeries made of cultured marble, the method may not be used with other types of forgeries that use real marble as their source since the method relies on compositional differences between the natural and cultured marble.

3- Although the study involves limited number of samples, independent samples t-test could successfully be applied. However, if the sample size could be increased, other statistical methods would become available.

4- Thin section investigations successfully distinguish between authentic and cultured marbles. However, since it is a destructive method, it can only be applied if samples from authentic marble sculptures are provided by the museums.

5- Trace elements like Pb in marble may be used for provenance analysis of marble sculptures since this element is hosted by calcite crystals which are the essential mineral in marbles affected by ore mineralization by metasomatism.

Suggestions for further study:

The PXRF technique used in this thesis work proved to be successful to distinguish cultured marbles and natural marbles. Also elemental (Pb and Co) differences appeared to be significant to distinguish marble compositions.

As a further study PXRF analyses with a larger sample number is suggested to be carried out to test this method for detection of marble authenticity. If a large enough sample is obtained, a linear regression equation may be calculated, which may be used to assess the authenticity of an unknown sculpture. By looking at the position of the unknown sculpture on the regression line, one can determine whether it stands within the confidence interval of authentic sculptures.

Besides portable XRF analyses, mineral composition of the samples could be analyzed by X-ray diffraction method, in order to get mineralogical composition. This is especially necessary for authentic marble sculptures which show greater amount of calcium than Marmara marble.

Provenance analysis by XRF of the authentic marble sculptures in the museums seems to be a subject for further investigation.

REFERENCES

Ashmole, B. (1961) *Forgeries of Ancient Sculpture: Creation and Detection*. Holywell Press: Oxford.

Başer, O. (2009) *Stabilization of Expansive Soils Using Waste Marble Dust.* MSc. Metu: Ankara.

Best, M.G., (1982), *Igneous and metamorphic petrology.* W.H. Freeman & Company.

Borghi, A., Vaggelli, G. MArcon, C. & Fiora, L. (2009) “The Piedmont White Marbles Used in Antiquity: An Archaeometric Distinction Inferred by a Minero-Petrographic and C-O Stable Isotope Study” in *Archaeotmetry* 51:6. pp. 913-931.

Council of Europe, *European Convention on the Protection of the Archaeological Heritage*. Valetta, Malta 16 January 1992. Last Accessed on 14 April 2012. http://conventions.coe.int/Treaty/en/Treaties/html/143.htm

Dietrich, R.V. & Skinner, B.J. (1979) *Rocks and Rock Minerals.* Wiley & Sons

Dunn, P. J. (2001) “Geochemistry” in *Franklin and Sterling Hill, New Jersey: the World’s Most Magnificent Mineral Deposits*. http://franklin-sterlinghill.com/dunn/ch10/hostminerals.stm .

Dutton, D. (2003) “Authenticity in Art” in *The Oxford Handbook of Aesthetics*. Oxford University Press: New York. Last Accessed on 21.06.2012. http://denis dutton. com/authenticity.htm

"EcoMarble (FP5-GROWTH-GRD1-1999-10404)." *GeoAnalysis S.A.* Last Accessed on 20 May 2012. http://www.geoanalysis.gr/index.jsp;jsessionid= 5FBCEA41865CEF3F066381030DCEE7CE?CMCCode=10050103&extLang=LG .

Ehlers, E.G. & Blatt, H. (1982) *Petrology: Igneous, Sedimentary and Metamorphic.* Freeman: San Francisco.

Fettes, D. & Desmons, J. (2007) *Metamorphic Rocks: a Classification and Glossary Terms: Recommendations of the International Union of Geological Sciences Subcommission on the Systematics of Metamorphic Rocks*. Cambridge University Press: New York.

Fitton, J. L. (1999) "Marble Figurine of a Woman." *British Museum.* Last Accessed on 7 May 2012. http://www.britishmuseum.org/explore/highlights/highlight_ objects/gr/m/marble_figurine_of_a_woman.aspx .

Fleming, S. J. (1975) *Authenticity in Art: the Scientific Detection of Forgery*. Crane, Russack: New York.

"Forgery" *University of Chicago: Theories of Media: Keywords Glossary.* Last Accessed on 29.06.2012. http://csmt.uchicago.edu/glossary2004/forgery.htm

Gürü, M., Akyüz, Y. & Akın, E. (2005) "Mermer Tozu/Polyester Kompozitlerde Dolgu Oranının Mekanik Özelliklere Etkileri" in *Politeknik Dergisi* 8:3. pp. 271-274.

Gürü, M., Tekeli, S. & Akin, E. (2007) "Manufacturing of Polymer Matrix Composite Material Using Marble Dust and Fly Ash" in *Key Engineering Materials* 336-338. pp.1353-1356.

Haywood, I. (1987). *The Missing Link: Archaeological Forgery and Fictions of the First HumanFaking it.* Last Accessed on 21.07.2012. http://www.clarku.edu/~ piltdown/map_expose/the_missing_link.html

Herz, N. (1988) “Geology of Greece and Turkey: Potential Marble Source Regions” in *Classical Marble: Geochemistry, Technology, Trade.* Kluwer Academic Publishers: Dordrecht. pp. 7-10.

Herz, N. & Waelkens, M. (1988) *Classical Marble: Geochemistry, Technology, Trade.* Kluwer Academic Publishers: Dordrecht.

“L’artigianato”Last Accessed on 16 May 2012. http://www.italianhandicraft.it/ products/ busto-di-marco-aurelio--marco-aurelioz.htm .

“Marble 1” *Glossary of Stone Industry Terms.* Last Accessed on 12 April 2012. http://www.marble-institute.com/consumers/glossary.pdf .

“Marble 2” *Oxford Dictionaries: the World’s Most Trusted Dictionaries*. Last Accessed on 17 April 2012. http://oxforddictionaries.com/definition/marble .

Margolis, S.V. & Showers, W. (1988) “Weathering Characteristics, Age, and Provenance Determinations on Ancient Greek and Roman Marble Artifacts” in *Classical Marble: Geochemistry, Technology, Trade.* Kluwer Academic Publishers: Dordrecht. pp. 233-242.

Michael , C.T., Zacharias, N., Maniatis, Y. and Dimotikali, D., (1997) “A new technique (foil technique) for measuring natural dose in TL dating and its application in the dating of a mortar containing ceramic fragments” in *Ancient TL* , 15:2-3. pp. 36-42.

Michael , C.T., Zacharias, N., Polikreti, K and Pagonis, V.,(1999) “Minimizing the Spurious TL of Recently Fired Ceramics Using the Foil Technique, *Radiat. Prot. Dosim.*, 84. pp. 1-49, 499-502.

Muscarella, O. W. (2000) *The Lie Became Great: The Forgery of Near Eastern Cultures.* Styx Publications: Groningen.

Palagia, O. (2006) *Greek Scuplture: Funciton, Materials and Techniques in the Archaic and Classical Periods.* Cambridge University Press: New York.

Polikreti, K., Michael, C.T. & Maniatis, Y. (2002) “Authenticating Marble Sculpture with Thermoluminescence” in *Ancient TL* 20:1. pp. 11-18.

Polikreti, K. (2007) “Detection of Ancient Marble Forgery: Techniques and Limitations” in *Archaeometry 49:4.* pp. 603-619.

Potts, P. J., (2008) “Introduction, Analytical Instrumentation and Application Overview” in *Portable X-Ray Fluorescence Spectrometry: Capabilities for In Situ Analysis.* RSC Publishing.

Sen, G. (2001) *Earth’s Materials: Minerals and Rocks* Prentice Hall

Ulens, K., Moens, L. & Dams, R. (1995) “Analytical methods useful in authenticating ancient marble sculptures” in *The Study of Marble and Other Stones Used in Antiquity.* Archetype Publications: London. pp. 199-205.

"Using SPSS and PASW." in *Wikibooks, Open Books for an Open World*. Last Accessed on 27 May 2012. http://en.wikibooks.org/wiki/Using_SPSS_and_PASW.

Waelkens, M., De Paepe P., Moens, L. (1988) “Quarries and the Marble Trade in Antiquity” in *Classical Marble: Geochemistry, Technology, Trade.* Kluwer Academic Publishers: Dordrecht. pp. 11-28.

Williams, H., Turner, F.J. & Gilbert, C.M. (1982) *Petrography: an Introduction to the Study of Rocks in Thin Sections.* W.H. Freeman: San Francisco.