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Isotopic Geochemistry Applied on Marble Samples of Kythnos Island in Greece

Petros Karalis
National Centre for Scientific Research (N.C.S.R.)

Elissavet Dotsika
National Centre for Scientific Research (N.C.S.R).

Alexandros Mazarakis -Ainian
University of Thessaly

Evaggelia Kolofotia
University of Thessaly

Iakovos Raptis
Centre for Research and Technology Hellas

Anastasia Electra Poutouki
University of Pavia

Anastasios Drosou
Centre for Research and Technology Hellas

Brunella Raco
Institute of Geoscience and Earth Recourses-CNR

Panagiotis Leandros Poutoukis
University of Patras

Dafni Kyropoulou
National Centre for Scientific Research (N.C.S.R.)

Dimitrios Tzovaras
Centre for Research and Technology Hellas

Abstract: The present contribution aims to study the isotopic characteristics of various marbles from the archaeological site of Kythnos Island in the Cyclades, Greece. The database of this research is very important and useful in the conservation and restoration of monuments as these tasks should aim at preserving their material status and their authenticity. The characterization of marble taken from this site contributes significantly to the determination of the origin of the raw materials used in monuments in the wider area of the Aegean Sea. Samples were obtained mainly from the inner layers of the findings, which were not exposed to the weather conditions and without remarkable traces or signs of severe corrosion. The methods that were used required very small quantities of material. The measurements are considered almost non-destructive and based on isotopic geochemistry.

Keywords: Oxygen isotopes, Carbon isotopes, Marbles, Kythnos, Tinos, Raw materials

Introduction

An island with a long history and particular archaeological importance is Kythnos, which is situated between Kea and Serifos. The ancient city of "Vryokastro", on the island's northwest shore, was a fortified polis that was continually inhabited from the first millennium B.C. to the sixth or seventh century A.D (Fig 1). The remains of the ancient city occupy an area of approximately 28,5 hectares, including the small islet of Vryokastraki, which was connected to the shore in antiquity by a narrow isthmus. During the systematic investigations that have been in progress since 1990 (survey and subsequent excavations) numerous finds and several ancient structures, such as temples, public buildings, houses, port facilities, burial monuments, etc., have been brought to light. These discoveries have provided valuable insights into the urban planning of the city and the sociopolitical and economic development of the ancient community.

Regarding the construction of the buildings, the island's ground is composed of various types of crystalline slates (metamorphic rock) with intervening marble horizons. Slate and limestone appear to have been used extensively for the buildings of the ancient city, and the discovery of marble fragments of architectural elements from the sanctuaries of the Upper Town confirms its parallel use. Several samples of marble were chosen in order to identify the marble's provenance (Fig.2).

During the field inspection of the intramural sanctuaries located on the Middle Plateau, a deliberate selection of marble samples was made. These samples encompassed both structural elements derived from the buildings and structural components originating from various artifacts, scattered throughout the archaeological site. More specifically, the chosen specimens were procured from the Upper Town precinct, housing the sanctuaries of Asklepios, Aphrodite, and the Samothracian Gods (Mazarakis Ainian, 2019), as well as from the Archaic sanctuary dedicated to Artemis and Apollo (Mazarakis Ainian 2017, 2019). Furthermore, the catalog of marble samples includes a subset originating from sculptures from the ancient harbor. Among these pieces, one find is a Hermaic stele, dating to the 2nd century A.D., subsequently reused as "spolia" during the Roman era, eventually being incorporated into the now-submerged fortification wall of Mandraki Bay. Additionally, there is a statue featuring a seated male figure, identified as Menander, who is credited as the founder of "New Comedy".

Figure 1. Aerial photograph of Vryokastro

In order to identify the origin of marble artifacts and understand the characteristics of marble, samples from the Kythnos quarries in Greece were analyzed using a variety of techniques. These included stable isotope analysis of carbonates (^{13}C, ^{18}O), SEM-EDXA analysis, and optical microscopy. Through these methods, information regarding the origin and texture of the marble used in the production of the artifacts was obtained (see Fig. 2).

Materials and Methods

We studied marble material from the island of Kythnos and of many islands in Cyclades. Samples were collected from Cyclades islands (Andros, Naxos, Syros, Sifnos, Paros and Tinos). In the current work, analytical results from samples extracted from Tino's quarries were presented. On Tinos, most of the island is a part of the Cycladic blueschist unit, which is represented by a marble–schist sequence. The whole succession can be subdivided by means of three mappable marble horizons, m3, m2 and m1 (Melidonis, 1980). From Tinos, we selected samples that represent the three major marble horizons m3, m2 and m1 (m1 calcte marble and M1 dolomite marble). We report petrographic characteristics and results of C, O isotopes analyses. From Tinos, the samples came from the three marble horizons M3, M2, and M1 and the fossil-bearing lowermost dolomite (Melidonis, 1980). The calcite marbles show all color gradations between white and grey, in alternating layers. The dolomites from the Panormos area on Tinos (> 100 m in thickness) are poorly bedded massive rocks. Their color is less white than the calcite marbles and shows a weak yellowish tint. We also collect samples from archaeological marble pieces (D2-D3-D4) from Kythnos. The samples come from buildings 1 and 2.

Figure 2. Marble samples

Table 1. SEM results identify the mineralogical structure of each material.

Samples	Mg	Al	Si	P	S	K	Ca	Fe	Marble
D2									
Max.	44,99	4,46	8,75	1,62	3,41	2,48	100	11,52	Calcite, with dolomite (Mg)
Min.	0,58	0,38	1,02	1,08	0,01	1,04	49,34	2,8	
D3									
Max.	2,78	28,42	47,88		1,38	16,71	99,04	3,95	Calcite
Min.	-1,13	-0,54	-0,74		-1,1	-0,43	9,23	-0,59	
D4									
Max.	12,32	0,69	1,69		1,55	0,97	0,97	0,99	Calcite, with Mg
Min.	0,75	-0,49	-1,38		-0,59	-0,25	-0,25	-1	

Based on that, the isotopic measurements ($\delta^{13}C$, $\delta^{18}O$) were used to determine the origin of the carbonate material. The isotopic analyses took place in the Stable Isotope Unit of the Institute of Materials Science (NCSR Demokritos) on a Thermo Delta V Plus IRMS equipped with GasBenchII. In order to distinguish the material of the tesserae in more detail, the maximum grain size (MGS) of each was determined by optical microscopy.

Results – Discussion

The full range of grain sizes and isotopic signatures that occur in a lot of different quarries has been measured and presented. In a $\delta^{13}C$ *versus* $\delta^{18}O$ diagram, the fields corresponding to all known ancient quarries from Penteli, Cyclades (especially Naxos, Keros, Paros), Thassos and Asia Minor (Ephesos, Proconnesus, Dokimeion, Aphrodisias, Usak) are reported (Moens et al., 1992a, Moens et al., 1992b, Moens, 2003). The plots

representing the analyzed samples are also shown on the same diagram. In the same samples we locate and isotopic values from Tinos island. This diagram indicates the origin of the carbonate material of the artifacts from each of the ancient monuments (Fig.3). In cases where the samples plot on overlapping areas, a further study is applied, using the maximum grain size (MGS) of the material (Polikreti & Maniatis, 2002; De Nuccio et al., 2000; Attanasio, 2003).

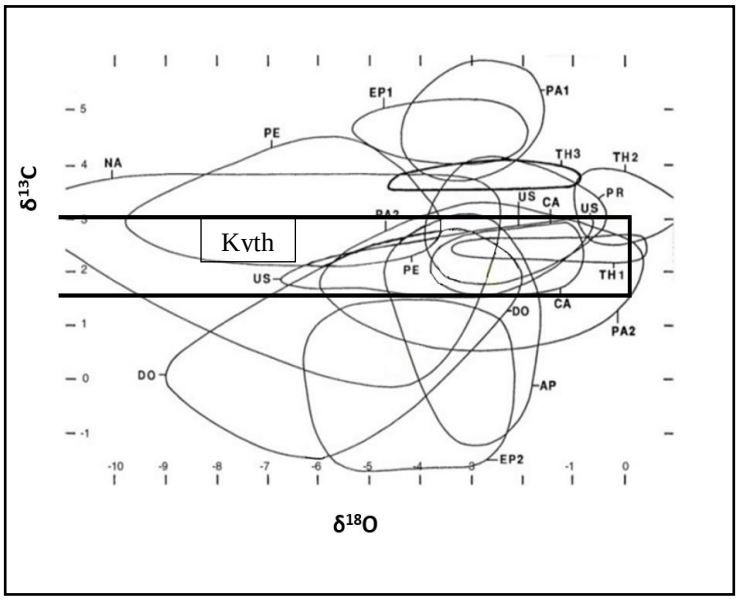

Figure 3. Isotopic signatures (vs PDB, ‰) of the marble pieces plotted against the quarry field parameters of most of the known ancient marble quarries (Moens, 2003). PE = Penteli, NA = Naxos, EP1 = Ephesos-1, EP2 = Ephesos-2, DO = Dokimeion, AP = Aphrodisias, US = Usak, CA = Carrara, PR = Proconnesus, PA1 = Paros-1, PA2 = Paros-2, TH1 = Thassos-1 (calcitic), TH2 = Thassos-2 (calcitic), TH3 = Thassos-3 (dolomitic).

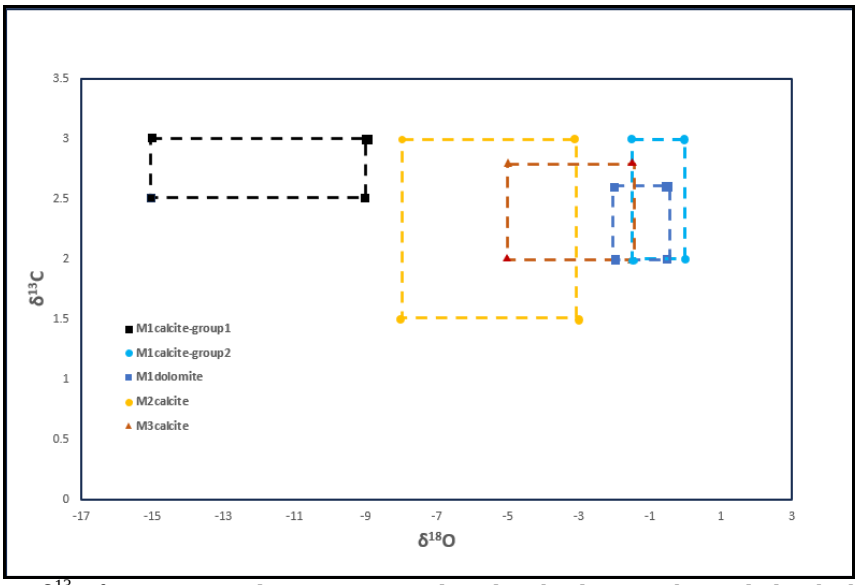

Figure 4. $\delta^{18}O$ vs $\delta^{13}C$ for Tinos samples quarries are plotted in the diagram that includes the known ancient marble quarries.

Marbles from the M1 horizon (Calcite marble, Tinos) present variable MgO contents (< 7 wt %; Mg/Ca range between 0 and 0,6), due to different contents of dolomite. Calcite marbles from M1 present Mg/Ca that range between 0 and 0,12, while dolomitic marbles from M1 present Mg/Ca that range between 0,4 and 0,6. Marbles from M2 and M3 horizons have MgO concentrations lower of 1.0 wt % and Mg/Ca range between 0 and 0,013 and 0 with 0,03 respectivelly. Table 1 demonstrates the chemical analysis of marbles from Kythnos island. SEM analysis of the archaeological samples (from Kythos) indicated that some pieces are not marbles, thus they were not considered suitable for isotopic fingerprinting. The rest samples (D2-D3-D4) were analyzed (Table 1).

Marbles from M3 horizon, present $\delta^{18}O$ that range between −5 ‰ and −1.5 ‰. Kythnos M2 marbles present $\delta^{18}O$ values varying between −8 ‰ and −3.1 ‰. Calcite marbles from the M1 horizon, present $\delta^{18}O$ that range between −1.5 ‰ and 0 ‰, while dolomitic marbles from the M1 horizon, present $\delta^{18}O$ that range between −2 ‰ and -0.5 ‰, $\delta^{13}C$ values of most samples from M1, M2, M3 horizons fall within the range of 1.5–3 ‰. Marbles from Kythnos display the highest variability in $\delta^{18}O$ with values between −15.1 ‰ and +0 ‰. While, the $\delta^{13}C$ of marbles from Kythnos present the same values opos the samples from M1, M2, M3 Tinos horizons. So, based on δ^{18} O and δ^{13} C values, the marbles from Tinos quarries can be separated into four groups, according to the different M1, M2, M3 horizons (Fig. 4). According to the Mg/Ca ratio the archaeological samples probably come from M1 and M2 horizons. The isotopic values (δ^{18} O and $\delta^{13}C$ values) of samples from Kythnos quarries are plotted in the diagram that includes the known ancient marble quarries (Figs3 and 4).

Conclusion

After analyzing the δ^{18} O and $\delta^{13}C$ values, the marbles from Tinos quarries (M1 and M2 horizons) were categorized into four groups based on the different M1, M2, and M3 horizons. The archaeological samples from Kythnos underwent elemental and microscopic analysis and some pieces were found not to be marbles, therefore they were not suitable for isotopic fingerprinting. The remaining samples (D2-D3-D4) were analyzed showing that the Mg/Ca ratio suggests that the archaeological samples most likely originated from the M1 and M2 horizons. Furthermore, the δ^{18} O and δ^{13} C values from Tino's marbles were located on a diagram that includes known ancient marble quarries.

Recommendations

In the continuation of this study, the residual stress effect together with the geometry effect can be evaluated. This experiment would be more appropriate because HFMI does not only perform geometry improving. The relationship between residual stress and geometry can be direct or inverse. A test bench for residual stress measurement will make the results more realistic and consistent. In addition, outputs in terms of life can be obtained with a fatigue test bench.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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Author Information

Petros Karalis
Stable Isotope and Radiocarbon Unit, Institute of Nanoscience and Nanotechnology, National Centre for Scientific Research (N.C.S.R.) "Demokritos", 15341, Attiki, Greece

Elissavet Dotsika
Stable Isotope and Radiocarbon Unit, Institute of Nanoscience and Nanotechnology, National Centre for Scientific Research (N.C.S.R.) "Demokritos", 15341, Attiki, Greece
Contacting author e-mail: e.dotsika@inn.demokritos.gr

Alexandros Mazarakis Ainian
Department of History, Archaeology and Social Anthropology, University of Thessaly, 38221, Volos, Greece

Evaggelia Kolofotia
Department of History, Archaeology and Social Anthropology, University of Thessaly, 38221, Volos, Greece

Iakovos Raptis
Information Technologies Institute, Centre for Research and Technology Hellas, 57001, Thessaloniki, Greece

Anastasia Electra Poutouki
Department of Pharmaceutical Sciences,
University of Pavia, 27100, Pavia, Italy

Anastasios Drosou
Information Technologies Institute, Centre for Research and Technology Hellas, 57001, Thessaloniki, Greece

Brunella Raco
Institute of Geoscience and Earth Recourses-CNR, Italy

Panagiotis-Leandros Poutoukis
Department of Physics, University of Patras, 26504, Patra, Greece

Dafni Kyropoulou
Stable Isotope and Radiocarbon Unit, Institute of Nanoscience and Nanotechnology, National Centre for Scientific Research (N.C.S.R.) "Demokritos", 15341, Attiki, Greece

Dimitrios Tzovaras
Information Technologies Institute, Centre for Research and Technology Hellas, 57001, Thessaloniki, Greece

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