ACCESSORY MINERALS, δ^{13} C AND δ^{18} O, AND PETROGRAPHIC STRUCTURES OF PENTELIC AND PROCONNESIAN QUARRY MARBLES: ANALYSIS WITH NONMETRIC MULTIDIMENSIONAL SCALING

FOR ARTIFACT PROVENANCE

by

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(Under the Direction of Samuel Swanson)

ABSTRACT

41 samples from the quarries of Mount Pentelikon (Attica, Greece) and Proconnesos (Marmara Island, Turkey) were analyzed for accessory minerals using an electron microprobe, stable isotope δ^{13} C and δ^{18} O, and maximum grain size to investigate the dissimilarities between the quarry regions. The multivariate data were statistically analyzed using nonmetric multidimensional scaling, a dimensionality-reducing ordination method that was previously used almost exclusively for psychological and ecological data. Results from the nonmetric multidimensional scaling analyses showed dissimilarities between Pentelic and Proconnesian marble based primarily on stable isotope δ^{13} C and δ^{18} O and maximum grain size, and separation to a slightly lesser degree based on accessory mineral content.

INDEX WORDS: Greek Marble, Mediterranean, Quarries, Provenance, Accessory minerals, Stable Isotopes, Nonmetric Multidimensional Scaling

ACCESSORY MINERALS, δ^{13} C and δ^{18} O, and petrographic structures of pentelic and proconnesian quarry marbles: analysis with nonmetric multidimensional scaling for artifact provenance

by

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MASTER OF SCIENCE

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ACCESSORY MINERALS, δ¹³C AND δ¹⁸O, AND PETROGRAPHIC STRUCTURES OF PENTELIC AND PROCONNESIAN QUARRY MARBLES: ANALYSIS WITH NONMETRIC MULTIDIMENSIONAL SCALING FOR ARTIFACT PROVENANCE

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DEDICATION

For Łukasz.

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CHAPTER 1

INTRODUCTION

MARBLE OF THE ANCIENT MEDITERRANEAN

Marble, a metamorphic rock with a protolith of limestone or dolostone, is composed of calcite (CaCO₃) or dolomite (CaMg(CO₃)₂), but may contain a variety of accessory minerals. Different types of accessory minerals are present in marble based on the composition of the marble (mainly the presence of Si, Al, K, Fe) and metamorphic grade. The accessory minerals may include relict sedimentary grains, such as quartz and apatite that were present in the sedimentary protolith, while porphyroblastic accessory minerals (e.g. biotite, tremolite) are produced via metamorphism (Capedri et al., 2004; Capedri and Venturelli, 2004). The compositions of some accessory minerals are variable (e.g. micas). Their compositions are determined by the bulk composition of the protolith, as well as the pressure and temperature conditions during metamorphism (Yardley, 1989).

The Mediterranean Region includes parts of Spain and France, Italy, Greece, the Aegean Islands, Turkey, Lebanon, Israel, and northern Africa (Abulafia, 2003; Figure 1.1). Within the Mediterranean region are numerous quarries of marble that have been economically important for at least the past three millennia (Renfrew, 1969). There are as many as 33 major groups of ancient and modern marble quarries in the Mediterranean (Lepsius, 1890; Washington 1898; Herz 1988; Capedri et al. 2004).



Figure 1.1. Map of the Mediterranean Region.

Notable use of marble in the Mediterranean began in the Third Millennium B.C. within the southern Aegean Sea's Cycladic Islands, also known as the Cyclades. Human activity with marble may have begun as early as 5000 B.C on the Greek mainland and Crete as well as the Cyclades. (Waelkens et al., 1988). The Cyclades are composed of about 220 islands, and are known for their ancient marble figurines, found in island grave sites (Renfrew 1969; Branigan 1971). The early Cycladic figurines are mostly female human shapes. (Fig. 1.2, 1.3, 1.4). On average, the figurines ranged in size from 5 cm to 1.5 m (Renfrew, 1969). The largest of the marble figurines were likely quarried from the islands of Naxos and Paros, while smaller figurines could easily be made from loose marble found on any number of Cycladic islands (Griffiths Pedley, 2007).

The three major Greek colonies during the Mediterranean's Bronze Age (Fig. 1.5) were Crete, the Cyclades, and mainland Greece. The Cyclades were among the first areas of the Mediterranean to be colonized, in the Early Bronze Age and Late Neolithic Period, ca. 3000 B.C. (Griffiths Pedley, 2007). The human inhabitants of these islands later migrated west to the present-day Greek mainland, and to southern Italy. It was also c. 3000 B.C. that groups of people in Anatolia (present-day Turkey) may have migrated to northern Greece (Griffiths Pedley, 2007).

The end of the Bronze Age, ca. 1100 B.C. signaled the Geometric Period, often referred to as the Dark Age of Greece (ca. 1100 B.C. – 700 B.C.). Artifacts with linear, geometric shapes painted on them and rigid statuettes from the Geometric Period are found across the Greek colonies. It was during this period of time that the Greek state and alphabet were established (Jeffery, 1961). Originating from the artisans of Athens, painted terracotta kraters and amphoras, often found buried with the dead or as grave markers, were seen more frequently than marble artifacts (Fig. 1.6). Burial sites at Corinth from this period contained terracotta vessels, local

sandstone grave slabs, and local sandstone sarcophagi, rather than marble artifacts (Brookes, 1981). Carter (1972) suggested the possibility that stone craftsmen during this time may have been trained in the east (i.e. Mesopotamia), although there is little evidence to prove or disprove this idea. The close of the 6th Century marked the end of Antiquity in the Mediterranean.



Figure 1.2. Cycladic marble female figure, Late Spedos-Type (ca. 2600-2400 B.C.). Image © The Metropolitan Museum of Art, used with permission through the Images for Academic Publishing (IAP) initiative.



Figure 1.3. Cycladic marble female figure (ca. 2300-2200 B.C.). Image © The Metropolitan Museum of Art, used with permission through the Images for Academic Publishing (IAP) initiative.



Figure 1.4. Cycladic marble head from the figure of a woman (ca. 2700-2500 B.C.). Image © The Metropolitan Museum of Art, used with permission through the Images for Academic Publishing (IAP) initiative.

BC	CYCLADES	GREECE
3000	Early Cycladic I	
2800		Early Hallonistic I
2600		
2500		
2400	Farly Cycladic II	Farly Hellenistic II
2300	Early Cycladic II	
2200	Early Cycladic III	Farly Hallenistic III
2100		
2000	Middle Cycledie I	
1000	Wilddie Cycladic I	
1900	Middle Creek die U	Middle Hellenistie
1800	Middle Cycladic II	
1700	Middle Cruele die III	
1600	Wilddie Cycladic III	
1000		Late Hellenistic I
1500		Late Hellenistic II
1400	Late Cycladic	
1300	-	Late Hellenistic III
1200		
1100		
1000	Dark Age (Geometric Period)	
900	_ `	

Fig. 1.5. Timeline of the Bronze Age in the Mediterranean, from Griffiths Pedley (2007).



Figure 1.6. Geometric Period krater, terracotta (ca. 750-735 B.C.). Image © The Metropolitan Museum of Art, used with permission through the Images for Academic Publishing (IAP) initiative.

The end of Antiquity led into the rise of Ancient Greece and the time of Archaic and Classical Greece (ca. 600 B.C. – 336 B.C.), a time that produced some of the most revered Ancient Greek marble artifacts. While marble artifacts are relatively common in museums, marble may not have been the most preferred sculptural medium, as marble artifacts were able to survive the centuries better than precious metal-laden wood and valuable bronze. (Lawrence, 1926). Some of the marble artifacts of Archaic Greece include temple kore figures (Figure 1.7) and ornate sarcophagi as well as large structures such as the Parthenon (Figure 1.8) the Temple of Apollo at Corinth, and the Temple of Artemis at Sardis (Fig. 1.9). Kore, young female figures, and kouros, young male life-sized figures, were sculpted from marble, limestone, or dolostone. These figures adorned the outside of many Greek temples.

Ancient Roman society borrowed much from Greek society, not the least of which was marble artisanship. Rome originally had access to far less marble than the Greeks, and so trade with Greek colonies was essential to Rome's use of the material. The ability to quarry and transport different types of marble from different places is a display of economic strength. In the Roman Period and late Roman Republic (509 B.C. – 27 B.C.), and the Roman Empire (27 B.C. – 393, A.D.) until c. 250 A.D., Roman artisans made life-sized or larger marble copies of many Greek bronze or precious metal plated wooden statues (Vermeule, 1967). Through these marble copies, famous Greek sculpture was brought to Roman citizens (Potts, 1980; Vermeule, 1967). While the majority of original wooden and bronze Greek sculptures have not lasted to modern times, many Roman marble copies remain. Marble was also used in major Roman structures such as the Colosseum (Fig. 1.10), the Pantheon, and the Baths of Diocletan. Roman colonies in Greece, such as the Roman Baths at Isthmia, also had multiple varieties of decorative marble from across the Mediterranean (Reinhard 2005).



Figure 1.7. Archaic marble statue of a kore (maiden) (ca. 6th Century B.C.) Image © The Metropolitan Museum of Art, used with permission through the Images for Academic Publishing (IAP) initiative.



Figure 1.8. "The Parthenon", Frederic Edwin Church, oil on canvas. Image © The Metropolitan Museum of Art, used with permission through the Images for Academic Publishing (IAP) initiative.



Figure 1.9. Hellenistic marble column from the Temple of Artemis at Sardis (ca. 300 B.C.). Image © The Metropolitan Museum of Art, used with permission through the Images for Academic Publishing (IAP) initiative.



Figure 1.10. "The Colosseum, Rome", by Louis Ducros, pen and brown ink, watercolor, heightened with white. Image © The Metropolitan Museum of Art, used with permission through the Images for Academic Publishing (IAP) initiative.

The primary transport method of marble by the Greeks and the Romans was by sea. Most of the major quarry regions active from ancient to present times are located near the coastline and harbors. Like almost any export, quarry marble proximity to the sea makes for more efficient transport. The advantage of sea transport allowed the Greeks and the Romans to utilize many varieties of marble on individual buildings.

On a basic level, different types of white or grey marble may be classified by their geographic location of quarry origin. For example, white marble from the Cycladic Islands of Naxos or Paros is considered to be "Naxian" or "Parian". Marbles with colors other than white or grey often have specific names. Reinhard (2005), under the direction of Lorenzo Lazzarini, tentatively assigned provenance to polychromatic marbles from the Roman Baths at Isthmia, to southern Euboa (*cipollino* and *fior de pesco*), Thessaly (*verde antico*), Asia Minor: Verzirken (*breccia corallina*), Docimion (*pavonazetto*) and *Greco scritto*, possibly from Asia Minor, or Tunisia, or Algeria.

OVERVIEW OF THE GEOLOGIC HISTORY OF THE MEDITERRANEAN

The present-day eastern Mediterranean region is a collage of tectonic plates brought together during the closing of the Tethyan Oceans during Alpine-Himalayan orogeny. Several different continental fragments came together with ophiolitic mélanges (former ocean basins) and belts of high-pressure metamorphic rocks (former subduction zones). In the Early Jurassic Period, the continents of Africa and Eurasia were united with North America as the super-continent, Pangaea. The Tethys Ocean separated the future continents of Africa and Eurasia, opening to the east (Higgins and Higgins, 1996). In the Mid Jurassic, the North Atlantic Ocean began to form by the rifting of Pangaea along normal faults. The new crust created in these rifts formed the North Atlantic Ocean, beginning with the separation of Africa from North America, moving Africa eastward. By 110 Ma, Eurasia began to separate from North America (Higgins and Higgins, 1996).

The Tethys Ocean was ultimately closed by the clockwise rotation of the African plate about an axis of Gibraltar. The rotation of the African plate was slowed by the collision of the Arabian plate portion of the African plate against Eurasia, which produced the mountains of Turkey. Presently, the rotation of the African plate in this manner has almost ceased. Major plate motion in the region is currently dominated by the westward movement of the Anatolian Plate (Turkey) into the Aegean region (Okay et al., 2008).

This study focuses on select marble quarries from Mount Pentelikon and the island of Marmara in the Marmara Sea. Older maps put Mount Pentelikon in the Pelagonian Zone of Greece (Higgins and Higgins, 1996), but more recent workers place Mount Pentelikon in the northern part of the Cycladic Blueschist Unit (Shaked et al., 2000). Marmara Island is on the northern edge of the Sakarya Zone. The Pelagonian Zone/ Cycladic Blueschist Unit and the

Sakarya Zone are isopic zones (groups of rocks that share a common history) within the Aegean Region of the Mediterranean, and have been influenced by some of the same tectonic events. The marble quarries on Mount Pentelikon and Marmara Island both formed from carbonate units deposited on a passive plate margin adjacent to older igneous and metamorphic rocks.

MOUNT PENTELIKON

One of the more active quarry regions of Ancient Greece is Mt. Pentelikon (Fig. 1.11). Mount Pentelikon, or "Penteli", is a mountain composed of Triassic to Upper Cretaceous marble that overlooks the north side of Attica, Greece (Pike, 2000; Fig. 1.11, 1.12). The marble of Penteli was first quarried in the 5th Century B.C. and was utilized in the construction of the Athenian Acropolis, the Parthenon, a temple on the Athenian Acropolis, Prostoon in Eleusis, a "porch" attached to the Telesterion of Demeter and Persephone, and the Olympieion in Athens, a sanctuary of the cult of Zeus (Herz 1988; Korres, 1995). There are at least 172 individual ancient and modern quarries on Mt. Pentelikon (Pike, 2000). The basic structure of the major Pentelikon quarries is shown in Figure 1.13, in which pure marble is quarried between layers of impure marble (Korres, 1995).

Geologic Setting of Mount Pentelikon

Mount Pentelikon is part of the north section of the Attic-Cycladic metamorphic belt. Mount Pentelikon consists of five units of rocks metamorphosed in the Mesozoic, from youngest to oldest: 5) Upper "Hymettian" marble, 4) Kaisariani schist and marbles, 3) Lower "Pentelic" marble, 2) Pirnari dolomite beds, and 1) Vari schist and Pentelicus gneiss (Herz and Pritchett, 1953). The Lower Pentelic marble unit is white crystalline material, with calcite grains usually from 0.5 to 1.0 mm in size, foliated in grey streaks or flakes of white mica, with iron-bearing minerals and quartz (Herz and Pritchett, 1953).

Pentelic marble may be classified by three main layers: 3) the Upper Marble formation, 2) the Intermediate Schist formation, and 3) the Lower Marble formation (Lepsius, 1893; Pike, 2000). These three layers are within the Lower "Pentelic" Marble formation defined by Herz and Pritchett (1953). The ancient quarries of Mount Pentelikon are located in the Lower Marble formation, on the west side of the mountain (Pike, 2000).

Among the 172 Pentelic quarries identified by Pike (2000) is quarry P85. This is an ancient quarry, with exact time of quarry activity unknown. Marble within P85 is foliated with layers of white mica, and the eastern wall of the quarry has inclusions of epidote-schist. The center of the quarry contains marble with less mineralogical impurities, where accessory minerals are not always visible to the naked eye.



Figure 1.11. Map of eastern Mediterranean showing Mt. Pentelikon and Proconnesos.



Figure 1.12. Geological map of Attica and Athens showing Pentelikon, modified from Higgins and Higgins (1996).



Figure 1.13. Geological and structural features of te main Pentelikon quarries, modified from Korres (1995). M = Veins of best marble; Z = Layers of unusable marble, schists; P = Main shear joints; 1,2,3 = natural sections; Λ = Sections left unexcavated to act as buttresses and partitions.

PROCONNESOS

"Proconnesos" is the Ancient Greek name for present-day Marmara Island, Turkey, located in the southwest part of the Marmara Sea (Fig. 1.11, 1.14). The ancient Roman name for the island is written "Proconnesus". The quarry marble on Marmara Island is from the late Permian, located on the northeast side of the island (Attanasio et al., 2008; Fig. 1.14). There are at least 23 separate ancient and modern quarries on the island (Fig. 1.15). These quarry groups contain sets of smaller quarries with different times of marble extraction. Some Proconnesos quarries have been active as early as the Archaic Period, when their material was likely used to construct the first Artemision at Ephesos (Attanasio et al., 2008; Monna and Pensabene, 1977). The greatest quarry activity on Proconnesos was after the 1st Century AD, when the quarries became the property of Imperial Rome (Attanasio et al., 2006). It was perhaps to the advantage of the marble industry that the quarries of Proconnesos are located near to the coastline, so the quarried marble could be efficiently shipped to a number of destinations in the Mediterranean Region.

Evidence of marble shipments from Proconnesos was uncovered from a shipwreck just off the coast of western Anatolia, known as Kizilburun (Carlson and Aylward, 2010). This ship is believed to have sunk sometime in the Late Hellenistic Period (ca. 160 B.C. – 30 B.C.). The ship sank with several marble drums likely meant for the columns of the Temple of Apollo at Claros. The final destination of the marble drums was likely the Temple of Apollo at Claros, based on measurements of the diameter of the column drums (stackable cylinders of marble used to construct columns) recovered from the seafloor (Carlson and Aylward, 2010). Dr. Scott Pike examined samples of the marble for maximum grain size, and Dr. Donato Attanasio examined samples with electron paramagnetic spectroscopy (EPR). After review of the EPR data and stable

isotope δ^{13} C and δ^{18} O, the marble column drums were assigned to Proconnesos (Carlson and Aylward, 2010). The Proconnesos source is in line with the probable shipping routes of the Late Hellenistic Period.

Geologic Setting of Proconnesos

Proconnesos, or Marmara Island, is situated in the southwest part of the Sea of Marmara, an area that is presently influenced by the movements of the 1500 km long North Anatolian Fault Zone, a large east-west right lateral strike-slip fault (Wong et al., 1995). The North Anatolian Fault first became active in the late Miocene to Pliocene (Barka, 1992; Yaltirak, 2002) The Sea of Marmara originally formed along the Intra-Pontide Suture Zone, a suture that was likely created in the early Eocene. The creation of the Intra-Pontide Suture Zone likely caused uplift and erosion of the Marmara Region. Marmara Island is part of the Sakarya Zone, and area that has a long and complex history Rocks on Marmara Island consist of Triassic metabasite, marble, and phyllite, metamorphosed in greenschist and blueschist facies (Okay and Goncuoglu, 2004). These rocks are intruded by an east-west trending Eocene-Oligocene granodiorite pluton (Aygul et al., 2012). The granodiorite intrusion is about 1.2 - 2.0 km wide, and is likely part of the larger Eocene granitoid belt in northern Turkey. The intrusion of these granitoids followed plate convergence and continent-arc collision (Koprubasi and Aldanmaz, 2004). To the north of the pluton are the quarry marble units. Marble protoliths are Lower to Mid Jurassic shallow marine clastic rocks and Upper Jurassic-Lower Cretaceous neritic limestones (Okay and Goncuoglu., 2004; Okay and Satir, 2006). The marbles and associated metasediemnts show evidence of Barrovian metamorphism. Marble units are overlain by a thin sheet of serpentinite (Aygul et al., 2012).

The rock units on Marmara Island can be defined from north to south as the Upper unit and the Lower unit, divided based on calcitic and dolomitic marbles vs. granodiorites, metaserpentines, meta-gabbros, amphibolites, calc-schists, mica schists, and crystallized carbonate minerals (Attanasio et al., 2008; Fig. 1.16). The Upper unit contains the calcitic Proconnesian quarry marbles.


Figure 1.14. Geologic map of Proconnesos, modified from Attanasio et al. (2008).



Figure 1.15. Proconnesos quarry sites on the northeast part of Marmara Island, first published by Asgari and Matthews (1995), modified by Attanasio et al. (2008).



Figure 1.16. Lithology of Marmara Island. Marble on Marmara Island is quarried from the coarse crystalline marbles of the Late Permian Marmara marbles. (Attanasio et al., 2008).

PROVENANCE

Provenance of an object may be found by finding the original source or origin of the object (Rapp and Hill, 1998; Tykot, 2004). Determining an artifact's provenance is important in distinguishing original work from forgeries, often by tracing an artifact's ownership throughout history. Having direct documentation of the human ownership of an artifact can ensure authenticity, and thereby preserve the value of the artifact. Many archaeological provenance studies recognize the value of provenance as tracing the exchange of artifacts between different groups of people (Rapp and Hill, 1998; Tykot, 2004).

Provenance of a stone artifact (i.e. marble, obsidian, granite) may be accomplished by evaluating petrographic and geochemical data from potential quarry sites. Once consistent data are obtained for both artifact and quarry samples, quarry regions where an artifact least likely came from can be eliminated as possible sources. Based on the number of marble quarry regions throughout the Mediterranean region, for example, an artifact could have 30 potential source areas and a large number of possible quarry sites. A useful approach is to rule out quarries where an artifact did not likely originate, rather than assign the artifact to one definitive location. Once the geoscientist has excluded quarries from which the artifact did not likely originate, archaeologists who have a better understanding of patterns of habitation and trade may be better equipped to assign provenance to one specific location.

Provenance of Marble

Provenance studies of Classical marble artifacts began over 120 years ago (Lepsius, 1890). "Classical," as used here, refers to Classical Greece and Rome and the related archaeological materials of Ancient Greece and Rome (Griffiths Pedley, 2007).

This may be from the Bronze Age (3000 – 900 BC, Fig. 1.2) to as recent as the early Byzantine Empire (ca. AD 395). The Early Byzantine Empire also coincides with Late Antiquity. *Current Method*

The current standard among researchers in the marble provenance community utilizes a combination of $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ values and the maximum calcite or dolomite grain size of a sample to find provenance of a marble artifact. The maximum calcite or dolomite grain is measured with a ruler or under a microscope, based on whether the protolith was limestone or dolomite. The null hypothesis in a marble provenance study is that the variables used to characterize a sample will not distinguish one region from another. The alternative hypothesis is that the results of a marble provenance study will show that two samples from different regions are clearly distinguishable from one another. For the study to be successful, the alternative hypothesis needs to be true.

Current Study

The method that uses stable isotope δ^{13} C and δ^{18} O and maximum grain size for marble provenance studies has become popular because it is generally effective at separating quarry regions and can be replicated by different laboratories. However, as with almost any set of variables, when more marble data points are collected, there is more potential for overlap of data between quarry sites (Attanasio et al., 2008). The answer to improving the standard method of marble provenance is to add more variables to the existing method, and to interpret the data statistically in a way that is reproducible by the rest of the marble research community.

Accessory minerals found in quarry marble samples were added as statistical variables to make the existing method of marble provenance more effective. Data were analyzed by nonmetric multidimensional scaling. The method of analyzing stable isotopes and maximum

calcite grain size is then expanded by accessory mineral content and nonparametric statistical analysis. To test the utility of accessory minerals, marble samples from two major quarry regions, Mt. Pentelikon in Attica, Greece, and Proconnesos, also known as Marmara Island, Turkey, were selected for this study. Mt. Pentelikon and Proconnesos were chosen for their significance to the ancient marble industry. Many artifacts and architectural materials were made from these quarries, such as the Temple at Ephesos (Proconnesos) and the Athenian Acropolis columns (Mt. Pentelikon) (Attanasio et al., 2008; Pike, 2000). The cultural and economic value of these quarry products necessitates accurate methods of provenance.

CHAPTER 2

PREVIOUS STUDIES OF MARBLE PROVENANCE

OVERVIEW

The task of assigning provenance to Classical marble artifacts once exclusively belonged to Classical archaeologists. Provenance was assigned based on where an artifact was excavated, (Gardner, 1890), color of the marble, and texture of the marble as observed by the naked eye (Gardner, 1896; Marquand, 1898). The available historical and archaeological data would also be evaluated (Wace, 1906).

Color and texture of a marble sample are two important places to start, but some studies suggest that these properties may be subjective (Washington, 1898; Renfrew and Springer Peacy, 1968). Geoscientists became involved with the process of Classical marble provenance in order to develop less subjective methods. Analysis of Classical marble by geoscientists began with petrographic descriptions of marble from different quarry sites (Lepsius 1890) and evolved to include stable isotopic analysis (Craig and Craig, 1972), trace element analysis (Conforto et al., 1975), cathodoluminescence (Barbin et al., 1989; Barbin et al., 1990; Barbin et al., 1992; Attanasio et al., 2000), and accessory mineral analysis. (Capedri et al., 2004; Capedri and Venturelli, 2004).

Presently, there is no *single* variable that is routinely used for finding provenance of marble. Many studies analyze marble based on a combination of variables, such as stable isotopes, maximum grain size, cathodoluminscence, and accessory mineral content (Moens et al., 1988; Germann et al., 1988; Roos et al., 1988). Frequently published is the multivariate method

that uses a combination of stable isotopes δ^{13} C and δ^{18} O and maximum calcite or dolomite grain size (Pike, 2000; Carlson and Aylward, 2010). This multivariate data may then be analyzed by statistical methods. In marble provenance studies, the most commonly used statistical method currently is discriminant function analysis, which analyzes separation between predefined groups (Tykot, 2004; Attanasio et al., 2008). The predefined groups are typically different quarry regions.

PETROGRAPHIC ANALYSIS

One of the simplest ways to analyze marble is to describe the texture in thin section using a petrographic microscope. Many marble provenance studies begin with petrographic analysis in order to observe the basic characteristics of the sample. Basic textural elements include color, maximum calcite or dolomite grain size, variability of grain sizes, shape of grains, and the presence or absence of intergrowths in grains.

Petrographic analysis was the first method to be used systematically in Classical marble provenance studies (Lepsius, 1890; Washington, 1898; Renfrew and Springer Peacy, 1968). Lepsius (1890) introduced the method to the marble provenance community through the publication "Griesche Marmostudien" – "Greek Marble Studies". Lepsius was a German geologist who was working in Greece on geologic maps. He took interest in Classical marble provenance and characterized a variety of Greek marble quarry samples based on simple petrographic characteristics such as calcite grain appearance and color.

Washington (1898) also discussed the role of petrography in marble provenance studies in an address to the Archaeological Institute of America. Washington was an American petrologist and argued against subjectivity in the provenance studies of marble *connoisseurs*. A marble *connoisseur* is an archaeologist or art historian with a deep knowledge of artifacts from

Classical antiquity. The *connoisseur* may be certain of an artifact's origin based on its general appearance, but he or she also may be using qualitative methods that are difficult to replicate. The work of Washington (1898) doesn't diminish the work of archaeologists in marble provenance, but it does call for a systematic petrographic method for marble provenance. It may be gathered from Washington (1898) that the work of Lepsius (1890) was an incredible contribution to marble provenance research, but the classification of marble may differ by researchers.

Herz and Pritchett (1953) presented petrographic descriptions of Attic marble from Mt. Hymettos and Mt. Pentelikon. The study referenced Lepsius (1890) as the first to describe Attic marble for provenance purposes. Importantly, Herz and Prichett (1953) outlined four basic characteristics that should be recorded in provenance studies. These characteristics include: 1) the color of the marble sample, 2) the grain size, 3) the structures visible in the marble, and 4) the accessory minerals found in the marble. The benefit to this petrographic method is that it could be done with relatively simple tools such as a millimeter scale, hand lens, and petrographic microscope.

Almost 80 years after Lepsius (1890), Renfrew and Springer Peacy (1968) presented criticism of petrographic analysis in marble provenance studies. The authors suggested that the work of Lepsius (1890) may be subjective. To investigate the reproducibility of Lepsius (1890), Renfrew and Springer Peacy (1968) attempted to replicate Lepsius' original study.

The categories of marble that Lepsius (1890) created include "Penteli", "Hymettian", "Parian", and "Naxian" based on their respective locations (Mt. Pentelikon, Mt. Hymettos, Paros, Naxos). Using a petrographic microscope, Renfrew and Springer Peacy (1968) examined samples of similar origin and were unable to describe the samples in the same manner as Lepsius

(1890). Specifically, the color of different marbles and grain sizes differed between Lepsius (1890) and Renfrew and Springer Peacy (1968). Even today, a systematic approach to petrography in marble provenance for all studies has not yet been developed.

In more recent studies (Pike 2000; Capedri et al. 2004; Attanasio et al. 2008) petrographic analysis is done as an introduction to the marble sample suite. It is not the primary focus of most studies. Petrographic analysis is an important accompaniment to a multivariate study, but has not yet been standardized for all studies. The findings of preliminary petrographic analyses may be useful in selecting samples for further analysis, such as stable isotope analysis.

STABLE ISOTOPE ANALYSIS

Stable isotopic analysis in carbonate rocks requires the measurement of the ratios of ${}^{13}\text{C}/{}^{12}\text{C}$ and ${}^{18}\text{O}/{}^{16}\text{O}$ relative to the international Peedee Belemnite (PDB) standard of South Carolina (Herz, 1988). Today, the PDB standard is in extremely short supply, so a synthetic standard was made relative to the original PDB are and labeled "Vienna Pee Dee Belemnite - VPDB", having been made in a Austria. The deviation of isotopic ratios relative to the standard is written as " δ " and expressed in parts per thousand or as ${}^{0}\!/_{00}$, per mil (Herz, 1988). The general equations for carbon and oxygen isotopes are:

Equation 2.1. Carbon stable isotope analysis. (Coplen, 1994)

$$\delta^{13}C(^{0}/_{00}) = \left[\frac{(^{13}C/^{12}C)sample}{(^{13}C/^{12}C)standard} - 1\right] * 1000$$

Equation 2.2. Oxygen stable isotope analysis. (Coplen, 1994)

$$\delta^{18}O(^{0}/_{00}) = \left[\frac{(^{18}O/^{16}O)sample}{(^{18}O/^{16}O)standard} - 1\right] * 1000$$

Analysis of stable isotope δ^{13} C and δ^{18} O in Mediterranean marble has been the most widely used method for Classical marble provenance studies since Craig and Craig (1972) first published on the method. Stable isotope analysis is popular because it only requires a small amount of powdered sample, .1 mg, often obtained using a dental drill. A small sample means minimum destruction to marble artifacts, and increases the likelihood that museums will grant permission for quantitative provenance investigations. A database of stable isotope values from different Mediterranean regions was first established by Herz (1988) and continues to grow with new studies (Manfra et al. 1975; Herz 1988; Herz 1992; Wenner et al.,1988; Pentia et al., 2000; Pike 2000; Capedri et al. 2004; Capedri and Venturelli 2004; and Attanasio et al. 2008).

Craig and Craig (1972) analyzed quarry marble samples from Naxos, Paros, Penteli, and Hymettos for stable isotope δ^{13} C and δ^{18} O (Fig. 2.1). The results indicate separate fields for each quarry on a plot of δ^{13} C vs. δ^{18} O, which was at the time extremely promising for the marble provenance community. Numerous studies that employed stable isotopes (δ^{13} C and δ^{18} O) have followed since Craig and Craig (1972)'s initial assessment (Manfra et al. 1975; Herz 1988; Herz 1992; Wenner et al.,1988; Pentia et al. 2000; Pike 2000; Capedri et al. 2004; Capedri and Venturelli 2004; and Attanasio et al. 2008). The expectation for the results in these studies is generally the same: different quarry regions may have statistically different isotopic signatures.



Figure 2.1. Original stable isotopic database for Greek marble quarries (Craig and Craig, 1972).

ACCESSORY MINERAL ANALYSIS

Capedri et al. (2004) and Capedri and Venturelli (2004) presented the first systematic studies for the determination of marble provenance based on accessory minerals. Capedri et al. (2004) analyzed 75 marble quarry samples from 32 ancient quarry sites with a scanning electron microscope in Greece (21 sites), Macedonia (1), Italy (1), and Turkey (9), averaging about one to four samples per quarry. The study also analyzed samples for stable isotope δ^{13} C and δ^{18} O and maximum grain size. Since this was the first accessory minerals study of its kind, the objective was to analyze a few samples from many sites across the Mediterranean Region, rather than to analyze many samples from one area. Capedri et al. (2004) utilized a scanning electron microscope with an energy dispersive X-ray spectroscopy system in order to qualitatively analyze accessory minerals that may be too small to identify using a petrographic microscope, and to obtain compositional data for each mineral. Several of the accessory minerals identified by Capedri et al. (2004) have the potential for compositional variation. These include apatite (F, Cl), chlorite (Fe, Mg, Mn, Ti, Al), phlogopite (Fe, Mg, Mn, Ti, Al) and margarite (Na, K, Ca) from the Proconnesos quarries and apatite (F, Cl) and phengetic muscovite (Fe, Mg, Mn, Ti, Al) from Pentelikon quarries (Table 2.1).

Ultimately, Capedri et al. (2004) suggested that separate quarries may be distinguished by the presence or absence of certain accessory minerals. In the case of Pentelic marbles vs. Proconnesos, quartz is present in three out of four Pentelic samples, whereas quartz has not been found in any of the four samples from Proconnesos. The reverse is true for phlogopite, where three out of four Proconnesos samples contain some amount of the mineral, and Pentelikon samples were found to not contain phlogopite (Table 2.1).

Α	С	Q	Ap	Su	F	0x	Ch	К	PM	Ph	As	Pa	Ма	G
Penteli	G9	Х	Х	Fe		Ti,	?		Х					
(Pentelikon)						Fe,								
						Mn,								
						Cr								
	G12	Х					Х		Х					Х
	G1	Х	Х	Fe					Х					
Marmara	M1		Х	Fe	Х	Ti		Х		Х	Х		Х	
(Proconnesus)	M2		Х							Х		Х		
	M3		Х	Fe	Х			Х		Х		Х	Х	
	M4		Х										Х	

Table 2.1. Accessory mineral data for Penteli and Proconnesos samples (Capedri et al., 2004).

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Capedri et al. (2004)

Capedri and Venturelli (2004) used the database developed from Capedri et al. (2004) to analyze 38 Roman and medieval marble artifact samples for accessory minerals, stable isotope δ^{13} C and δ^{18} O, and maximum grain size. The published database of Capedri et al. (2004) is entirely quarry data, so the 38 artifact samples could be compared to it for provenance possibilities. Capedri and Venturelli (2004) concluded that this multivariate approach was more effective for provenance than isotope and maximum grain size data alone, assigning provenance to one most likely location in 37 out of 38 samples.

Accessory minerals found in marble are useful because they characterize marble samples based on the composition of the protolith and the metamorphic history of the sample. If accessory mineral content can be summarized for each sample, the method can be used in combination with maximum calcite grain size and stable isotope analysis. This combination of variables might then be analyzed by nonparametric statistical methods, which are statistical methods that make few assumptions about the data set beyond random sampling (Legendre and Legendre 1998; McCune and Grace 2002).

CHAPTER 3

METHODS

SAMPLES

The majority of the samples of the quarries of Pentelikon and Proconnesos for this study marble provenance came from previous studies (Pike, 2000; Attanasio et al., 2008). A total of 41 samples were used in this study. Of the 41 total samples, 10 are from Pentelikon, and were analyzed by Pike (2000) for stable isotopes, and 31 are from Proconnesos. Two sets of samples are from Proconnesos. Attanasio et al. (2008) previously analyzed 16 of the samples (Proconnesos A) for stable isotopes. Dr. Vildan Esenli amassed a new collection of 15 samples (Proconnesos B; Table 3.1). Accessory minerals for all samples were analyzed for this study. The Proconnesos B samples were also analyzed for stable isotopes and maximum grain size in this study.

Dr. Scott Pike originally sampled marble from Pentelikon for his Ph.D. dissertation at the University of Georgia, completed in 2000. Dr. Donato Attanasio of the Istituto di Struttura della Materia of the Consiglio Nazionale delle Ricerche (Institute of Structural Materials of the National Research Counsel) in Rome originally obtained Proconnesos A samples as part of a larger Marmara Island database (Attanasio et al., 2008). Dr. Vildan Esenli of Istanbul Technical University obtained 15 Proconnesos B samples specifically for this study. The use of previously analyzed samples (Pentelikon and Proconnesos A) provides a direct comparison of accessory mineral outcomes to a commonly accepted stable isotope and maximum grain size method. The Proconnesos B samples provide an opportunity to expand the Proconnesos database with new stable isotope and grain size data.

Table 3.1. Summary of sample set.

SAMPLES							
Penteliko (Pike,	Pentelikon (10 total) (Pike, 2000)		Proconnesos A (16 total) (Attanasio et al., 2008)		Proconnesos B (15 total) (sampled by Esenli)		
Sample	Description	Sample	Description	Sample	Description		
P85-1		C1.18	Ancient	Proc-1			
P85-2		C2.7	quarry at Ilik	Proc-2			
P85-4	-	C3.2s	Mermer	Proc-3			
P85-5	Querry	C4.4	Ancient quarry near the big column of Mandira	Proc-4a			
P85-6	Qually	C5.2	Big quarry	Proc-4b			
P85-7	(Pike, 2000)	C5b.13	wall west of Aksoy	Proc-5			
P85-8	2000)	C6.4	Ancient quarry including OC236	Proc-6	Proconnesos marble samples		
P85-9	-	C7i.8	Ancient	Proc-7			
P85-10		C8.5	quarry in the area of Mandira	Proc-8			
		C10.3		Proc-9			
		C11.2		Proc-10			
		C12.3	Ancient	Proc-11			
		C.13.6	quarry at	Proc-12			
		C14.7	Altintas	Proc-13			
		C15.1	-	Proc-14			
		C16.6					

PETROGRAPHIC ANALYSIS

Criteria for analyzing marble samples petrographically included identification of: 1) the color of the marble sample, 2) the maximum calcite grain size and variation, 3) the structures visible in the marble, and 4) the presence/absence of accessory minerals, as recommended by Herz and Pritchett (1953). The color of the marble sample was noted by viewing a hand sample. The maximum calcite grain size was also measured from hand samples with a metric ruler. Thin sections of the marble were commercially produced and polished for further electron microprobe analysis. The thin sections were first examined using a petrographic microscope in plane polarized light and cross-polarized light in order to identify grain structures and non-opaque accessory minerals. A reflected light microscope was used to preliminarily identify the possible opaque minerals based on reflected light color, prior to microprobe analysis. Smaller grain size of many accessory minerals made traditional petrographic identification impossible.

Maximum Calcite Grain Size

The maximum calcite grain size was found by using a ruler to measure the largest calcite grain visible in each of the 41 hand samples. For this entire sample set, calcite was the dominant carbonate mineral, so maximum calcite grain size was measured rather than maximum dolomite grain size. Calcite was mainly visible in thin section, with trace amounts of dolomite visible prior to the electron microprobe analysis. Grain sizes were measured in millimeters. No petrographic microscope was needed for this obtaining the maximum calcite grain size measurements, because the largest grain in each sample was visible to the naked eye.

STABLE ISOTOPE ANALYSIS

Pike (2000) provided stable isotope δ^{13} C and δ^{18} O values for Pentelikon. Attanasio et al. (2008) analyzed Proconnesos A samples prior to this work for δ^{13} C and δ^{18} O. This study obtained new data for Proconnesos B samples at the University of Georgia's Stable Isotope Laboratory, in the Department of Geology.

Stable isotopic analyses for Proconnesos B were accomplished using a method modified from McCrea (1950). Powdered samples (approximately 5.0 mg) were reacted under vacuum in 100% phosphoric acid at 50 °C. Carbon dioxide gas was extracted on a conventional vacuum line and analyzed on a Finnigan MAT 252 mass spectrometer.

Laboratory standards were prepared and analyzed with each set of samples. There were approximately eight samples in each batch. These standards were calibrated to NBS-19 (δ^{13} C = +1.95 per mil, δ^{18} O = -2.2 per mil) and NBS-18 (δ^{13} C = -5.0 per mil and δ^{18} O = -23.0 per mil). Sample isotopic results are normalized to the lab standards using a two-point scale, and all δ^{13} C and δ^{18} O values are reported relative to VPDB. The 2-sigma precision limit is 0.04 per mil for δ^{13} C and 0.05 per mil for δ^{18} O. Correction for reaction temperature assumes all samples are calcite, which can be confirmed by the calcite grains viewed in thin section. Less than 10% dolomite was present in each sample, and the majority of the samples contained under 5% dolomite.

ELECTRON MICROPROBE ANALYSIS

Polished thin sections were carbon-coated for accessory mineral analysis on a JEOL JXA-8600 Superprobe. The Superprobe ran Geller Microanalytical Laboratory's dQANT32 stage and spectrometer automation, operating in wavelength dispersive mode at the University of Georgia's Electron Microprobe Laboratory. For this study, accessory minerals were identified as

any mineral found in trace amounts that was obviously not the calcite matrix. Little was known about the accessory mineral content before electron microprobe analysis, as many of the grains are too small to identify using a petrographic microscope. Samples were characterized based on the presence or absence of a specified mineral, not on the percent of the mineral found in the sample. The percent of the mineral found in the sample was difficult to determine based on the small grain sizes, some of which were less than 5 microns.

The microprobe analyses were set up for reconnaissance under four routines: 1) sulfides, 2) oxides, 3) pyroxene, and 4) apatite. The sulfide routine analyzed element weight percent data for Fe, Cu, S, Ni, and sometimes Zn. It is suited for common sulfides such as pyrite, chalcopyrite, and sphalerite. The oxide routine analyzed weight percentages of Si, Ti, Al, Mg, Fe, Ca, Mn, Cr, and Ni. Minerals such as rutile, quartz, and titanite, can be identified by the oxide routine. The oxide routine also reveals the presence of certain micas and dolomite, although the totals are too low to publish because of the lack of certain elements such as K, F, and Cl for micas. The pyroxene routine can be used to preliminarily identify micas such as muscovite, biotite, phlogopite, paragonite, and margarite. The apatite routine analyzed P, Ca, Al, Mn, Cl, and F in apatite grains.

The 41 samples were analyzed with these reconnaissance routines in order to determine their accessory mineral content. While some of the initial totals may be less than ideal in reconnaissance, the data are useful to mineral identification. Reconnaissance provides enough information to state whether a mineral is present or absent in a sample. The routines were also used to note differences in compositional variation, as is the case for the micas in the pyroxene routine. The compositional data should only be considered qualitative. Totals are sometimes low and good stoichiometry is not always reported.

Carbonate Analysis for Temperature

Electron microprobe analyses of calcite in equilibrium with dolomite can be used to determine the temperature of equilibration of the two carbonate minerals based on the exchange of MgCO₃ (Anovitz and Essene, 1987). Using the electron microprobe, calcite and dolomite grains were located next to one another in several of the samples. When calcite and dolomite are found in contact with one another in a sample, it is assumed that they are in equilibrium. The calcite and dolomite grains were then analyzed with the electron microprobe. The weight percent of CaO, MgO, and CO₂ were then recalculated for their cation proportions. Calcium and magnesium share a site in the calcite mineral (Ca,Mg)CO₃. With the cation proportions of MgCO₃ calculated, the MgCO₃ value could be used with the calcite-dolomite thermometry equation of Anovitz and Essene (1987) (Equation 3.1).

Equation 3.1. Calcite-dolomite thermometry (Anovitz and Essene, 1987).

$T = A(X MgCO_3.Cc) + B(X MgCO_3.Cc) + C(X MgCO_3.Cc) + D(X MgCO_3.Cc) + E$ *Where A, B, C, D, and E are unit-less constants.*

\mathbf{T} = Temperature in Kelvin

X MgCO₃.Cc = Mole fraction of MgCO₃ in calcite (Cc) analysis

A = -2360.0 B = -0.01345 C = 2620.0 D = 2608.0E = 334.0

The composition of coexisting calcite and dolomite in marble is often used to calculate temperatures of metamorphic recrystallization, but it has not been used previously in marble provenance studies. Using Equation 3.1, we calculated equilibrium temperatures for each sample. The calculated temperatures from Equation 3.1 depend on the consistency of

temperature results from multiple calcite grains in a single sample, as well as the consistency of the results across multiple calcite grains in a set of quarry samples. The results of Equation 3.1 also have broader implications for the metamorphic history of a quarry region.

STATISTICAL METHODS

Nonmetric Multidimensional Scaling (NMDS)

An ordination is an exploratory statistical method that reduces the dimensionality of a data set. Nonmetric multidimensional scaling (NMDS) is a numerical ordination method that uses a predefined number of axes to reduce dimensionality based on the dissimilarity among samples in the dataset, effectively reducing the number of variables. NMDS was chosen over other ordination methods (such as principle components analysis and correspondence analysis) because NMDS makes few assumptions about the dataset beyond random sampling. NMDS is a nonparametric method, so the data do not have to be normally distributed, nor do they have to be homoscedastic. NMDS provides a relatively simple way to quickly note similarities and differences between data points in Pentelikon vs. Proconnesos A and B in a decreased dimensional space.

The NMDS algorithm is a multi-step process. First, the number of dimensions for the NMDS ordination has to be chosen. Multiple trials of the ordination with different numbers of dimensions may be necessary in order to make the best decision regarding the number of dimensions used to evaluate the data set.

An initial starting configuration of the ordination is then generated with the chosen number of dimensions. From this ordination, the distances from each pair of data are calculated. Dissimilarities between the distances are also calculated. Using distances between each pair of points (y-axis) versus the dissimilarity between each pair of points (x-axis), a Shepard diagram is

generated. A monotone regression is calculated for this distance of pairs of points vs. dissimilarity, from which the stress value may be calculated (Kruskal, 1964). Stress, the "goodness of fit" of the monotonic regression, is calculated using the sum of the squares of the ordination distance between two samples and the sum of squares of the distance between two samples predicted from the monotonic regression (Equation 3.2).

Equation 3.2. Kruskal's equation for stress (Kruskal, 1964).

$$stress = S = \sqrt{\frac{\sum_{1 < j} (d_{ij} - \hat{d}_{ij})^2}{\sum_{1 < j} d_{ij}^2}}$$

Where d_{ij} = ordination distance between samples *i* and *j*, and d-hat_{ij} is the distance predicted from the monotonic regression.

Stress decreases the fit between distances and dissimilarities improves, based on the calculated monotonic regression. Changing the number of dimensions or restarting the ordination multiple times to achieve lower stress can manipulate stress. Different numbers of dimensions directly affect stress because they change how the monotonic regression is calculated, based on the distance between points in multidimensional space. Since every dataset is different, the best-fitting number of dimensions may vary between analyses. It is typically possible to obtain a lower stress value with an increased number of dimensions, but increasing the number of dimensions doesn't always improve the visual pattern of the data points.

NMDS is a numerical ordination method, and its objective is to convert nonmetric data into a metric output, based on rank order of dissimilarities between data points. When calculated by hand or by inadequate software, NMDS may have issues with local minima. Local minima are stress values that are not the best solutions but are better than other solutions in close proximity. To avoid local minima, multiple restarts may be used to calculate stress until the best minimum stress value is found. The data are plotted in Shepard diagrams (distance vs. dissimilarity) in multiple combinations, from which the monotonic regression is calculated. This iterative process allows stress to be calculated multiple times, until the solutions are consistent with one another or until the restarts are finished. When the stress values are calculated multiple times and are very close to one another, the solution converges. Whether or not a solution is said to converge depends on the established criteria for convergence. The criteria for how close stress values have to be for a convergent solution to be reached may be very strict, but it can be increased or decreased based on the data set.

The final output of NMDS may adapt the multidimensional data to different dimensional spaces, based on the selection of the user. Samples that are similar will plot closer to one another, and samples that are more dissimilar will plot farther away from one another. Different combinations of axes may be viewed separately in order to visualize patterns among the data. The degree of variance is greatest on axis 1, and decreases with each following axis.

The dataset consists of maximum grain size, stable isotope δ^{13} C and δ^{18} O, and accessory mineral data, for a total of 15 variables. Maximum grain size data are ratio data, stable isotopes are interval data, and accessory minerals are nominal data. Several different numbers of dimensions were evaluated for the fit of the ordination, but three dimensions and 100 restarts were chosen for the best fit and interpretation of the data set. An increased number of dimensions lowered the stress value, but three dimensions showed enough separation between each sample set to be sufficient.

A percent range transformation was applied to each variable. The data were scaled between 0 and 1 according to their status as ratio, interval, or nominal data. For ratio data (maximum grain size) and interval data (stable isotopes), all data points were scaled between 0

and 1 based on the minimum and maximum of the dataset (Okasen, 1983; Legendre and Gallagher, 2001). The range transformation makes the minimum value equal to 0, and the maximum value in the set equal to 1 (Equation 3.3). All values in between the minimum and the maximum fall proportionately between the minimum and the maximum. For nominal data that are treated as present or absent in a sample, present values may be assigned a "1", and absent values may be assigned a "0" (Okasen, 1983; Legendre and Gallagher, 2001).

Equation 3.3. Scaling the data between 0 and 1.

Scaled Value =
$$\frac{x - Min}{|Max - Min|}$$

1 6 4

Where x = the numerical value of a sample, Min = the minimum value in the sample set, and Max = the maximum value in the sample set. |Max - Min| is the absolute value of the maximum minus the minimum value.

Euclidean distance was used in this ordination to calculate the monotonic regression, and ultimately the stress value. In two-dimensional space, the Euclidean distance between two points is given by the Pythagorean formula (Equation 3.4). The Euclidean distance is the shortest distance between two points.

Equation 3.4. The Euclidean distance between two points (x_1, y_1) and (x_2, y_2) is given by the Pythagorean distance formula, where d = distance (Libeskind, 2008).

$$d = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2}$$



Figure 3.1. Line represents the Euclidean distance between points (x_1, y_1) and (x_2, y_2) in twodimensional space.

An ordination utilizes a Euclidean distance measure that accounts for the distance between two points i and j in multidimensional space (Equation 3.5). With multiple dimensions to consider, an ordination's Euclidean distance is more complex than that of Equation 3.4.

Equation 3.5. Euclidean distance in a multidimensional ordination (Cox and Cox, 2001). The distance d_{ij} between points *i* and *j* is defined as:

$$d_{ij} = \sqrt{\sum (x_{ia} - x_{ja})^2}$$

Where x_{ia} specifies the position or coordinate of point *i* on dimension *a*.

All NMDS calculations were performed in the statistical program R, version 2.14.0 (R Development Team, 2011). The NMDS can be calculated using the vegan 2.0, an ecological software package for R. The percent range transformations were performed using the function decostand("range") for scaling ratio and interval data between 0 and 1, (Okasen, 1983; Legendre and Gallagher, 2001). The NMDS specifically used the function metaMDS() within the vegan library, which transforms the final ordination with a principal components analysis. The metaMDS() function was performed using the Euclidean distance measure, and the default transform for ecological data was disabled.

CHAPTER 4

<u>RESULTS</u>

PETROGRAPHIC ANALYSIS

Mt. Pentelikon

Petrographic characteristics of 10 samples from quarry P85 are summarized in Table 4.1. Each hand sample of this Pentelic marble is white with orange to brown crusts of oxidation. This color is consistent with previous observations of Pentelic marble (Renfrew and Springer Peacy 1968). A variety of micas are visible in P85 thin sections, which appeared to be muscovite under the petrographic microscope. Also visible were a number of pyrite grains, as confirmed using a reflected light microscope. All other accessory grains were too small to be identified using only a transmitted or reflected light microscope.

The maximum grain size of calcite in the 10 samples ranges from 0.5 - 1.1 mm (Table 4.1; Figs. 4.1, 4.2, 4.3). The maximum calcite grain size is related to the rate of recrystallization during metamorphism. For this information to be most effective, maximum calcite grain size must differ by quarry region.

Proconnesos A

Proconnesos A are each from a different quarry on Marmara Island. These quarries may be more up to 2 km apart from each other on the northeast part of the island. Viewed in hand sample, Proconnesos A samples appear to be grey with no visible oxidation. Trace amounts of muscovite were found in thin section, as well as pyrite and several other unidentified opaque minerals. Other accessory grains were too small to definitively identify in thin section.

Proconnesos A samples also had higher maximum calcite grain sizes than Pentelikon samples. Maximum calcite grain sizes in Proconnesos A samples ranged from 1.3 to 1.9 mm (Table 4.2; Figs. 4.1, 4.2, 4.3).

Sample ID	Quarry Region	Previous Work	Hand Sample Color	Structure	MGS (mm)
P85-1	Penteli	Pike (2000)	White, brown crust	Calcite structure, no banding, some evidence of accessory mineral oxidation	0.9
P85-2	Penteli	Pike (2000)	White, brown crust	Mainly white calcite with microscopic accessory content	1.0
P85-3	Penteli	Pike (2000)	White, brown crust	Brown minerals, near banding throughout fine- grained	0.5
P85-4	Penteli	Pike (2000)	White, brown crust	Mainly white calcite with microscopic accessory content	0.7
P85-5	Penteli	Pike (2000)	White, brown crust	Mainly white calcite with microscopic accessory content	1.1
P85-6	Penteli	Pike (2000)	White, brown crust	Mainly white calcite with microscopic accessory content	0.6
P85-7	Penteli	Pike (2000)	White, brown crust	Mostly calcite, can see effects of surface crust on top of sample	0.7
P85-8	Penteli	Pike (2000)	White, brown crust	Mainly white calcite with microscopic accessory content	0.6
P85-9	Penteli	Pike (2000)	White, brown crust	Subtle grey banding with calcite	0.8
P85-10	Penteli	Pike (2000)	White, brown crust	Some brown banding, Fe oxidation	0.9

Table 4.1. Grain size and structure of marble samples from Mt. Pentelikon.



Figure 4.1. Selected marble samples as analyzed for maximum calcite grain size. See Appendix B for more images.

Sample ID	Quarry Region	Previous Work	Hand Sample Color	Structure	MGS (mm)
C1.18	Proconnesos	Attanasio et al. 2008	Grey- white	No apparent metamorphic banding	1.7
C2.7	Proconnesos	Attanasio et al. 2008	Grey	One lighter band - silicate	1.9
C3.2s	Proconnesos	Attanasio et al. 2008	Grey- white	No apparent metamorphic banding	1.8
C4.4	Proconnesos	Attanasio et al. 2008	Grey	No apparent metamorphic banding, larger grey and white crystals, dolomitic	1.3
C5.2	Proconnesos	Attanasio et al. 2008	Grey	No apparent metamorphic banding	1.7
C5b.13	Proconnesos	Attanasio et al. 2008	Grey- white	No apparent metamorphic banding	1.7
C6.4	Proconnesos	Attanasio et al. 2008	Grey	No apparent metamorphic banding, larger grey and white crystals, dolomitic	1.3
C7i.8	Proconnesos	Attanasio et al. 2008	Grey- white	No apparent metamorphic banding	1.3
C8.5	Proconnesos	Attanasio et al. 2008	Grey	No apparent metamorphic banding, larger grey and white crystals, dolomitic	1.3
C10.3	Proconnesos	Attanasio et al. 2008	Grey- white	No apparent metamorphic banding	1.3
C11.2	Proconnesos	Attanasio et al. 2008	Grey	No apparent metamorphic banding, larger grey and white crystals, dolomitic	1.5
C12.3	Proconnesos	Attanasio et al. 2008	Grey	No apparent metamorphic banding, larger grey and white crystals, dolomitic	1.6
C13.6	Proconnesos	Attanasio et al. 2008	Grey	No apparent metamorphic banding, larger grey and white crystals, dolomitic	1.3
C14.7	Proconnesos	Attanasio et al. 2008	Grey	No apparent metamorphic banding, larger grey and white crystals, dolomitic	1.7
C15.1	Proconnesos	Attanasio et al. 2008	Grey	No apparent metamorphic banding, larger grey and white crystals, dolomitic	1.8
C16.6	Proconnesos	Attanasio et al. 2008	Darker grey	No apparent metamorphic banding	1.4

Table 4.2. Grain size and structure of marble samples from Proconnesos A.

Proconnesos B

Proconnesos B samples were taken from quarry areas on the northeast side of Marmara Island. The exact sample locations of Proconnesos B are unknown, unlike the Proconnesos A sample set. Proconnesos B samples also appear generally grey in hand sample. Muscovite and phlogopite grains were visible in thin section. Like Pentelikon and Proconnesos A, pyrite grains could also be tentatively identified using a reflected light microscope, although there were several other opaque minerals that could not be identified with the reflected light microscope alone. The maximum calcite grain size in Proconnesos B sample ranges from 1.1 - 2.1 mm, overlapping with Proconnesos A samples and also the largest maximum calcite grain size range of the three sample sets (Table 4.3, Figs. 4.1, 4.2, 4.3).

Sample ID	Quarry Region	Source	Hand Sample Color	Structure	MGS (mm)
Proc-1	Proconnesos	Esenli	Grey-white	No apparent metamorphic banding	1.8
Proc-2	Proconnesos	Esenli	Grey-white	No apparent metamorphic banding	1.3
Proc-3	Proconnesos	Esenli	Grey	No apparent metamorphic banding	2.1
Proc-4a	Proconnesos	Esenli	Grey	No apparent metamorphic banding	1.9
Proc-4b	Proconnesos	Esenli	Grey-white	One darker band	2.2
Proc-5	Proconnesos	Esenli	Grey	One darker band	1.2
Proc-6	Proconnesos	Esenli	Grey	No apparent metamorphic banding	1.9
Proc-7	Proconnesos	Esenli	Darker grey	No apparent metamorphic banding	1.5
Proc-8	Proconnesos	Esenli	Grey-white	No apparent metamorphic banding	2.0
Proc-9	Proconnesos	Esenli	Grey-white	Grey banding	1.6
Proc-10	Proconnesos	Esenli	Grey	One lighter band	1.0
Proc-11	Proconnesos	Esenli	Grey-white	No apparent metamorphic banding	1.3
Proc-12	Proconnesos	Esenli	Grey-white	Finer grained, no metamorphic banding	1.1
Proc-13	Proconnesos	Esenli	Grey-white	One lighter band	1.5
Proc-14	Proconnesos	Esenli	Grey-white	No apparent metamorphic banding; even distribution of differing crystals	2.1

Table 4.3. Grain size and structure of marble samples from Proconnesos B.



Figure 4.2. Maximum calcite grain size frequency distribution of Pentelikon, Proconnesos A, and Proconnesos B.



Figure 4.3. Maximum calcite grain size box plots of Pentelikon, Proconnesos A, and Proconnesos B.

STABLE ISOTOPE ANALYSIS

The results of the stable isotopic analysis for δ^{13} C and δ^{18} O are summarized in Figure 4.4 and Table 4.4. Pike (2000) reported stable isotope values for Pentelikon P85 samples. Attanasio et al. (2008) reported isotopic values for Proconnesos A samples. New data were obtained for Proconnesos B samples. Existing isotopic results for Pentelikon and Proconnesos A were pointchecked at the University of Georgia, with results that fit in the range of both quarries (Table 4.5).

Figure 4.4 displays δ^{13} C (‰ VPDB) vs. δ^{18} O (‰ VPDB) for all samples. Isotopic data is listed in Table 4.5. Much focus is typically placed on a plot like this because it is part of the standard method for marble provenance analysis (Pike, 2000). The null hypothesis for this data was that Pentelikon would show no isotopic difference from Proconnesos A and Proconnesos B. However, Penteli samples generally plot to the left of the figure, and Proconnesos A and B samples generally plot to the right of the figure. This information by itself is promising for statistical analyses that attempt to differentiate between the quarry regions.



Figure 4.4. Stable isotope δ^{13} C (‰ VPDB) vs. δ^{18} O (‰ VPDB).

	Quarry	C	s 13 o	c 180
Sample ID	Region	Source	0 C	0.0
P85-1	Penteli	Pike (2000)	2.90	-8.30
P85-2	Penteli	Pike (2000)	2.90	-5.60
P85-3	Penteli	Pike (2000)	2.70	-6.90
P85-4	Penteli	Pike (2000)	2.80	-5.60
P85-5	Penteli	Pike (2000)	2.80	-6.20
P85-6	Penteli	Pike (2000)	2.80	-5.50
P85-7	Penteli	Pike (2000)	3.10	-8.50
P85-8	Penteli	Pike (2000)	3.00	-4.30
P85-9	Penteli	Pike (2000)	2.70	-8.30
P85-10	Penteli	Pike (2000)	4.20	-7.50
C1.18	Proconnesos	Attanasio et al. (2008)	2.68	-2.19
C2.7	Proconnesos	Attanasio et al. (2008)	2.75	-2.58
C3.2s	Proconnesos	Attanasio et al. (2008)	3.00	-2.28
C4.4	Proconnesos	Attanasio et al. (2008)	2.61	-3.14
C5.2	Proconnesos	Attanasio et al. (2008)	2.64	-6.00
C5b.13	Proconnesos	Attanasio et al. (2008)	2.70	-1.69
C6.4	Proconnesos	Attanasio et al. (2008)	2.46	-2.54
C7i.8	Proconnesos	Attanasio et al. (2008)	2.82	-1.96
C8.5	Proconnesos	Attanasio et al. (2008)	2.00	-2.54
C10.3	Proconnesos	Attanasio et al. (2008)	3.12	-2.91
C11.2	Proconnesos	Attanasio et al. (2008)	1.95	-2.54
C12.3	Proconnesos	Attanasio et al. (2008)	3.01	-2.34
C13.6	Proconnesos	Attanasio et al. (2008)	2.70	-1.91
C14.7	Proconnesos	Attanasio et al. (2008)	2.78	-2.04
C15.1	Proconnesos	Attanasio et al. (2008)	2.54	-2.56
C16.6	Proconnesos	Attanasio et al. (2008)	3.07	-3.50
Proc-1	Proconnesos	This study	2.10	-4.20
Proc-2	Proconnesos	This study	2.20	-0.40
Proc-3	Proconnesos	This study	2.60	-0.30
Proc-4a	Proconnesos	This study	2.30	-1.60
Proc-4b	Proconnesos	This study	3.00	-3.00
Proc-5	Proconnesos	This study	2.70	-2.00
Proc-6	Proconnesos	This study	2.30	-1.50
Proc-7	Proconnesos	This study	2.80	-1.70
Proc-8	Proconnesos	This study	3.70	-1.60
Proc-9	Proconnesos	This study	2.60	-0.40
Proc-10	Proconnesos	This study	2.90	-1.60
Proc-11	Proconnesos	This study	2.00	-3.10
Proc-12	Proconnesos	This study	2.00	-3.20
Proc-13	Proconnesos	This study	2.80	-3.70
Proc-14	Proconnesos	This study	2.10	-4.40

Table 4.4. Stable isotope data for the sample set.

Study, Sample	Original δ^{13} C vs. VPDB	New δ ¹³ C vs. VPDB	Original δ ¹⁸ O vs. VPDB	New δ ¹⁸ O vs. VPDB
Pike (2000), P85-3	2.70	2.70	-6.90	-6.40
Attanasio et al. (2008), C1.18	2.70	3.20	-2.20	-1.60

Table 4.5. Point-checked isotopic data.

ELECTRON MICROPROBE ANALYSIS

Accessory mineral assemblages were identified using a petrographic microscope and an electron microprobe. In most cases, the small grain size of the accessory minerals (< 0.1 mm) necessitated use of the electron microprobe over the petrographic microscope. Accessory minerals found in each sample were recorded as "present" with no attempt to quantify percent abundances of the mineral in thin section. Abundances were not recorded because of the small grain sizes and the subsequent difficulty of identification. Overall results from the accessory mineral analysis are presented in Table 4.6 and Appendix A.
e Margarite																															x									
Paragonite							x																																	
Phlogopite																											x							x	x				x	x
Muscovite	X	×		x	x	x	x		×		×		x	X							X										×			×	×		X			x
Titanite																																x								
Quartz	X	×		x	x			x	×																						×	x		x						
Goethite		×				x				x				x		x					×				x	×						x			×					
Rutile		X																								x						×								
Sphalerite													x																											
Pyrite X	×			X	x	X	X	X	x	X	X	X		x	X	X	x				X			X		x	X	X	X	X	x	X		X	X	x	X	X	X	x
Apatite X	×	×	×	X	x	x	×			x		x			x		x								x	x		x	x	X		x						x		
Dolomite				x	x	x	x	x	x		x		x			x	x	x				x	x				x				x				x	x	x	x	x	X
Sample P85-1	P85-2	P85-3	P85-4	P85-5	P85-6	P85-7	P85-8	P85-9	P85-10	C1.18	C2.7	C3.2s	C4.4	C5.2	C5b.13	C6.4	C7i.8	C8.5	C10.3	C11.2	C12.3	C13.6	C14.7	C15.1	C16.6	Proc-1	Proc-2	Proc-3	Proc-4a	Proc-4b	Proc-5	Proc-6	Proc-7	Proc-8	Proc-9	Proc-10	Proc-11	Proc-12	Proc-13	Proc-14

Table 4.6. Presence of accessory minerals, indicated by "X".

Carbonate Minerals

Calcite

Calcite, CaCO₃, was the primary mineral in all 41 of the marble quarry samples, suggesting a limestone protolith (Table 4.6). Calcite and dolomite both occur in equilibrium in 31 of the 41 total samples (Table. 4.6). Since Mg often substitutes for Ca in calcite (Deer et al. 1992), the MgCO₃ content of select calcite grains was analyzed. The substitution of Mg for calcite is a solvus relation (Figure 4.5). These calcite grains were analyzed when found next to dolomite grains, under the assumption that they were in equilibrium.

The reported mole fractions of MgCO₃ (magnesite) in calcite are typically less than 0.080 (Anovitz and Essene, 1987). For this study, the mole fraction of MgCO₃ in calcite grains was between .015 and .049. These values were used with the formula from Anovitz and Essene (1987) (Equation 3.1) to calculate the calcite-dolomite equilibration temperature. Results are shown from select samples from Pentelikon, Proconnesos A, and Proconnesos B samples in Table 4.7, and Appendix A.



Figure 4.5. The calcite-dolomite solvus fit to reversals, from Anovitz and Essene (1987). The head of the above arrows on the solvus curve represent final compositions. Direction of arrow = direction of compositional shift. Points on dolomite side of curve are compositions of dolomite coexisting with calcite

Table 4.7. Atomic proportions and calcite-dolomite thermometry. T = Temperature. K = Kelvin. C = degrees Celsius.

	Result	Т, К	Τ, C
	P85-9-1		
CaO	0.979	(0.4	220
MgO	0.018	604	330
CO_2	1.001		
	P85-9-2		
CaO	0.982		••••
MgO	0.015	564	290
CO_2	1.001		
	P85-10-1		
CaO	0.978		
MgO	0.020	627	350
CO_2	1.001		
	Proc-9-1		
CaO	0.949		
MgO	0.049	796	520
CO_2	1.001		
	Proc-9-2		
CaO	0.986		
MgO	0.018	597	320
CO_2	0.998		
	Proc-12-1		
CaO	0.968		
MgO	0.031	709	440
CO2	1.000		
	Proc-12-2		
CaO	0.954		
MgO	0.044	776	500
CO_2	1.001		
_	C14.7-1		
CaO	0.979		
MgO	0.019	612	340
CO_2	1.00		
-	C8.5-1		
CaO	0.964		
MgO	0.035	730	460
CO ₂	1.001		
2	C8.5-2		
CaO	0.969		
MgO	0.029	697	420
CO_2	1.000		

Dolomite

Dolomite, $CaMg(CO_3)_2$, was found in trace amounts in 31 of 41 total samples. Neither Pentelikon nor Proconnesos is considered to be dolomitic marble based on the observation from these samples that 1) calcite was the only matrix material and 2) dolomite is only found in trace amounts, i.e. >5% of the sample. It is difficult to distinguish calcite from trace grains of dolomite in thin section, however, the back-scattered electron images on the electron microprobe show differences in density between calcite and dolomite, and make the distinction obvious. The molecular structure of dolomite is similar to calcite, but differs based on Mg content (Deer et al., 1992). This structure is the equivalent of combining one layer of CaCO₃ and one layer of MgCO₃.

Dolomite analyses were mostly obtained through reconnaissance routines, such as the oxide and pyroxene routines described in Chapter 3. Although these routines analyzed for Ca, Mg, and Fe, the routines didn't calculate the estimated CO₂. Select dolomite analyses are displayed in Table 4.8.

Table 4.8. Select dolomite analyses. Values below minimum detection limit are indicated by strikethrough.

Sample	P85-9	P85-10	C8.5	C14.7	Proc-9	Proc-12
CaO	30.78	30.10	31.72	32.25	30.41	31.73
MgO	20.38	21.65	21.94	21.99	21.35	22.41
FeO	0.87	0.70	0	0.18	0.18	0.09
MnO	0.77	0	0.0592	0	0.03	0
SrO	0.01	0.03	0	0.06	0.06	0.04
CO ₂	47.42	47.7	48.88	49.46	47.33	49.44
Total	100.23	100.18	102.59	103.94	99.3 7	103.70

Phosphate Minerals

Apatite

Apatite, Ca₅(PO₄)₃(F,Cl,OH), forms small (.01 to .05 mm) rounded grains in the majority of the samples. The grains have very low birefringence and are difficult to distinguish from quartz with the petrographic microscope. Due to small size of the grains and the similarity to other minerals, the electron microprobe is the most effective tool for apatite identification. Apatite appears as bright grains against the darker calcite matrix in backscattered electron images on the microprobe and can easily be distinguished from quartz, which is dark relative to the calcite matrix.

All samples with apatite were found to be the apatite (CaF) endmember. Apatite (CaF) is found in samples from Pentelikon, Proconnesos A, and Proconnesos B. This form of apatite is referred to as fluor-apatite, and is more commonly found than end-members chlor-apatite (Ca₅(PO₄)₃Cl), hydroxyapatite (Ca₅(PO₄)₃OH), and carbonate-apatite (Ca₅(PO₄,CO₃,OH)₃(F,OH)) (Deer et al, 1992). Selected results are displayed in Tables 4.9-4.11.

Weight %				
Sample	P85-1	P85-2	P85-3	P85-4
P_2O_5	41.01	42.24	42.15	42.95
CaO	56.83	55.13	53.78	55.06
Al_2O_3	0.01	0.01	0.68	0.01
MnO	0	0.03	0.05	0
Cl	0	0.01	0.02	0
F	3.54	3.69	3.91	4.30
Fe ₂ O ₃	0	0	0.09	0.09
Total	99.90	99.54	99.04	100.60
Atomic Pr	oportions			
Р	6.108	6.268	6.283	6.347
Ca	10.712	10.351	10.146	10.297
Al	0.001	0.001	0.142	0.003
Mn	0	0.004	0.007	0
Cl	0	0.003	0.004	0
F	1.969	2.046	2.180	2.371
Fe	0	0	0.012	0.012
0	25	25	25	25
Cation				
Total	18.791	18.673	18.775	19.030
Total	43.790	43.673	43.775	44.030

Table 4.9. Selected apatite analyses from Pentelikon. Values below minimum detection limit are indicated by strikethrough.

Weight %				
Sample	C 3.2s 4 20k	C5b.13 1 40k	C 7i.8 6	C 7i.8 9
P_2O_5	41.71	42.23	43.67	42.96
CaO	55.97	56.10	56.22	56.89
Al_2O_3	0	0	0.02	0.01
MnO	0	0	0	0
Cl	0.03	0.01	0.06	0.03
F	3.92	3.94	3.75	3.83
Fe ₂ O ₃	0	0	0.09	0
Total	99.98	100.62	102.21	102.09
Atomic Pro	portions			
Р	6.216	6.239	6.295	6.235
Ca	10.555	10.490	10.257	10.452
Al	0	0	0.004	0
Mn	0	0	0	2.075
Cl	0.010	0.001	0.016	0.001
F	2.182	2.177	2.020	0
Fe	0	0	0.012	0.008
0	25	25	25	25
Cation				
Total	18.964	18.909	18.603	18.770
Total	43.964	43.909	43.604	43.770

Table 4.10. Selected apatite analyses from Proconnesos A. Values below minimum detection limit are indicated by strikethrough.

Weight %				
Sample	Proc-1 9	Proc 38	Proc-4b 22	Proc-6 7
P_2O_5	40.76	42.49	39.58	40.00
CaO	58.42	54.40	56.28	55.98
Al_2O_3	0	0	0	0
MnO	0	0	0	0
Cl	0	0.01	0	0.02
F	4.38	3.63	3.82	3.38
Fe ₂ O ₃	0	0	0	0
Total	101.71	99.00	98.07	97.95
A 4 D				
Atomic Pro	oportions	(212	()()	(079
P	6.078	0.313	6.069	6.078
Ca	11.024	10.227	10.922	10.765
Al	0	0	0	0
Mn	0	0	0	0
Cl	0	0.002	0	0.005
F	2.437	2.016	2.191	1.917
Fe	0	0	0	0
0	25	25	25	25
Cation				
Total	19.539	18.557	19.182	18.765
Total	44.539	43.557	44.182	43.765

Table 4.11. Selected apatite analyses from Proconnesos B. Values below minimum detection limit are indicated by strikethrough.

The theoretical limit of F in apatite is 3.77 weight %. Weight % values (wt%) of fluorine in apatite were often above the theoretical limit of 3.77 wt %. This is likely because of the analytical apatite routine. Any chlorine amounts were under the minimum detection limit (>.06% Cl). Detectable limits of chlorine were typically above ~ 0.062 wt %. The microprobe does not analyze for water and the OH- component is typically estimated by the difference of F^- plus Cl⁻.

Capedri et al. (2004) found that apatite was the most frequently found accessory mineral in Mediterranean quarry marble. Apatite grains from Penteli and Proconnesos in the study of Capedri et al. (2004) were less than 40 μ m, often anhedral and rounded in shape. Our results are consistent with these findings.

Sulfide Minerals

Pyrite

The majority of the samples contained pyrite, FeS_2 (Table 4.7; Table 4.12). Marcasite also has the formula FeS_2 , but forms in low temperature sedimentary rocks, and these marbles are medium to high temperature metamorphic rocks. Pyrite can contain minor elements other than Fe or S (Deer et al., 1992), so the grains were often analyzed for additional Ni and Cu. Like the findings of Capedri et al. (2004) and Capedri and Venturelli (2004), pyrite was found much more frequently than sulfide minerals containing Ni, Cu, and Zn.

Table 4.12 Select pyrite analyses. Values below minimum detection limit are indicated by strikethrough.

Weight %						
Sample	P85-1	P85-1 3	P85-1-12	P85-2-16	P85-2-17	P85-2-18
Fe	45.79	45.03	45.51	45.13	45.76	45.36
S	53.96	54.48	54.33	54.77	54.75	54.55
Ni	0.07	0.20	0	0.15	0.07	0.01
Cu	0.02	0.11	0.08	0	0.09	0
Total	99.84	99.82	99.92	100.06	100.67	99.92
Sample		C6.4 4	C12.3	Proc-9	Proc-12	Proc-13
Fe		44.97	44.92	44.03	45.81	46.34
S		51.76	51.09	55.25	53.85	54.64
Ni		0.8822	0.1535	0.0903	0.7211	0.185
Cu		0	0	0.0334	0	0
Total		97.62	96.17	99.40	100.38	101.17

Sphalerite

Sphalerite, (Zn,Fe)S, was only found definitively in one sample, C4.4 of Proconnesos A, but it is likely present in more Proconnesos A samples that were not analyzed with a sulfide routine containing Zn on each day. The wt % of Fe and S in the samples likely containing sphalerite was consistent with a sphalerite analysis, but the lack of Zn in the routine resulted in low totals. The successful sphalerite analysis is listed in Table 4.13.

Table 4.13. Sphalerite analysis from sample C4.4 in Proconnesos A. Values below minimum detection limit are indicated by strikethrough.

Weight %						
	C4.4					
Fe	0.44					
S	31.89					
Ni	0					
Zn	59.29					
Cu	0					
Total	91.61					

Other Nonsilicate Minerals

Rutile

Rutile, TiO₂, was found in P85-3 of Pentelikon, and Proc-1 and Proc-6 of Proconnesos B. Although some rutile may contain significant amounts (in our case, above detection limit on the microprobe) of Fe (Deer et al., 1992), these samples were almost exclusively Ti and O. Since the ionic radius of Ti^{4+} is similar to that of Nb and Ta, there is a possibility for substitution of Ti^{4+} with Nb and Ta (Deer et al., 1992). The routine analyzing these rutiles however did not analyze for Nb and Ta. Results from the rutile analyses may be viewed in Table 4.14.

Weight %			
Sample	Proc-1	Proc-6	P85-3
SiO ₂	0.60	0.66	1.33
TiO ₂	84.14	97.24	93.40
Al_2O_3	1.17	0.43	0.93
MgO	0.05	0	0
FeO	0.43	0	0.88
CaO	5.37	1.02	0.96
MnO	0.08	0.08	0.02
Cr2O3	0.48	0.10	0
NiO	0	0.07	0
Total	92.31	99.62	97.68
Atomic Prop	ortions		
Si	0.009	0.009	0.018
Ti	0.926	0.977	0.958
Al	0.020	0.007	0.015
Mg	0.001	0	0
Fe	0.005	0	0.010
Ca	0.084	0.015	0.014
Mn	0.001	0.001	0
Cr	0.006	0.001	0
Ni	0	0.001	0
Ο	2	2	2
Cation			
Total	1.052	1.010	1.018
Total	3.052	3.010	3.018

Table 4.14. Rutile analyses from Proconnesos B (Proc-1, Proc-6) and Pentelikon (P85-3). Values below minimum detection limit are indicated by strikethrough.

Goethite

Goethite, FeO(OH), was identified in 10 of the 31 samples, at least once in each sample set. Goethite is a hydroxide mineral, and the electron microprobe does not analyze for H₂O, or OH⁻. Therefore, the totals for goethite are up to ~20% lower than 100. The ideal weight % composition of goethite is 89.86 % Fe₂O₃ and 10.14 % H₂O. Results for goethite analyses can be viewed in Table 4.15.

Table 4.15. Select goethite analyses. Values below minimum detection limit are indicated by strikethrough.

Weight %	6		
Sample	P85-3	C6.4	Proc-1
SiO ₂	3.10	3.41	3.90
TiO ₂	0.02	0	0.05
Al_2O_3	0.20	0.21	0.67
MgO	0.39	0.35	0.44
FeO	73.10	75.15	73.98
CaO	1.51	1.67	1.83
MnO	0.86	0	0.05
Cr ₂ O ₃	0.03	0.03	0.03
NiO	0.48	2.36	0
Total	79.69	83.17	80.97
Atomic P	roportion	15	
Si	0.174	0.183	0.212
Ti	0.007	0	0.002
Al	0.012	0.013	0.043
Mg	0.033	0.027	0.035
Fe	3.441	3.385	3.360
Ca	0.091	0.096	0.106
Mn	0.041	0	0.002
Cr	0.001	0.002	0.001
Ni	0.021	0.102	0
0	4	4	4
Cation			
Total	3.818	3.809	3.763
Total	7.818	7.809	7.763

Framework Silicates

Quartz

Grains of quartz, SiO₂, were found in both Pentelikon and Proconnesos B, although quartz grains were more frequently found in Pentelikon samples. In general these quartz grains were between .08 and .5 mm in diameter and some exhibited a hexagonal crystal shape (Figure 4.6). These quartz grains were likely of detrital origin in the limestone protolith, but since they are euhedral, they probably recrystallized with metamorphism.Results from select quartz analyses can be viewed in Table 4.16.

Capedri et al. (2004) stated that accessory quartz grains in Pentelic marble are likely of detrital origin, possibly from a sandy limestone protolith. They found that quartz grains from four different Penteli samples might be up to .5 mm. Capedri et al. (2004) did not find accessory quartz grains in its four samples from Proconnesos. Out of this study's 31 Proconnesos samples, three from Proconnesos B contained accessory quartz.

Sample	P85-2	P85-2	P85-2	P85-3	P85-3	P85-5
SiO ₂	98.54	100.01	99.32	98.45	98.23	99.15
TiO ₂	0	0	0.001	0	0	0
Al_2O_3	0.01	0	0	0	0	0.01
MgO	0	0	0.02	0.02	0	0
FeO	0.04	0	0.07	0	0.02	0.02
CaO	0.02	0.04	0.03	0.04	0.02	0.12
MnO	0	0.04	0.02	0	0.07	0.04
Cr ₂ O ₃	0.048	0	0.07	0	0	0.10
NiO	0.030	0	0	0.109	0.030	0.01
Total	98.69	100.08	99.53	98.62	98.3 7	99.44
Si	1.998	1.999	1.997	1.998	1.998	1.996
Ti	0	0	0	0	0	0
Al	0	0	0	0.001	0	0.002
Mg	0	0.001	0.007	0.005	0	0
Fe	0.001	0	0.0011	0	0	0.002
Ca	0.001	0.008	0.006	0.009	0	0.002
Mn	0	0.006	0.003	0	0.0012	0.006
Cr	0.001	0	0.001	0	0	0.002
Ni	0.001	0	0	0.002	0.005	0.002
0	4	4	4	4	4	4
Cation						
Total	2.001	2.001	2.002	2.002	2.001	2.002
Total	6.001	6.001	6.002	6.002	6.001	6.002

Table 4.16 Select quartz analyses. Values below minimum detection limit are indicated by strikethrough.

Orthosilicates

Titanite

Titanite, CaTi[SiO₄](O,OH,F), was positively identified in Proc-6 of Proconnesos B. If more grains were found within the sample set, the compositional variation could be investigated on a comparative basis. Deer et al. (1992) stated that the chemical substitutions of greatest importance in titanite are (Al,Fe³⁺) + (F,OH)- = Ti⁴⁺ + O²⁻. In this case, Al and Fe³⁺ occupy octahedral sites in titanite and rare earth elements such as ytterbium may substitute for Ca (Deer et al., 1992).

Titanite in metamorphic rocks is typically found in schists and gneisses rich in ferromagnesian minerals and calcium, and may be common in metamorphosed or impure calcsilicate rocks and skarns. In sedimentary rocks such as limestone, titanite may occur as a detrital grain, which may be an explanation for its limited occurrence in these samples (Deer et al., 1992). The composition of the titanite grain in Proc-6 is listed in Table 4.17.

Weight %	6
Sample	Proc-6 11
SiO ₂	27.93
TiO ₂	37.90
Al_2O_3	3.72
MgO	0
FeO	0
CaO	28.04
MnO	0
Cr ₂ O ₃	0.05
NiO	0
Total	97.65
Atomic P	roportions
Si	1.120
Ti	1.143
Al	0.176
Mg	0
Fe	0
Ca	1.205
Mn	0
Cr	0.001
Ni	0
0	6
Cation	
Total	3.6465
Total	9.6465

Table 4.17. Titanite analysis for Proc-6 of Proconnesos B. Values below minimum detection limit are indicated by strikethrough.

Sheet Silicates

Muscovite

Muscovite, K₂Al₄[Si₆Al₂O₂₀](OH,F)₄, was found in various samples of Pentelikon,

Proconnesos A, and Proconnesos B. Muscovite is one of the most common micas and occurs in many different environments (Deer et al., 1968), so it is not surprising that grains of muscovite were found more than once in each of the quarry sample sets.

Special attention was given to the compositional variation of the muscovite grains. According to

Deer et al. (1968), the isomorphous replacements of sites in mica are:

For K: Na, Rb, Cs, Ca, Ba For octahedral Al: Mg, Fe^{2+} , Fe^{3+} , Mn, Li, Cr, Ti, V For (OH): F (Si₆Al₂) may vary to (Si₇Al)

Of greatest importance to this study was the replacement of K by Na to form paragonite, and the variation of Mg and Fe^{2+} as replacement for octahedral Al, which is classified as phengitic muscovite. Results of the electron microprobe analysis are displayed in Table 4.18.

Weight %						
Sample	P85-3 5	P85-5 2	C 5.2 2	C 2.7 5		
SiO ₂	49.39	50.44	48.75	50.82		
TiO ₂	0.09	0.09	0	0.11		
Al_2O_3	34.94	32.23	35.72	32.77		
MgO	2.82	4.43	0.98	3.75		
FeO	0.14	0.18	0.11	0.04		
CaO	0.13	0.04	0.68	0.49		
MnO	0.03	0	0.04	0.01		
K ₂ O	7.68	8.50	6.51	5.79		
Na ₂ O	1.30	0.55	0.17	0.28		
Cr ₂ O ₃	0.09	0.01	1.46	0.35		
Total	96.60	96.48	94.42	94.41		
Atomic Pro	oportions					
Si	6.338	6.498	6.346	6.566		
Ti	0.008	0.009	0	0.011		
Al	5.285	4.894	5.480	4.990		
Mg	0.540	0.851	0.190	0.721		
Fe	0.015	0.019	0.012	0.005		
Ca	0.018	0.006	0.094	0.069		
Mn	0.003	0	0.004	0.001		
Κ	1.257	1.397	1.080	0.954		
Na	0.323	0.137	0.044	0.070		
Cr	0.009	0.001	0.150	0.035		
0	22	22	22	22		
Cation						
Total	13.798	13.812	13.402	13.424		
Total	35.798	35.812	35.402	35.424		

Table 4.18. Select muscovite analyses (22 oxygens) Values below minimum detection limit are indicated by strikethrough.

The compositional variation of atomic proportions of Fe + Mg and Si was evaluated in order to determine if the muscovites were phengitic and varied by quarry region. Figure 4.6 displays Fe+Mg vs. Si-6. Si-6 was used so that the x –scale was closer to the y-scale. The compositions vary from one another slightly, but not enough to be used as a discriminating variable between Pentelikon and Proconnesos.



Fig. 4.6. Fe+Mg vs. Si-6 in muscovites from Pentelikon, Proconnesos A, B.

Paragonite

One grain of paragonite, $Na_2Al_4[Si_6Al_2O_{20}](OH)_4$, was identified in sample P85-8 of Pentelikon. Paragonite is often mistaken for muscovite or talc in thin section. The major difference between muscovite and paragonite is that Na substitutes for K. Natural muscovites have a maximum Na₂O content of ~2.0%, while Na₂O in paragonite is closer to 6.4% (Deer et al., 1968). Paragonite has a similar crystal structure to muscovite and is colorless in thin section and colorless to pale yellow in thin section, so it is often misidentified (Deer et al., 1968). Results from the analysis of this paragonite grain are displayed in Table 4.19.

Sample	P85-8			
SiO ₂	46.23			
TiO ₂	0.02			
Al ₂ O ₃	39.95			
MgO	0.53			
FeO	0.15			
CaO	0.42			
MnO	0			
K ₂ O	0.82			
Na ₂ O	5.59			
Cr_2O_3	0.09			
Total	93.79			
Atomic Pr	Atomic Proportions			
Si	5.965			
Ti	0.002			
Al	6.075			
Mg	0.102			
Fe	0.016			
Ca	0.058			
Mn	0			
Κ	0.135			
Na	1.398			
Cr	0.009			
0	22			
Cation	13.757			
Total	10.101			
Total	35.757			

Table 4.19. Paragonite analysis of sample P85-8 in Pentelikon. Values below minimum detection limit are indicated by strikethrough.

The electron microprobe totals for mica endmembers were not always optimal. Most of the totals were lower than 100 % because the routine may not have been properly calibrated for elements such as K, F, and Cl. Every mica grain found in the samples however has an accompanying analysis, which resulted in abundant muscovite data and just this one paragonite grain. The routine for micas always contained both K and Na. Paragonite was the least frequently found mica phase by Capedri et al. (2004) and Capedri and Venturelli (2004). This study also found paragonite less frequently than other mica phases, such as muscovite, margarite, and phlogopite.

Phlogopite

Phlogopite, $K_2(Mg,Fe^{2+})_6[Si_6Al_2O_{20}](OH,F)_4$, also a mica end-member, was only found in Proconnesos B samples. Deer et al. (1968) stated that if the Mg:Fe ratio falls below 2:1 in phlogopite, it should actually be classified as biotite. Biotite however has more substitution of Al by Mg or Fe. Select phlogopite analyses may be viewed in Table 4.20

Weight %					
Sample	Proc-2 (1)	Proc-2 (2)	Proc-8	Proc-14	Proc-9
SiO ₂	39.03	40.46	42.04	39.96	41.27
TiO ₂	0.19	0.26	0.01	0.34	0.10
$A_{l2}O_3$	21.48	22.13	13.07	20.67	16.07
MgO	24.61	24.35	28.05	24.61	27.00
FeO	0.13	0.06	0	0.09	0
CaO	0.17	0.20	1.08	0.28	0.23
MnO	0	0	0.04	0.03	0
K ₂ O	6.76	7.57	8.49	8.90	7.87
Na ₂ O	0.74	1.03	0.98	0.43	1.10
Cr_2O_3	0.23	0.10	0.10	0.12	0.19
Total	93.33	96.16	93.86	95.42	93.82
Atomic Pro	portions				
Sample	Proc-2 (1)	Proc-2 (2)	Proc-8	Proc-14	Proc-9
Si	5.414	4.28	5.903	5.484	5.749
Ti	0.02	0.006	0.001	0.035	0.01
Al	3.513	5.084	2.163	3.344	2.64
Mg	5.088	5.547	5.87	5.036	5.608
Fe	0.015	0.001	0	0.01	0
Ca	0.026	0.059	0.163	0.041	0.034
Mn	0	0.01	0.005	0.003	0
Κ	1.196	0.061	1.521	1.558	1.398
Na	0.199	0.26	0.266	0.113	0.296
Cr	0.025	0.016	0.011	0.013	0.021
0	22	22	22	22	22
Cation	15.495	15.323	15.902	15.638	15.756
l otal	25 405			25 (20	28 85 (
		,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,			1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1

Table 4.20. Select phlogopite analyses, all from Proconnesos B samples. Values below minimum detection limit are indicated by strikethrough.

The compositional variation of these phlogopites was investigated by plotting atomic proportions of Fe vs. Si (Fig. 4.7). Of the nine samples that were plotted, two plotted toward the left of the plot with lower Si, while seven others had higher Si and slightly higher Mg.



Fig. 4.7. Fe+Mg vs. Si in phlogopites from only Proconnesos B.

Margarite

Two grains of margarite, $CaAl_4[Si_4Al_4O_{20}](OH_4)$, were found in Proc-5 of Proconnesos B. Margarite fundamentally differs from muscovite, paragonite and phlogopite because Ca is the interlayer cation. In margarite, Ca is stabilized by an increased $[Al]^4$:Si ratio (Deer et al., 1968).

Margarite is also colorless in thin section, with weak to absent pleochroism. Optically it differs from muscovite by having higher refractive indices and lower birefringence. In hand sample, sizable crystals of margarite have a typical mica structure, but are harder than other micas, with less elastic cleavage (Deer et al., 1968). Table 4.21 contains results of the margarite analyses.

Weight %						
Sample	Proc-5	Proc-5				
SiO ₂	30.81	35.49				
TiO ₂	0.06	0.01				
Al ₂ O ₃	52.18	43.81				
MgO	0.41	1.00				
FeO	0.04	0.05				
CaO	12.28	8.70				
MnO	0.01	0				
K ₂ O	0.16	2.02				
Na ₂ O	0.91	0.71				
Cr ₂ O ₃	0.40	0.21				
Total	97.25	91.99				
Atomic Pro	Atomic Proportions					
Sample	Proc-5	Proc-5				
Si	4.005	4.833				
Ti	0.006	0.001				
Al	7.996	7.033				
Mg	0.08	0.204				
Fe	0.005	0.006				
Ca	1.711	1.27				
Mn	0.001	0				
Κ	0.026	0.35				
Na	0.23	0.187				
Cr	0.041	0.022				
0	22	22				
Cation	14.098	13.908				
1 Otal Total	36 000	35 000				
10181	30.098	22.208				

Table 4.21. Analysis of margarite in Proconnesos A. Values below minimum detection limit are indicated by strikethrough.

<u>Summary</u>

Accessory minerals in the marble samples (Table 4.6) are related to several different processes. Apatite, titanite, and rutile are all resistant to weathering and are concentrated in clastic sediments. The grains of apatite are small and rounded, consistent with a detrital

sedimentary source. These minerals could be have been added to the carbonate sediments prior to the formation of the limestone. Quartz is also resistant to weathering and is concentrated in clastic sediments. The quartz grains are subhedral (Fig. 4.8). If the quartz grains were originally detrital grains derived form clastic sediments, the crystal faces must have developed after deposition in the carbonate, perhaps during metamorphism. Pyrite grains are subhedral to euhedral (Figs. 4.8 and 4.9). Formation of pyrite during diagenesis prior to metamorphism is consistent with the euhedral crystals. The one identified grain of sphalerite is from quarry C4 (Fig. 1.15). This is one of the most southern of the samples quarries and is closer to the granodiorite pluton in the center of Marmara Island (Fig. 1.14, 1.16). The sphalerite may be related to some hydrothermal fluid associated with intrusion of the granodiorite pluton. However, no other obvious evidence of hydrothermal fluids are evident in the marbles and the sphalerite origin remains unknown. Grains of goethite are related to the weathering of some Fe-bearing mineral, probably pyrite. The micas, along with the final compositions of calcite and dolomite, are the only definitive metamorphic minerals in the marbles.

The two sample collections from Marmara Island (Proconnesos A and Proconnesos B, Table 4.6) were obtained by different workers for different purposes. Proconnesos A samples were collected by geoarchaeologists (Attanasio et al., 2008) from the marble quarries and were to be representative of the quarried marble. Proconnesos marble was desirable, in part, because of its visually homogeneous color. Proconnesos A samples were selected to be as pure (devoid of accessory minerals) as possible. The Proconnesos A samples do not contain any quartz or phlogopite (Table 4.6). Proconnesos B samples were collected by a geologist (Vildan Esenli of Istanbul Technical University) and were collected to be representative of the marble in each

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location (no attempt to find purest marble). The Proconnesos B samples contain accessory minerals (quartz and phlogopite, Table 4.6).

Definitive estimates of metamorphic conditions are difficult with the limited assemblage of metamorphic minerals (muscovite, phlogopite, margarite). Marbles of the Mt. Penteli region experienced high pressure (blueschist-eclogite) metamorphism during the Alpine Orogeny in the Late Cretaceous to Middle Eocene (Shaked et al., 2000). This event was followed by a lower grade (greenschist to amphibolite) metamorphism during the Oligocene/Miocene collision (Shaked et al., 2000). Calcite in the marbles is equigranular (Fig. 4.10) and does not show any of the rod-like textures (e.g. Seaton et al., 2009) associated with calcite replacement of high pressure aragonite. The recrystallization accompanying the lower grade Oligiocene/Miocene event seems to dominate the Pentelikon marble fabric. Paragonite (after zoisite and kyanite) is reported in retrograded high pressure marbles from Austria (Spear and Franz, 1986) and the paragonite in the Pentelikon muscovite (Fig. 4.10) relative to muscovite from Proconnesos also supports the notion of higher pressures for the Pentelikon rocks.

Margarite occurs in Ca-Al metamorphic rocks ranging from pelitic rocks to impure marbles. A wide range of metamorphic conditions (including ultra high pressure) stabilizes margarite, but often margarite forms as a replacement of some high grade phase (Fleet, 2003). Most commonly margarite occurs with muscovite, such as in sample Proc-5 (Table 4.6). With such a large stability field, the margarite occurrence at Proconnesos is easily justified based on the inferred Barrovian metamorphism for these rocks.

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Figure 4.8. Back scattered electron images (BSI) of accessory minerals in marble from Pentelikon. A) Sample P85-3. Apatite (bright) and muscovite (micaceous, grey) in calcite matrix. B) Sample P85-5. Pyrite (bright) and muscovite (micaceous, grey) in calcite matrix. C) Sample P85-5. Quartz (dark, center) in calcite matrix. D) Apatite (bright) and muscovite (micaceous and grey) in calcite matrix.



Figure 4.9. Back scattered electron images (BSI) of accessory minerals in marble from Proconnesos A. E) Sample C1.18. Pyrite (bright) in calcite matrix. F) Sample 5b.13. Apatite (lighter) in calcite matrix. G) Sample C10.3. Pyrite (bright) in calcite matrix. H) Sample C10.3. Pyrite (bright) and apatite (less bright) in darker calcite matrix.



Figure 4.10. Back scattered electron images (BSI) of accessory minerals in marble from Proconnesos B. I) Sample Proc-12. Pyrite (brightest), apatite (second brightest) and dolomite (black mineral) in calcite matrix. J) Sample Proc-9. Apatite (light) in calcite matrix. K) Sample Proc-10. Dolomite (dark) and apatite (light) in calcite matrix. L) Sample Proc-14. Muscovite (dark) in calcite matrix.

STATISTICAL ANALYSIS

Nonmetric multidimensional scaling (NMDS)

The NMDS with three dimensions resulted in a stress of .12 and a convergent solution after 86 restarts. Figure 4.12 shows the two-dimensional projection of the three-dimensional ordination, oriented based on NMDS axis 2 vs. NMDS axis 1. NMDS axis 1 has the greatest variance then NMDS axis 2, then NMDS axis 3. Figure 4.13 shows where the variables plot in ordination space.

Accessory minerals that are present in only 1 of the 41 samples plot on the outer edges of the ordination. These infrequently found accessory minerals include titanite, rutile, margarite, and sphalerite, and paragonite. Paragonite appears to be very close to quartz in two-dimensional space, but likely far away from the other variables in three dimensions. The variables maximum grain size (represented by MGS in this ordination) and stable isotope δ^{13} C and δ^{18} O fall closer to one another in the ordination presumably because their sample scores have fairly similarly spaced values between 0 and 1, and vary less between quarries than an accessory mineral found in only one or two samples in the entire sample set. More frequently found minerals such as goethite, pyrite, apatite, quartz, phlogopite, muscovite, and dolomite appear to encircle maximum grain size and stable isotope signatures.

In Figure 4.11, sample scores from Pentelikon, Proconnesos A, and Proconnesos B do not notably vary from one another along axis one. However, on axis 2, Pentelikon samples have generally higher samples scores than Proconnesos A and Proconnesos B, with some overlap. Figure 4.11 shows some separation between Pentelikon and Proconnesos.

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Figure 4.11. Sample scores from three-dimensional ordination on NMDS axis 2 and NMDS axis 1.

The sample scores on NMDS axis 2 vs. NMDS axis 1 (Fig. 4.11) are directly related to the apparent placement of the variables in Figure 4.12. Prior to this statistical analysis, we knew that maximum grain size and stable isotope δ^{13} C and δ^{18} O values were generally dissimilar between Pentelikon, Proconnesos A and Proconnesos B. Separation would be expected in an NMDS ordination based on these maximum grains sizes and stable isotopes alone. The addition of each accessory mineral to the ordination brings some similarities such as shared minerals between all quarry areas like muscovite, apatite, quartz, and pyrite. These shared minerals were also found frequently in the 41 samples. Five Proconnesos B samples contained accessory phlogopite, not found in Pentelikon or Proconnesos B. Pentelikon contained grains of both quartz and paragonite, variables that plotted at the top of this figure. Accordingly, Pentelikon samples in general plot toward the top of the figure. Proconnesos A and Proconnesos B samples plot generally toward the bottom of the figure, with some overlap from two Pentelikon samples in two-dimensional space.



Figure 4.12. Variables of a three-dimensional ordination on NMDS axis 2 and NMDS axis 1.

Figure 4.13 presents the NMDS axis 3 vs. the NMDS axis 1. This pattern looks similar to axis 2 vs. axis 1, except the Pentelikon samples scores are now at the bottom of the twodimensional space, and the Proconnesos A and Proconnesos B are at the top of the figure. Variance is least on axis 3 and greatest on axis 1, so the axes may be contrasted based on variance. Axis 3 shows Proconnesos A and B samples with higher variance, and Pentelikon with lower variance. Figure 4.14 shows all variables proportionately in the same space, but across a wider span than axis 2 vs. axis 1. The samples for axis 3 vs. axis 1 (Fig. 4.13) plot between an x limit of -2 and 1, and a y limit of 0 and 1, but the variables have an x limit of -4 and 4, and a y limit of -2 and 2.



Figure 4.13. Sample scores from three-dimensional ordination on NMDS axis 3 and NMDS axis 1.



4.14. Variables of a three-dimensional ordination on NMDS axis 3 and NMDS axis 1.

Axes somewhat closer in variance are NMDS axis 3 and NMDS axis 2, as seen in Figure 4.15. Axis 3 vs. axis 2 shows the greatest amount of separation between Pentelikon and Proconnesos A and B sample scores. This separation is likely driven by differences in grain size and isotopic data, and the more frequent presence of quartz and micas in Pentelikon than Proconnesos A and Proconnesos B. Pentelikon samples vary from Proconnesos A and B axis 2, plotting generally toward the right, with higher variance. Pentelikon also varies from Proconnesos A and B along axis 3, having generally lower sample scores than Proconnesos A and B.
For these reasons, Figure 4.15 is the most visually discriminating plot between Pentelikon and Proconnesos A, B. Figure 4.16 shows the placement of the variables in axis 3 vs. axis 2, covering a larger space than the sample scores in Figure 4.17.



Figure 4.15. Sample scores from three-dimensional ordination space on NMDS axis 3 and NMDS axis 2.



4.16. Variables of a three-dimensional ordination on NMDS axis 3 and NMDS axis 2.

CHAPTER 5

DISCUSSION AND CONCLUSIONS

Separately, maximum calcite grain size, stable isotope δ^{13} C and δ^{18} O, and accessory mineral content all have the potential to distinguish Pentelikon from Proconnesos A and Proconnesos B. This study investigated the power of a multivariate statistical method in determining similarities or differences between marble quarry regions and provided new accessory mineral data for 41 quarry samples, as well as stable isotope data for 15 samples. In this case, maximum calcite grain size and stable isotopes may have been enough to characterize the samples by region. With the addition of accessory minerals as a distinguishing parameter, statistical analysis is necessary for interpretation of the data sets, due to the large number of variables.

This work focused on the beginning stage of a marble provenance study – quarry characterization. With so much emphasis placed on NMDS and its ability to display differences between quarries, it is important to suggest how the method could be used to provenance artifact samples in the future. Since NMDS is only concerned with a scaled value and not a predetermined group for each sample, an artifact sample could easily be entered into the ordination with potential quarry site data, provided the artifact sample is uniquely labeled in the ordination plot. When the NMDS reaches a solution for the data set, the artifact sample can be analyzed in reference to where it falls in the NMDS plot. Similarities or differences between the artifact sample and the quarry samples can be seen quickly, compared to poring over tables of data, or attempting to fit the sample into a crowded stable isotope database plot.

The major focus of this study was the procurement of electron microprobe data for accessory minerals in the marble samples. Sampling for quarry marbles with accessory minerals should follow the same practice as is used for sampling of marbles for stable isotope analysis. The marble should appear texturally homogeneous with few accessory minerals visible to the naked eye. From these findings, there are typically abundant accessory minerals in samples that appear to be entirely calcite to the naked eye. Visually homogeneous quarry marble would have been the most common marble used by the Greeks and Romans for sculpture, because it is structurally consistent for carving.

The temperature of equilibrium between calcite and dolomite was calculated in order to determine whether or not there were similar temperatures between Pentelikon, Proconnesos A, and Proconnesos B (Table 4.7). Further investigation of calcite in equilibrium with dolomite using Equation 3.1 should be done in order to determine how much the calculated temperatures vary within one sample and within a set of quarry samples. The results from the thermometry data of this study show that Pentelikon samples have fairly similar values within quarry P85 (290 – 330 °C), while Proconnesian marble are more variable. Proconnesios A had a range of 320 – 520 °C and Proconnesios B had a range of 340 - 460 °C. Proconnesian samples cover multiple quarries and may vary to this extent because of the Eocene granitoid intrusion.

Several of the accessory minerals were present with similar compositions in both Penteli and Proconnesos, such as apatite-(CaF), quartz, pyrite, and muscovite. Compositional variation of Fe + Mg and Si in muscovites from Pentelikon, Proconnesos A, and Proconnesos B was evaluated with the idea that different quarry regions may vary from one another based on the composition of muscovite. The three quarries appear to be visually indistinguishable (Fig. 4.6) from this plot alone.

Future work should continue to investigate compositional variation in accessory minerals, especially apatites, micas, and carbonate minerals, as demonstrated in this study. Although notable compositional variation was not observed in apatites and muscovites between Penteli and Proconnesos, there is the potential that other Mediterranean marble quarries will contain accessory minerals with distinct compositional variation.

Nonmetric multidimensional scaling worked well for these samples because there was enough similarity between multiple samples for a pattern to be seen in each NMDS plot. If NMDS were used on a sample set in which points had few similarities, the ordination's results would reflect few similarities in the data. Finding that there are few similarities between samples is also useful information. However, in provenance studies involving quarries, one looks for groups with a fair amount of samples that show similarity to one another and can be distinguished from other groups of data.

The separation between Pentelikon and Proconnesos A and B was notable in Figure 4.15, based on axis 3 vs. axis 2. The variables plotted in Figure 4.16 suggest that this separation is a reflection mainly of maximum grain size (MGS), and stable isotopes, values that were known to differ between Pentelikon and Proconnesos prior to the statistical analysis. The separation between Pentelikon and Proconnesos A and B is centered on these values in Figures 4.11, 4.13, and 4.15. From there, separation between quarry regions is influenced by differences in goethite, apatite, pyrite, and muscovite – minerals found in several samples of Pentelikon, Proconnesos A, and Proconnesos B. Titanite, rutile, quartz, paragonite, margarite, phlogopite, and sphalerite caused separation among Pentelikon and Proconnesos as well, since not all of those minerals were present in each sample area.

The NMDS ordination provides a visual assistance in making observations about the geologic history of both Pentelikon and Proconnesos. The ordination reflected differences between Pentelikon and Proconnesos based on maximum grain size (Figs. 4.11 - 4.16). Marble samples from Pentelikon were from a small area (~10-20 meters apart from one another) on the northern part of the Attic-Cycladic metamorphic belt. Calcite grain sizes were similar to one another, ranging from 0.5 to 1.1 mm. On average, Proconnesian marble samples ranged from 1.0 to 2.2 mm. Proconnesian samples covered a broader range, up to 2 km apart for a few samples. The maximum calcite grain sizes barely overlap between Pentelikon and Proconnesos. Pentelic marble may have recrystallized faster than Proconnesian, and the variability of maximum grain size in Proconnesos reflects multiple events of recrystallization, supported by the island's Eocene granitoid intrusion.

The NMDS also reflected differences in stable isotope δ^{13} C and δ^{18} O for Pentelikon and Proconnesos (Figs. 4.11 – 4.16). Pentelic marble generally has higher δ^{13} C values (2.70 to 4.20_{VPDB}) than Proconnesos A (1.95 to 3.01_{VPDB}) and Proconnesos B (2.00 to 3.70_{VPDB}). δ^{18} O values in Pentelic samples (-8.50 to -4.30_{VPDB}) are somewhat lower than Proconnesos A (-6.00 to -1.69_{VPDB}) and Proconnesos B (-4.40 to -0.40_{VPDB}). This further separates the samples scores in the ordination. Stable isotopes in Proconnesian marbles are again more variable than Pentelikon, possibly due to their larger distribution across the island, and the impact of the Eocene granitoid.

Most of the samples contained apatite (CaF), which is resistant to weathering and was likely present in the limestone protolith. Quartz in Pentelikon and Proconnesos B was also likely present in the protolith, of detrital origin. The ordination separated the areas of Pentelikon and Proconnesos B from Proconnesos A to some degree based on the presence of quartz. Apatite appears to be less influential (Figs. 4.11 - 4.16). Titanite and rutile, less present in the samples

and at the edge of the ordination, were also likely present in the protolith as detrital grains resistant to weathering. Titanite and rutile however were less influential on the entire dataset, since they were infrequently present.

Pyrite grains were present in samples from Pentelikon, Proconnesos A, and Proconnesos B, which means that pyrite was unlikely to separate the areas from one another. Pyrite likely formed diagenetically in the limestone protoliths of Pentelikon and Proconnesos. Goethite was also present in samples from each area, possibly formed by the weathering of pyrite. Sphalerite, only in Proconnesos A, may have been a product of hydrothermal fluids brought on by the Eocene granitoid intrusion.

The mica minerals included muscovite (present in Pentelikon, Proconnesos A, B), phlogopite (Proconnesos B), margarite (Proconnesos), and paragonite (Pentelikon). These minerals formed during metamorphism. The greater frequency of muscovite in Pentelikon over Proconnesos A and B further separated Pentelikon from Proconnesos in the ordination. Phlogopite also separated Proconnesos B samples from Proconnesos A and Pentelikon to a certain extent. The presence of margarite in Proconnesos B and paragonite in Pentelikon was limited to one sample for each mineral, unlike muscovite.

The method of analyzing accessory minerals with isotopic data and maximum grain size and summarizing the results with NMDS is still in the stage of quarry data collection. The case study of Pentelikon vs. Proconnesos shows promise for larger quarry studies, and the provenancing of unknown marble artifact samples. The challenge of the method lies in the increased amount of time that it takes to analyze accessory minerals with the electron microprobe. The NMDS analysis is not time consuming once commands are written for execution in R. Although there may be significant added time, the electron microprobe analysis of accessory minerals combined with maximum grain size and stable isotopes addresses the characteristics of a marble sample thoroughly. When these data are analyzed simultaneously with NMDS, the method may lead to more accurate provenance assignments.

This study affirms the importance of petrographic and stable isotope analysis as a standard component of marble provenance studies. Maximum calcite grain size and stable isotopes for Pentelikon and Proconnesos samples generally differed by quarry region. The accessory mineral content was not extremely different between Pentelikon and Proconnesos, since samples from both areas frequently contained minerals such as dolomite, apatite(CaF), pyrite, goethite, quartz, and muscovite. However, these are only two quarry areas in the Mediterranean Region, and accessory minerals may vary to a greater degree among more quarry areas (Capedri et al., 2004). NMDS provided a visual way to note dissimilarity between Pentelikon and Proconnesos, and can be used with grain size and stable isotopes alone, or with any other parameter that can be scaled accordingly, such as the presence or absence of accessory minerals. The benefit of NMDS is that nominal, ordinal, interval, and ratio data can be analyzed together once they are scaled systematically between 0 and 1. The ability to quantify and analyze any variable systematically is promising for future marble provenance studies, whether or not future studies utilize this combination of variables.

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APPENDIX A

ELECTRON MICROPROBE DATA

MINERALS

Carbonate Minerals

Calcite analyses (4 oxygens)

Weight %						
Sample	P85-9 1-2	P85-9 2-2	P85-10 1-2	C6.4 2-2	C15.1 -1	Proc-91
CaO	56.400	55.310	55.100	56.160	57.830	54.480
MgO	0.758	0.622	0.825	0.519	0.486	2.024
FeO	0.268	0.022	0.067	0	0	0.067
MnO	0	0.148	0.029	0	0	0.118
SrO	0.071	0.137	0.055	0	0.066	0.047
CO_2	45.280	44.250	44.230	44.640	45.940	45.100
Total	102.770	100.490	100.310	101.320	104.320	101.830
Atomic Prop	portions					
Ca	1.303	1.308	1.304	1.316	1.317	1.264
Mg	0.024	0.021	0.027	0.017	0.015	0.0653
Fe	0.005	0.004	0.001	0	0	0.001
Mn	0	0.003	0.006	0	0	0.002
Sr	0.009	0.002	0.007	0	0.008	0.006
С	1.333	1.333	1.333	1.333	1.333	1.333
0	4	4	4	4	4	4
Cation						
Total	2.667	2.667	2.667	2.667	2.667	2.667
Total	6.667	6.667	6.667	6.667	6.667	6.667

Calcite analyses (continued)

Weight %	ó					
Sample	Proc-12 2	Proc-12 1-2	C13.6 1-1	C13.6 1-2	C14.7 1-2	C8.5 1-2
CaO	53.770	55.300	55.080	56.890	56.490	55.140
MgO	1.787	1.280	1.046	0.383	0.789	1.433
FeO	0.156	0	0	0	0.134	0.089
MnO	0	0	0	0	0.030	0.030
SrO	0	0.138	0.083	0.031	0	0.020
CO_2	44.250	44.860	44.400	45.080	45.300	44.920
Total	99.960	101.580	100.610	102.390	102.740	101.640
Atomic P	roportions					
Ca	1.272	1.290	1.298	1.321	1.305	1.285
Mg	0.059	0.042	0.034	0.012	0.025	0.046
Fe	0.003	0	0	0	0.002	0.002
Mn	0	0	0	0	5.000	5.000
Sr	0	0.002	0.001	4.000	0	2.000
С	1.333	1.333	1.333	1.333	1.333	1.333
0	4.000	4.000	4.000	4.000	4.000	4.000
Cation Total	2.667	2.667	2.667	2.667	2.667	2.667
Total	6.667	6.667	6.667	6.667	6.667	6.667

Weight %						
Sample	P85-91	P85-9 2-1	P85-10 1-1	P85-10 2-1	Proc-9 1-1	Proc-9 2-1
CaO	30.780	29.990	31.970	30.100	33.500	30.410
MgO	20.380	19.790	22.470	21.650	22.320	21.350
FeO	0.872	1.452	0	0.695	0.112	0.179
MnO	0.768	1.210	0	0	0	0.030
SrO	0.013	0.046	0.038	0.034	0	0.059
CO ₂	47.420	46.790	49.640	47.700	50.720	47.330
Total	100.230	99.270	104.110	100.180	106.640	99.370
Atomic Prop	portions					
Ca	0.679	0.671	0.674	0.660	0.691	0.672
Mg	0.626	0.616	0.659	0.661	0.641	0.657
Fe	0.015	0.025	0	0.012	0.002	0.003
Mn	0.013	0.021	0	0	0	5.000
Sr	1.000	6.000	4.000	4.000	0	7.000
С	1.333	1.333	1.333	1.333	1.333	1.333
0	4.000	4.000	4.000	4.000	4.000	4.000
Cation Total	2.667	2.667	2.667	2.667	2.667	2.667
Total	6.667	6.667	6.667	6.667	6.667	6.667

Dolomite analyses from Pentelikon and Proconnesos B (4 oxygens)

Weight %				
Sample	Proc-12 1	C14.7 1-1	C8.5 1-1	C8.5 2-1
CaO	31.730	32.250	31.490	31.720
MgO	22.180	21.990	23.140	21.940
FeO	0	0.179	0.112	0
MnO	0	0	0.030	0.059
SrO	0.084	0.059	0.046	0
CO ₂	49.150	49.460	50.080	48.880
Total	103.150	103.940	104.890	102.590
Atomic Pr	oportions			
Ca	0.676	0.682	0.658	0.679
Mg	0.657	0.647	0.673	0.653
Fe	0	0.003	0.002	0
Mn	0	0	5.000	0.001
Sr	0.001	7.000	5.000	0
С	1.333	1.333	1.333	1.333
0	4.000	4.000	4.000	4.000
Cation	2 667	2 667	2 667	2 667
Total	2.007	2.007	2.007	2.007
Total	6.667	6.667	6.667	6.667

Dolomite analyses from Proconnesos A and B (4 oxygens)

Phosphate minerals

Weight %						
Sample	P85-1	P85-2	P85-3	P85-4	P85-5	P85-6
P_2O_5	41.010	42.240	42.150	42.950	42.080	43.100
CaO	56.830	55.130	53.780	55.060	55.300	55.970
Al_2O_3	0.005	0.005	0.683	0.013	0	0.037
MnO	0	0.025	0.049	0	0.198	0
Cl	0	0.010	0.015	0	0.005	0
F	3.540	3.690	3.910	4.300	4.170	3.990
Fe ₂ O ₃	0	0	0.091	0.091	0.159	0.023
Total	99.900	99.540	99.040	100.600	100.160	101.450
Atomic Prop	portions					
Р	6.108	6.268	6.283	6.347	6.281	6.292
Ca	10.712	10.351	10.146	10.297	10.530	10.341
Al	0.001	0.001	0.142	0.003	0.002	0.008
Mn	0	0.004	0.007	0	0.019	0
Cl	0	0.003	0.004	0	0.011	0
F	1.969	2.046	2.180	2.371	2.568	2.173
Fe	0	0	0.012	0.012	0.022	0.003
0	25.000	25.000	25.000	25.000	25.000	25.000
Cation						
Total	18.791	18.673	18.775	19.030	19.433	18.817
Total	43.790	43.673	43.775	44.030	44.433	43.815

Pentelikon apatite analyses (25 oxygens)

Weight %					
Sample	C 3.2s 4 20k	C5b.13 1 40k	C 7i.8 6	C 7i.8 9	C 3.2s 5 20k
P_2O_5	41.710	42.230	43.670	42.960	41.220
CaO	55.970	56.100	56.220	56.890	54.990
Al ₂ O ₃	0	0	0.018	0.005	0.016
MnO	0	0	0	0	0
Cl	0.034	0.005	0.055	0.028	0.021
F	3.920	3.940	3.750	3.830	4.160
Fe ₂ O ₃	0	0	0.092	0	0
Total	99.980	100.620	102.210	102.090	98.650
Atomic Pro	portions				
Р	6.216	6.239	6.295	6.235	6.250
Ca	10.555	10.490	10.257	10.452	10.551
Al	0	0	0.004	0	0.003
Mn	0	0	0	2.075	0
Cl	0.010	0.001	0.016	0.001	0.006
F	2.182	2.177	2.020	0	2.357
Fe	0	0	0.012	0.008	0
0	25.000	25.000	25.000	25.000	25.000
Cation					
Total	18.964	18.909	18.603	18.770	19.167
Total	43.964	43.909	43.604	43.770	44.168

Proconnesos A apatite analyses (25 oxygens)

Weight %				
Sample	Proc-1 9	Proc 3 8	Proc-4b 22	Proc-6 7
P_2O_5	40.760	42.490	39.580	40
CaO	58.420	54.400	56.280	55.980
Al ₂ O ₃	0	0	0	0
MnO	0	0	0	0
Cl	0	0.007	0	0.016
F	4.380	3.630	3.820	3.380
Fe ₂ O ₃	0	0	0	0
Total	101.710	99.000	98.070	97.950
Atomic Pro	portions			
Р	6.078	6.313	6.069	6.078
Ca	11.024	10.227	10.922	10.765
Al	0	0	0	0
Mn	0	0	0	0
C1	0	0.002	0	0.005
F	2.437	2.016	2.191	1.917
Fe	0	0	0	0
0	25.000	25.000	25.000	25.000
Cation				
Total	19.539	18.557	19.182	18.765
Total	44.539	43.557	44.182	43.765

Proconnesos B apatite analyses (25 oxygens)

Weight %											
Sample	P85-6	P85-9	P85-9	P85-10	Proc-5	Proc-6					
SiO ₂	99.310	95.940	98.470	98.590	99.510	97.480					
TiO ₂	0	0	0.016	0.026	0	0.284					
Al2O3	0.011	0	0	0.024	0	0.066					
MgO	0.021	0.006	0.007	0.032	0	0.025					
FeO	0.029	0	0.065	0	0	0.042					
CaO	0.041	0.046	0.008	0.113	0.199	0.332					
MnO	0.071	0	0.017	0	0.009	0.08 4					
Cr2O3	0	0.025	0	0.049	0.061	0					
NiO	0	0	0	0	0	0.017					
Total	99.500	96.020	98.580	98.890	99.790	98.330					
Atomic Pro	portions			Atomic Proportions							
	P85-6	P85-9	P85-9	P85-10	Proc-5	Proc-6					
Si	P85-6 1.998	P85-9 1.999	P85-9 1.999	P85-10 1.996	Proc-5 1.997	Proc-6 1.989					
Si Ti	P85-6 1.998 0	P85-9 1.999 0	P85-9 1.999 0	P85-10 1.996 0	Proc-5 1.997 0	Proc-6 1.989 0.004					
Si Ti Al	P85-6 1.998 0 0	P85-9 1.999 0 0	P85-9 1.999 0 0	P85-10 1.996 0 0.001	Proc-5 1.997 0 0	Proc-6 1.989 0.004 0.002					
Si Ti Al Mg	P85-6 1.998 0 0 0.001	P85-9 1.999 0 0 0	P85-9 1.999 0 0 0	P85-10 1.996 0 0.001 0.001	Proc-5 1.997 0 0 0	Proc-6 1.989 0.004 0.002 0.001					
Si Ti Al Mg Fe	P85-6 1.998 0 0 0.001 0	P85-9 1.999 0 0 0 0	P85-9 1.999 0 0 0 0 0.001	P85-10 1.996 0 0.001 0.001 0	Proc-5 1.997 0 0 0 0	Proc-6 1.989 0.004 0.002 0.001 0.001					
Si Ti Al Mg Fe Ca	P85-6 1.998 0 0 0.001 0 0.001	P85-9 1.999 0 0 0 0 0 0 0.001	P85-9 1.999 0 0 0 0 0.001 0	P85-10 1.996 0 0.001 0.001 0 0.002	Proc-5 1.997 0 0 0 0 0 0 0.004	Proc-6 1.989 0.004 0.002 0.001 0.001 0.007					
Si Ti Al Mg Fe Ca Mn	P85-6 1.998 0 0 0.001 0 0.001 0.001	P85-9 1.999 0 0 0 0 0 0.001 0	P85-9 1.999 0 0 0 0 0 0.001 0 0	P85-10 1.996 0 0.001 0.001 0 0.002 0	Proc-5 1.997 0 0 0 0 0 0.004 0	Proc-6 1.989 0.004 0.002 0.001 0.001 0.007 0.002					
Si Ti Al Mg Fe Ca Mn Cr	P85-6 1.998 0 0.001 0.001 0.001 0.001	P85-9 1.999 0 0 0 0 0 0 0.001 0 0	P85-9 1.999 0 0 0 0 0 0.001 0 0 0 0	P85-10 1.996 0 0.001 0.001 0 0.002 0 0.001	Proc-5 1.997 0 0 0 0 0 0 0.004 0 0.001	Proc-6 1.989 0.004 0.002 0.001 0.001 0.007 0.002 0					
Si Ti Al Mg Fe Ca Mn Cr Ni	P85-6 1.998 0 0 0.001 0.001 0.001 0 0 0	P85-9 1.999 0 0 0 0 0 0 0.001 0 0 0 0	P85-9 1.999 0 0 0 0 0 0 0 0 0 0 0 0 0	P85-10 1.996 0 0.001 0.001 0 0.002 0 0.001 0	Proc-5 1.997 0 0 0 0 0 0 0.004 0 0.001 0	Proc-6 1.989 0.004 0.002 0.001 0.001 0.007 0.002 0 0					
Si Ti Al Mg Fe Ca Mn Cr Ni O	P85-6 1.998 0 0 0.001 0.001 0.001 0 0 4.000	P85-9 1.999 0 0 0 0 0 0 0 0 0 4.000	P85-9 1.999 0 0 0 0 0 0 0 0 0 4.000	P85-10 1.996 0 0.001 0 0.001 0 0.001 0 4.000	Proc-5 1.997 0 0 0 0 0 0 0.004 0 0.001 0 4.000	Proc-6 1.989 0.004 0.002 0.001 0.001 0.007 0.002 0 0 4.000					
Si Ti Al Mg Fe Ca Mn Cr Ni O Cation	P85-6 1.998 0 0 0.001 0.001 0.001 0 4.000	P85-9 1.999 0 0 0 0 0 0 0 0 0 4.000	P85-9 1.999 0 0 0 0 0 0 0 0 4.000	P85-10 1.996 0 0.001 0.001 0 0.002 0 0.001 0 4.000	Proc-5 1.997 0 0 0 0 0 0 0 0.004 0 0.001 0 4.000	Proc-6 1.989 0.004 0.002 0.001 0.007 0.002 0 0 4.000					
Si Ti Al Mg Fe Ca Mn Cr Ni O Cation Total	P85-6 1.998 0 0 0.001 0.001 0.001 0 4.000 2.002	P85-9 1.999 0 0 0 0 0 0.001 0 0 0 4.000 2.001	P85-9 1.999 0 0 0 0 0 0 0 0 0 4.000 2.001	P85-10 1.996 0 0.001 0 0.002 0 0.001 0 4.000 2.003	Proc-5 1.997 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Proc-6 1.989 0.004 0.002 0.001 0.007 0.002 0 0 4.000 2.006					

Pentelikon and Proconnesos B apatite analyses (25 oxygens)

Sulfide Minerals

Pyrite analyses from Pentelikon

Weight %	/ 0					
Sample	P85-1	P85-1 3	P85-1-12	P85-2-16	P85-2-17	P85-2-18
Fe	45.790	45.030	45.510	45.130	45.760	45.360
S	53.960	54.480	54.330	54.770	54.750	54.550
Ni	0.073	0.202	0	0.154	0.073	0.013
Cu	0.024	0.110	0.081	0	0.086	0
Total	99.840	99.820	99.920	100.060	100.670	99.920
Sample	P85-2 19	P85-2 20	P85-2 23	P85-2 25	P85-2 26	P85-2 27
Fe	45.930	46.230	45.120	45.750	44.720	44.360
S	55.430	55.280	53.460	54.310	53.470	54.720
Ni	0	0.137	0.112	0.111	0.142	0.133
Cu	0.052	0	0	0	0	0.043
Total	101.420	101.640	98.700	100.180	98.330	99.250
Sample	P85-5 1	P85-5 7	P85-5 9	P85-5 10	P85-6 2	P85-64
Fe	46.260	46.550	47.380	46.340	45.930	46.470
S	51.570	53.300	53.010	52.170	53.960	51.930
Ni	0.372	0.232	0.044	0.237	0.403	0
Cu	0	0	0.053	0.005	0	0
Total	98.200	100.080	100.490	98.750	100.290	98.410
Sample	P85-6 5	P85-6 8	P85-6 9	P85-6 12	P85-77	P85-8 9
Fe	45.880	47.190	46.560	46.320	46.360	46.640
S	53.890	53.220	53.760	53.400	52.730	52.110
Ni	0.123	0.057	0.009	0.276	0.147	0.415
Cu	0.024	0.063	0.034	0	0	0.048
Total	99.910	100.530	100.360	100	99.240	99.220
Sample	P85-8 12	P85-8 13	P85-9 1	P85-96	P85-10 3	P85-10 4
Fe	46.560	44.730	46.560	45.190	46.300	46.010
S	49.990	52.750	53.080	51.890	51.890	52.100
Ni	0.264	0.615	0.229	1.134	0.234	0.052
Cu	0	0.053	0	0	0.082	0.005
Total	96.810	98.140	99.870	98.210	98.510	98.170

Pyrite d	analyses	from	Proconnesos	A
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Weight %					
Sample	C3.2s 1	C3.2s 2	C3.2s 3	C6.4 1	C6.4 2
Fe	46.360	46.040	45.780	45.730	46.110
S	51.270	51.470	50.740	52.530	52.490
Ni	0.025	0.641	0.876	0.367	0.140
Cu	0.068	0	0.044	0	0.061
Total	97.740	98.270	97.540	98.630	98.800
Sample	C6.4 3	C6.4 4	C12.3	C15.1	C15.1
Fe	34.530	44.970	44.920	45.440	45.620
S	0.024	51.760	51.090	51.040	52.330
Ni	1.746	0.882	0.153	0.340	0
Cu	0.075	0	0	0	0
Total	36.380	97.620	96.170	96.970	98.080

Pyrite analyses from Proconnesos B

Weight %					
Sample	Proc-1 1	Proc-1 2	Proc-2 1	Proc-2 2	Proc-3
Fe	37.960	42.210	46.760	45.590	43.780
S	44.130	47.970	53.720	51.740	53.260
Ni	0.065	0.119	0.124	0.008	0.742
Cu	0	0	0	0	0.004
Total	82.160	90.290	100.600	97.340	97.790
Sample	Proc-4a	Proc-4b 1	Proc-4b 2	Proc-5	Proc-6
Fe	45.270	45.890	44.590	44.580	46.400
S	52.150	51.130	54.540	53.720	54.240
Ni	0.238	0.110	1.869	1.255	0.212
Cu	0	0	0	0	0
Total	97.660	97.130	101.000	99.560	100.850
Sample	Proc-9	Proc-12	Proc-13	Proc-13 2	
Fe	44.030	45.810	46.340	44.110	
S	55.250	53.850	54.640	53.060	
Ni	0.090	0.721	0.185	0.541	
Cu	0.033	0	0	0.061	
Total	99.400	100.380	101.170	97.770	

Sphalerite analysis from Proconnesos A

Weight %	ó
Sample	C4.4
Fe	0.440
S	31.890
Ni	0
Zn	59.290
Cu	0
Total	91.610

Nonsilicates

Rutile analyses from Proconnesos A and Pentelikon (4 oxygens)

Weight %			
Sample	Proc-1	Proc-6	P85-3
SiO ₂	0.600	0.662	1.335
TiO ₂	84.140	97.240	93.400
Al_2O_3	1.167	0.433	0.934
MgO	0.051	0	0.001
FeO	0.430	0	0.884
CaO	5.370	1.019	0.961
MnO	0.081	0.081	0.017
Cr_2O_3	0.482	0.104	0
NiO	0	0.075	0
Total	92.310	99.620	97.680
Atomic Prop	portions		
Si	0.018	0.018	0.036
Ti	1.852	1.954	1.915
Al	0.040	0.014	0.030
Mg	0.002	0	0
Fe	0.011	0	0.020
Ca	0.168	0.029	0.028
Mn	0.002	0.002	0
Cr	0.011	0.002	0
Ni	0	0.002	0
0	4.000	4.000	4.000
Cation			
Total	2.104	2.020	2.037
Total	6.104	6.020	6.037

Weight %			
Sample	P85-3 7-1	C6.4	Proc-1
SiO ₂	3.100	3.410	3.900
TiO ₂	0.016	0	0.054
Al_2O_3	0.195	0.205	0.672
MgO	0.393	0.347	0.444
FeO	73.100	75.150	73.980
CaO	1.507	1.670	1.829
MnO	0.864	0	0.052
Cr_2O_3	0.027	0.034	0.034
NiO	0.478	2.356	0
Total	79.690	83.170	80.970
Atomic Pr	oportions		
Si	0.174	0.183	0.212
Ti	0.007	0	0.002
Al	0.012	0.013	0.043
Mg	0.033	0.027	0.035
Fe	3.441	3.385	3.360
Ca	0.090	0.096	0.106
Mn	0.041	0	0.002
Cr	0.001	0.001	0.001
Ni	0.021	0.102	0
0	4.000	4.000	4.000
Cation			
Total	3.818	3.809	3.763
Total	7.818	7.809	7.763

Goethite analyses from Pentelikon Proconnesos A, and Proconnesos B (4 oxygens)

Framework Silicates

Weight %)						
Sample	P85-2	P85-2	P85-2	P85-3	P85-3	P85-3	P85-5
SiO ₂	98.540	100.010	99.320	98.450	98.230	97.470	99.150
TiO ₂	0	0	0.001	0	0.003	0.029	0
Al_2O_3	0.014	0	0	0.005	0	0.003	0.010
MgO	0.002	0.003	0.023	0.015	0	0.001	0
FeO	0.036	0	0.065	0	0.022	0	0.015
CaO	0.022	0.037	0.029	0.042	0.019	0.052	0.121
MnO	0	0.035	0.017	0	0.071	0	0.036
Cr ₂ O ₃	0.048	0	0.072	0	0	0.037	0.100
NiO	0.030	0	0	0.109	0.030	0	0.012
Total	98.690	100.080	99.530	98.620	98.370	97.590	99.440
Atomic Pr	roportions						
Si	1.998	1.999	1.998	1.998	1.999	1.999	1.997
Ti	0	0	0	0	0	0	0
Al	0	0	0	0	0	0	0
Mg	0	0	0.001	0.001	0	0	0
Fe	0.001	0	0.001	0	0	0	0
Ca	0.001	0.001	0.001	0.001	0	0.001	0.003
Mn	0	0.001	0	0	0.001	0	0.001
Cr	0.001	0	0.001	0	0	0.001	0.002
Ni	0.001	0	0	0.002	0.001	0	0
0	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Cation							
Total	2.001	2.001	2.002	2.002	2.001	2.001	2.002
Total	6.001	6.001	6.002	6.002	6.001	6.001	6.002

Pentelikon quartz analyses (4 oxygens)

Orthosilicates

Weight %	
Sample	Proc-6 11
SiO ₂	27.930
TiO ₂	37.900
Al_2O_3	3.720
MgO	0
FeO	0
CaO	28.040
MnO	0
Cr_2O_3	0.047
NiO	0
Total	97.650
Atomic Prop	portions
Si	0.747
Ti	0.762
Al	0.117
Mg	0
Fe	0
Ca	0.803
Mn	0
Cr	0.001
Ni	0
0	4
Cation	
Total	2.431
Total	6.431

Titanite analysis from Proconnesos B (4 oxygens)

Sheet Silicates

Weight %						
Sample	P85-3 5	P85-5 2	P85-5 4	P85-5 5-1	P85-5 6	P85-5 12
SiO ₂	49.390	50.440	47.420	50.680	50.900	50.210
TiO ₂	0.088	0.093	0.120	0.105	0.147	0.123
Al_2O_3	34.940	32.230	36.580	31.940	32.540	32.740
MgO	2.823	4.430	1.489	3.800	3.060	3.840
FeO	0.138	0.181	0.073	0.327	0.160	0.182
CaO	0.128	0.043	0.207	0.280	0.066	0.046
MnO	0.027	0	0.035	0.035	0	0.035
K ₂ O	7.680	8.500	6.020	4.450	6.980	6.470
Na ₂ O	1.301	0.549	0.404	0.419	0.211	0.428
Cr ₂ O ₃	0.087	0.012	0	0.025	0.025	0
Total	96.600	96.480	92.340	92.060	94.090	94.080
Atomic Pro	oportions					
Si	6.338	6.498	6.267	6.656	6.626	6.537
Ti	0.008	0.009	0.012	0.010	0.014	0.012
Al	5.285	4.894	5.699	4.943	4.993	5.024
Mg	0.540	0.851	0.293	0.743	0.594	0.745
Fe	0.015	0.019	0.008	0.036	0.017	0.020
Ca	0.018	0.006	0.029	0.039	0.009	0.006
Mn	0.003	0	0.004	0.004	0	0.004
Κ	1.257	1.397	1.014	0.746	1.160	1.075
Na	0.323	0.137	0.103	0.107	0.053	0.108
Cr	0.009	0.001	0	0.003	0.003	0
0	22.000	22.000	22.000	22.000	22.000	22.000
Cation						
Total	13.798	13.812	13.431	13.288	13.468	13.530
Total	35.798	35.812	35.431	35.288	35.468	35.530

Muscovite from Pentelikon (22 oxygens)

Weight %						
Sample	P85-5 15	P85-5 16	P85-6 1	P85-6 10	P85-6 13	P85-616
SiO ₂	46.690	51.340	49.970	50.700	50.260	51.090
TiO ₂	0.089	0.043	0.057	0.186	0.058	0.058
Al_2O_3	35.810	31.180	31.750	34.340	28.400	32.990
MgO	1.022	3.780	3.140	2.849	4.370	3.550
FeO	0.073	0.189	0.094	0.123	0.225	0.196
CaO	0.344	0.076	0.536	0.525	0.389	0.355
MnO	0.071	0	0.035	0.027	0.027	0.027
K20	6.400	6.120	6.140	7.460	9.180	5.690
Na2O	0.249	0.363	0.346	0.467	0.230	0.419
Cr2O3	0.074	0.062	0	0	0.124	0.012
Total	90.820	93.140	92.080	96.670	93.250	94.390
Atomic Pr	oportions					
Si	6.293	6.720	6.632	6.465	6.735	6.593
Ti	0.009	0.004	0.006	0.018	0.006	0.006
Al	5.687	4.811	4.965	5.161	4.485	5.017
Mg	0.205	0.737	0.622	0.542	0.873	0.683
Fe	0.008	0.021	0.011	0.013	0.025	0.021
Ca	0.050	0.011	0.076	0.072	0.056	0.049
Mn	0.008	0	0.004	0.003	0.003	0.003
Κ	1.100	1.021	1.040	1.213	1.569	0.936
Na	0.065	0.092	0.089	0.116	0.060	0.105
Cr	0.008	0.006	0	0	0.013	0.001
0	22.000	22.000	22.000	22.000	22.000	22.000
Cation						
Total	13.435	13.424	13.446	13.600	13.823	13.413
Total	35.435	35.424	35.446	35.600	35.823	35.413

Muscovite from Pentelikon (continued) (22 oxygens)

Weight %	⁄0					
Sample	P85 7 1	P85 7 2	P85 7 6	P85 7 15	P85 8 3	P85 8 5
SiO ₂	47.600	49.840	50.440	49.860	49.430	51.140
TiO ₂	0.286	0.332	0.163	0.145	0.090	0.054
Al_2O_3	35.850	30.860	29.370	30.790	33.070	29.580
MgO	1.899	3.550	4.340	4.090	3.180	4.610
FeO	0.092	0.014	0.163	0.092	0.284	0.391
CaO	0.301	0.368	0.320	0.385	0.133	0.296
MnO	0.043	0	0.017	0.043	0	0.052
K ₂ O	8.150	7.670	5.930	7.890	5.500	6.120
Na ₂ O	0.361	0.266	0.198	0.444	1.055	0.475
Cr ₂ O ₃	0.012	0.049	0.037	0.110	0	0.024
Total	94.590	92.950	90.970	93.860	92.740	92.750
Atomic I	Proportions					
Si	6.239	6.619	6.765	6.585	6.507	6.753
Ti	0.028	0.033	0.017	0.014	0.009	0.006
Al	5.539	4.831	4.643	4.792	5.132	4.604
Mg	0.371	0.702	0.867	0.806	0.624	0.908
Fe	0.010	0.001	0.018	0.010	0.031	0.043
Ca	0.042	0.052	0.046	0.055	0.019	0.042
Mn	0.005	0	0.002	0.005	0	0.006
Κ	1.363	1.300	1.015	1.329	0.924	1.031
Na	0.092	0.069	0.052	0.114	0.270	0.121
Cr	0.001	0.005	0.004	0.011	0	0.003
0	22.000	22.000	22.000	22.000	22.000	22.000
Cation						
Total	13.691	13.614	13.427	13.721	13.515	13.515
Total	35.691	35.614	35.427	35.721	35.515	35.515

Muscovite from Pentelikon (continued, 2) (22 oxygens)

Weight %				
Sample	P85 8 10	P85 9 2	P85 10 8	P85 10 10
SiO ₂	51.960	48.390	50.350	51.250
TiO ₂	0.106	0.149	0.092	0.130
$A_{l2}O_3$	27.070	32.280	30.020	27.960
MgO	4.830	2.772	4.180	4.550
FeO	0.390	0.121	0	0.050
CaO	0.343	0.336	0.745	0.186
MnO	0	0.051	0	0
K ₂ O	8.190	7.720	7.480	6.170
Na ₂ O	0.143	0.259	0.503	0.422
Cr_2O_3	0	0.012	0.122	0
Total	93.020	92.080	93.490	90.720
Atomic Pro	portions			
Si	6.920	6.496	6.660	6.896
Ti	0.011	0.015	0.009	0.013
Al	4.249	5.107	4.679	4.434
Mg	0.958	0.554	0.824	0.913
Fe	0.043	0.014	0	0.006
Ca	0.049	0.048	0.106	0.027
Mn	0	0.006	0	0
Κ	1.391	1.322	1.261	1.060
Na	0.037	0.067	0.129	0.110
Cr	0	0.001	0.013	0
0	22.000	22.000	22.000	22.000
Cation				
Total	13.658	13.629	13.680	13.457
Total	35.658	35.629	35.680	35.457

Muscovite from Pentelikon (continued, 3) (22 oxygens)

Weight %			
Sample	C4.4 -5	C 5.2 2	C 2.7 5
SiO ₂	47.110	48.750	50.820
TiO ₂	0.011	0	0.109
Al_2O_3	29.730	35.720	32.770
MgO	1.966	0.982	3.750
FeO	0.035	0.114	0.043
CaO	0.489	0.676	0.497
MnO	0	0.035	0.009
K ₂ O	5.290	6.510	5.790
Na ₂ O	0.056	0.172	0.280
Cr_2O_3	0.467	1.462	0.346
Total	85.150	94.420	94.410
Atomic Pro	portions		
Si	6.719	6.346	6.566
Ti	0.001	0	0.011
Al	4.997	5.480	4.990
Mg	0.418	0.190	0.721
Fe	0.004	0.012	0.005
Ca	0.075	0.094	0.069
Mn	0	0.004	0.001
Κ	0.962	1.080	0.954
Na	0.015	0.044	0.070
Cr	0.053	0.150	0.035
0	22.000	22.000	22.000
Cation			
Total	13.244	13.402	13.424
Total	35.244	35.402	35.424

Muscovite from Proconnesos A (continued, 4) (22 oxygens)

Muscovite from Proconnesos B

Weight %		
	Possible parag	onite
Sample	Proc-14 7-3	Proc-9 4
SiO ₂	63.460	42.700
TiO ₂	0.013	0.072
Al_2O_3	22.760	27.810
MgO	0	3.250
FeO	0.014	0.007
CaO	3.140	0.337
MnO	0	0
K ₂ O	0.043	4.460
Na ₂ O	4.440	1.907
Cr_2O_3	0	0
Total	93.880	80.540
Atomic Prop	ortions	
Si	7.982	6.498
Ti	0.001	0.008
Al	3.374	4.987
Mg	0	0.737
Fe	0.001	0.001
Ca	0.424	0.055
Mn	0	0
Κ	0.007	0.865
Na	1.084	0.562
Cr	0	0
0	22.000	22.000
Cation		
Total	12.874	13.713
Total	34.874	35.713

Phlogopite from	Proconnesos B
-----------------	---------------

Weight %					
Sample	Proc-2 (1)	Proc-2 (2)	Proc-8	Proc-14	Proc-9
SiO ₂	39.03	40.46	42.04	39.96	41.27
TiO ₂	0.189	0.263	0.005	0.34	0.096
$A_{12}O_3$	21.48	22.13	13.07	20.67	16.07
MgO	24.61	24.35	28.05	24.61	27
FeO	0.127	0.056	0	0.086	0
CaO	0.172	0.199	1.083	0.282	0.23
MnO	0	0	0.044	0.026	0
K ₂ O	6.76	7.57	8.49	8.9	7.87
Na ₂ O	0.741	1.031	0.976	0.426	1.096
Cr ₂ O ₃	0.229	0.097	0.095	0.119	0.193
Total	93.33	96.16	93.86	95.42	93.82
Atomic Prop	portions				
a 1	D 0 (1)	\mathbf{D} \mathbf{O}		D 14	
Sample	Proc-2 (1)	Proc-2 (2)	Proc-8	Proc-14	Proc-9
Sample Si	Proc-2 (1) 5.414	Proc-2 (2) 4.28	Proc-8 5.903	Proc-14 5.484	Proc-9 5.749
Sample Si Ti	Proc-2 (1) 5.414 0.02	Proc-2 (2) 4.28 0.006	Proc-8 5.903 0.001	Proc-14 5.484 0.035	Proc-9 5.749 0.01
Sample Si Ti Al	Proc-2 (1) 5.414 0.02 3.513	Proc-2 (2) 4.28 0.006 5.084	Proc-8 5.903 0.001 2.163	Proc-14 5.484 0.035 3.344	Proc-9 5.749 0.01 2.64
Sample Si Ti Al Mg	Proc-2 (1) 5.414 0.02 3.513 5.088	Proc-2 (2) 4.28 0.006 5.084 5.547	Proc-8 5.903 0.001 2.163 5.87	Proc-14 5.484 0.035 3.344 5.036	Proc-9 5.749 0.01 2.64 5.608
Sample Si Ti Al Mg Fe	Proc-2 (1) 5.414 0.02 3.513 5.088 0.015	Proc-2 (2) 4.28 0.006 5.084 5.547 0.001	Proc-8 5.903 0.001 2.163 5.87 0	Proc-14 5.484 0.035 3.344 5.036 0.01	Proc-9 5.749 0.01 2.64 5.608 0
Sample Si Ti Al Mg Fe Ca	Proc-2 (1) 5.414 0.02 3.513 5.088 0.015 0.026	Proc-2 (2) 4.28 0.006 5.084 5.547 0.001 0.059	Proc-8 5.903 0.001 2.163 5.87 0 0.163	Proc-14 5.484 0.035 3.344 5.036 0.01 0.041	Proc-9 5.749 0.01 2.64 5.608 0 0.034
Sample Si Ti Al Mg Fe Ca Mn	Proc-2 (1) 5.414 0.02 3.513 5.088 0.015 0.026 0	Proc-2 (2) 4.28 0.006 5.084 5.547 0.001 0.059 0.01	Proc-8 5.903 0.001 2.163 5.87 0 0.163 0.005	Proc-14 5.484 0.035 3.344 5.036 0.01 0.041 0.003	Proc-9 5.749 0.01 2.64 5.608 0 0.034 0
Sample Si Ti Al Mg Fe Ca Mn K	Proc-2 (1) 5.414 0.02 3.513 5.088 0.015 0.026 0 1.196	Proc-2 (2) 4.28 0.006 5.084 5.547 0.001 0.059 0.01 0.061	Proc-8 5.903 0.001 2.163 5.87 0 0.163 0.005 1.521	Proc-14 5.484 0.035 3.344 5.036 0.01 0.041 0.003 1.558	Proc-9 5.749 0.01 2.64 5.608 0 0.034 0 1.398
Sample Si Ti Al Mg Fe Ca Mn K Na	Proc-2 (1) 5.414 0.02 3.513 5.088 0.015 0.026 0 1.196 0.199	Proc-2 (2) 4.28 0.006 5.084 5.547 0.001 0.059 0.01 0.061 0.26	Proc-8 5.903 0.001 2.163 5.87 0 0.163 0.005 1.521 0.266	Proc-14 5.484 0.035 3.344 5.036 0.01 0.041 0.003 1.558 0.113	Proc-9 5.749 0.01 2.64 5.608 0 0.034 0 1.398 0.296
Sample Si Ti Al Mg Fe Ca Mn K Na Cr	Proc-2 (1) 5.414 0.02 3.513 5.088 0.015 0.026 0 1.196 0.199 0.025	Proc-2 (2) 4.28 0.006 5.084 5.547 0.001 0.059 0.01 0.061 0.26 0.016	Proc-8 5.903 0.001 2.163 5.87 0 0.163 0.005 1.521 0.266 0.011	Proc-14 5.484 0.035 3.344 5.036 0.01 0.041 0.003 1.558 0.113 0.013	Proc-9 5.749 0.01 2.64 5.608 0 0.034 0 1.398 0.296 0.021
Sample Si Ti Al Mg Fe Ca Mn K Na Cr O	Proc-2 (1) 5.414 0.02 3.513 5.088 0.015 0.026 0 1.196 0.199 0.025 22	Proc-2 (2) 4.28 0.006 5.084 5.547 0.001 0.059 0.01 0.061 0.26 0.016 22	Proc-8 5.903 0.001 2.163 5.87 0 0.163 0.005 1.521 0.266 0.011 22	Proc-14 5.484 0.035 3.344 5.036 0.01 0.041 0.003 1.558 0.113 0.013 22	Proc-9 5.749 0.01 2.64 5.608 0 0.034 0 1.398 0.296 0.021 22
Sample Si Ti Al Mg Fe Ca Mn K Na Cr O Cation	Proc-2 (1) 5.414 0.02 3.513 5.088 0.015 0.026 0 1.196 0.199 0.025 22 15.495	Proc-2 (2) 4.28 0.006 5.084 5.547 0.001 0.059 0.01 0.061 0.26 0.016 22 15.323	Proc-8 5.903 0.001 2.163 5.87 0 0.163 0.005 1.521 0.266 0.011 22 15.902	Proc-14 5.484 0.035 3.344 5.036 0.01 0.041 0.003 1.558 0.113 0.013 22 15.638	Proc-9 5.749 0.01 2.64 5.608 0 0.034 0 1.398 0.296 0.021 22 15.756
Sample Si Ti Al Mg Fe Ca Mn K Na Cr O Cation Total	Proc-2 (1) 5.414 0.02 3.513 5.088 0.015 0.026 0 1.196 0.199 0.025 22 15.495	Proc-2 (2) 4.28 0.006 5.084 5.547 0.001 0.059 0.01 0.061 0.26 0.016 22 15.323	Proc-8 5.903 0.001 2.163 5.87 0 0.163 0.005 1.521 0.266 0.011 22 15.902	Proc-14 5.484 0.035 3.344 5.036 0.01 0.041 0.003 1.558 0.113 0.013 22 15.638	Proc-9 5.749 0.01 2.64 5.608 0 0.034 0 1.398 0.296 0.021 22 15.756

Margarite from Proconnesos B

Weight %					
Sample	Proc-5	Proc-5			
SiO ₂	30.81	35.49			
TiO ₂	0.059	0.012			
Al_2O_3	52.18	43.81			
MgO	0.411	1.003			
FeO	0.042	0.049			
CaO	12.28	8.7			
MnO	0.009	0			
K ₂ O	0.156	2.015			
Na ₂ O	0.912	0.708			
Cr_2O_3	0.398	0.205			
Total	97.25	91.99			
Atomia Proportions					
Sample	Proc-5	Proc-5			
Si	4 005	4 833			
Ti	0.006	0.001			
A1	7 996	7 033			
Mg	0.08	0 204			
Fe	0 005	0.006			
Ca	1.711	1.27			
Mn	0.001	0			
Κ	0.026	0.35			
Na	0.23	0.187			
Cr	0.041	0.022			
0	22	22			
Cation	14 009	12 009			
Total	14.098	15.908			
Total	36.098	35.908			
Paragonite from Pentelikon

Sample	P85-8
SiO ₂	46.23
TiO ₂	0.019
Al_2O_3	39.95
MgO	0.53
FeO	0.149
CaO	0.417
MnO	0
K ₂ 0	0.817
Na ₂ O	5.59
Cr ₂ O ₃	0.085
Total	93.79
Atomic Proportions	
Si	5.965
Ti	0.002
Al	6.075
Mg	0.102
Fe	0.016
Ca	0.058
Mn	0
Κ	0.135
Na	1.398
Cr	0.009
0	22
Cation	13.757
Total	25.757
Total	35.757

APPENDIX B:

SAMPLE IMAGES

HAND SAMPLES

Pentelikon





Proconnesos A



Proconnesos B







BACK SCATTERED ELECTRON IMAGES - PHOTOMICROGRAPHS (PM)

Pentelikon



BEI P85-5

PM.1. Top: Muscovite (dark, micaceous) and apatite (light) in calcite matrix. Bottom: Muscovite (dark, micaceous) and pyrite (bright, 5-sided) in calcite matrix.



BEI P85-5



BEI P-85 6

PM.2. Top: Quartz (center) in calcite matrix. Bottom: Scattered apatites (light) in calcite matrix.



BEI P85-3 5



PM.3. Top: Muscovite in calcite matrix. Bottom: Dolomite (dark) with apatite (light) and very small (~5 microns) pyrite grains.



BEI P85-8



BEI P85-9

PM.4. Top: Muscovite (dark, micaceous) apatite (light), and small pyrite grains (bright) in calcite matrix. Bottom: Dolomite (center) in calcite matrix.

Proconnesos A







BEI C1.18 sulfide1



BEI C1.18





BEI C5b.13



PM.7. Top and Bottom: Apatites in calcite matrix.



BEI C6.4





BEI C12.3







Proconnesos B



BEI Proc-1



BEI Proc-1

PM.10. Top: Pyrite grain in calcite matrix. Bottom: Phlogopite with dolomite in calcite matrix.



BEI Proc-1



BEI Proc-1





BEI Proc-1



BEI Proc-4a

PM.12. Top: Goethite in calcite matrix. Bottom: Pyrite in calcite matrix.



BEI Proc-4a



BEI Proc-4a

PM.13. Top: Apatite in calcite matrix. Bottom: pyrite in calcite matrix.



BEI Proc-4a



BEI Proc-4a

PM.14. Top: Apatite in calcite matrix. Bottom: Pyrite in calcite matrix.



BEI Proc-4a



BEI Proc-6

PM.15. Top: Apatite and bright pyrite grains in calcite matrix. Bottom: Rutile in calcite matrix.



BEI Proc-6



BEI Proc-6

PM.16. Top: Apatite in calcite matrix. Bottom: Pyrite in calcite matrix.



BEI Proc-6



BEI Proc-6

PM.17. Top: Sphalerite grain in calcite matrix (although no accompanying analysis). Bottom: Rutile in calcite matrix.

APPENDIX C

STATISTICAL METHODS

R COMMANDS

Nonmetric Multidimensional Scaling Multivariate Analysis

This NMDS analyzed maximum calcite grain size, stable isotopes, and accessory minerals from each quarry together.

```
library(vegan)
marble <- read.csv("untransmarble.csv",header=TRUE,sep=",",row.names=1)
marble
```

marblescaled <- decostand(marble, "range")</pre>

```
marble.mds <- metaMDS(marblescaled, distance="euclidean", k=3, trymax=100, autotransform=FALSE)
```

names(marble.mds)

marble.mds

dev.new()
plot(marble.mds)

```
dev.new()
plot(marble.mds, type="t", display=c("species"))
```

QsampleScores <- marble.mds\$points

ProconnesosA <- grep("xC", rownames(marblescaled))</pre>

ProconnesosB <- grep("Proc",rownames(marblescaled))</pre>

Pentelikon <- grep("P85-",rownames(marblescaled))

#Axis 1 and 2 dev.new() plot(QsampleScores[,1], QsampleScores[,2],xlab="NMDS 1", ylab="NMDS 2", las=1, type="n")

points(QsampleScores[ProconnesosA, 1], QsampleScores[ProconnesosA, 2], col="limegreen", pch=16)

points(QsampleScores[ProconnesosB, 1], QsampleScores[ProconnesosB, 2], col="blue", pch=16)

points(QsampleScores[Pentelikon, 1], QsampleScores[Pentelikon, 2], col="chocolate3", pch=16)

legend(-1.5, .7, legend=c("Pentelikon", "ProconnesosA", "ProconnesosB"), pch=c(16,16,16), col=c("chocolate3", "limegreen", "blue"))

#Axis 1 and 3
dev.new()
plot(QsampleScores[,1], QsampleScores[,3],xlab="NMDS 1", ylab="NMDS 3", las=1,
type="n")

points(QsampleScores[ProconnesosA, 1], QsampleScores[ProconnesosA, 3], col="limegreen", pch=16)

points(QsampleScores[ProconnesosB, 1], QsampleScores[ProconnesosB, 3], col="blue", pch=16)

points(QsampleScores[Pentelikon, 1], QsampleScores[Pentelikon, 3], col="chocolate3", pch=16)

legend(-1.5, 1.0, legend=c("Pentelikon", "ProconnesosA", "ProconnesosB"), pch=c(16,16,16), col=c("chocolate3", "limegreen", "blue"))

dev.new()
plot(QsampleScores[,1], QsampleScores[,3],xlab="NMDS 1", ylab="NMDS 3", las=1,
type="n",xlim=c(-4,4), ylim=c(-2,2))
text(marble.mds, display=c("species"), col="red", cex=.7)

#Axis 2 and 3
dev.new()
plot(QsampleScores[,2], QsampleScores[,3],xlab="NMDS 2", ylab="NMDS 3", las=1,
type="n")

points(QsampleScores[ProconnesosA, 2], QsampleScores[ProconnesosA, 3], col="limegreen", pch=16)

points(QsampleScores[ProconnesosB, 2], QsampleScores[ProconnesosB, 3], col="blue", pch=16) points(QsampleScores[Pentelikon, 2], QsampleScores[Pentelikon, 3], col="chocolate3", pch=16)

legend(-.5, 1.0, legend=c("Pentelikon", "ProconnesosA", "ProconnesosB"), pch=c(16,16,16), col=c("chocolate3", "limegreen", "blue"))

dev.new() plot(QsampleScores[,2], QsampleScores[,3],xlab="NMDS 2", ylab="NMDS 3", las=1, type="n", xlim=c(-4,4), ylim=c(-2,2)) text(marble.mds, display=c("species"), col="red",cex=.7)