Reports

Greek Marbles: Determination of Provenance by Isotopic Analysis

Abstract. *A study has been made of carbon-13 and oxygen-18 variations in Greek marbles from the ancient quarry localities of Naxos, Paros, Mount Hymettus, and Mount Pentelikon. Parian, Hymettian, and Pentelic marbles can be clearly distinguished by the isotopic relationships; Naxian marbles fall into two groups characterized by different oxygen-18/oxygen-16 ratios. Ten archeological samples were also analyzed; the isotopic data indicate that the "Theseion" is made of Pentelic marble and a block in the Treasury of Siphnos at Delphi is probably Parian marble.*

The problem of identifying the locality from which a given specimen of Greek marble was quarried has been studied for almost 100 years (*1*). In addition to the obvious applications such as detection of copies and forgeries (*2*, p. 189) there are more general problems of great importance which could be solved by a method capable of uniquely assigning a piece of marble to its place of origin. The major quarrying localities in use from preclassical to Hellenistic and Roman periods shifted successively from the Cycladic islands of Naxos, and later Paros, to Mount Pentelikon on the Attic mainland, and finally during Roman times, to nearby Mount Hymettus (*1*; *2*, p. 137; *3*). Thus in many instances the specification of the provenance of a piece of statuary or a building can be used to date the object from the known periods of quarrying operations in each area (*4*). Finally, there are geological problems at hand such as the question of whether the Pentelic and Hymettian marbles represent two formations or a single formation repeated by folding or faulting (*5*).

Methods applied to Greek marbles for provenance determination in the past include petrographic techniques (*1*, *3*), petrofabric studies (*3*, *6*), and Na and Mn analysis by neutron activation (*7*). Although Herz and Pritchett (*5*) were able to solve a problem of a mismatch of inscription fragments by a foliation study, and Ryback and Nissen (*7*) were able to characterize Marmara and Parian marble as low in Mn, none of these methods has been generally very successful (*8*). Trace element studies suffer inherently from the high variability in concentration (factors of over 100 for Na and Mn) due to highly localized interaction with inclusions and surrounding rocks. On the other hand, petrofabric studies are difficult and time consuming, require relatively large amounts of material, and depend on statistical treatments of what are, in these marbles, rather poorly developed fabrics.

Our approach to this problem was the idea that the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ variations in Greek marbles probably provided the best chance for unique characterization by locality. The isotopes ^{13}C and ^{18}O vary by at least 10 and 20 per mil (1 to 2 percent), respectively, in marbles from different areas (*9*), so that with two isotopes there is a reasonable probability of obtaining some distinctive differences. Moreover, we expected that the very process which originally formed the marbles might well smooth out the variations within a single quarrying area by local isotopic equilibration with fluid phases. In general both these expectations were fulfilled.

We made detailed collections in the four major quarrying areas which provided marble for statuary and building purposes in ancient Greece (*10*). In each area we concentrated our sampling at the sites of ancient quarries, as indicated by old chisel marks, worked faces, grooves, and other evidence. Samples were collected over the maximum extent of each locality and from representative phases, in order to de-

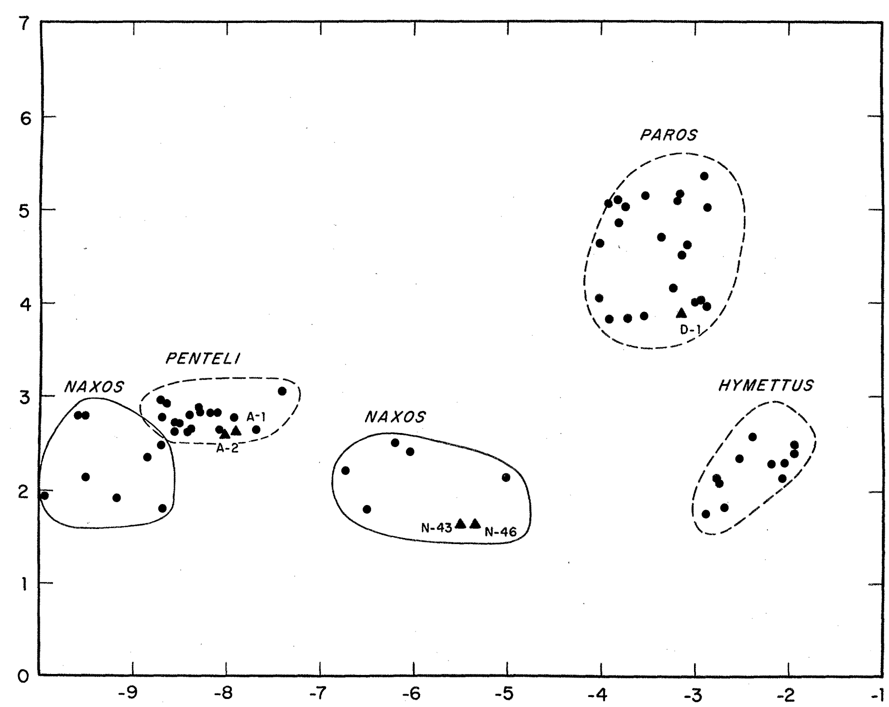

Fig. 1. Carbon-13 and oxygen-18 variations in marble samples from ancient Greek quarries relative to the PDB isotopic standard. Triangles denote some of the archeological samples listed in Table 1.

Table 1. Isotopic analyses of archeological marble samples.

Sample No.	Description	$\delta^{13}C$ (per mil)	$\delta^{18}O$ (per mil)	Probable provenance
A-1	Athens: "Theseion" (Hephaesteion) in the Agora, column on north side	2.63	−7.90	Pentelic
A-2	Athens: basal slab on south side of "Theseion"	2.63	−8.03	Pentelic
D-1	Delphi: carved block lying inside Treasury of Siphnos	3.89	−3.10	Parian
D-2	Delphi: drum of column of the Naxian Sphinx	1.96	−4.15	?
E-1	Epidaurus: carved block (lintel?), 10 m from Tholos	2.01	−1.12	?
E-2	Epidaurus: Corinthian capital next to the "triple circle" of Tholos	2.16	−0.78	?
E-3	Epidaurus: cut slab of white marble, 13 m from Tholos	2.58	−3.96	?
N-43	Naxos: Apollon Gate, Palatia, Naxos Harbour; flake from inside of gate	1.67	−5.51	Naxian
N-46	Naxos: Apollon Gate, large block at foot of hill toward Naxos	1.64	−5.35	Naxian
C-1	Caesarea, Israel: Corinthian capital of grey marble	3.51	−2.64	?

termine the variability in each area. A total of 170 quarry samples and some 20 archeological samples were taken. The marbles studied, in order of age of the workings, were as follows.

Naxian marble, on the island of Naxos in the Cyclades (6th and 7th centuries). The ancient Naxian quarries occur in two main localities, in two formations (*11*). Near Kinidaros, in the central interior, ancient quarries (probably used only locally) occur in the Keramoti marble. On the north point of the island, at Apollon, the ancient quarries are in the Amomaxi marble, which is separated from the older Keramoti marble by Komiaki schist. Each of these ancient sites is marked by the presence of a very large recumbent figure (Kouros), the earliest Greek statuary.

Parian marble, on the Cycladic island of Paros (5th and 6th centuries). The Lychnites marble occurs at Aghias Minas near Marathi, in the interior of the island (*12*). The quarries are underground and are reached by two steeply dipping shafts that follow the bedding. This is the finest statuary marble known.

Pentelic marble, Mount Pentelikon, 18 km northeast of Athens (5th century to Roman era). The ancient quarries begin at the cave of Spilia on the south slope and extend up the mountain. Six ancient and two recent quarries were located and sampled. The white Pentelic marble which was quarried is the "lower marble" of Lepsius (*1*).

Hymettian marble, Mount Hymettus, southeast of Athens, on the western slope (*13*). The marbles are grey, white, and blue, and are the "upper marble" of Lepsius (*1*). Seven ancient quarries were located and sampled.

General descriptions of these marbles are given in the references (*1, 3, 5*). The marbles are often (though not always) distinguishable with high probability in outcrop or fresh hand specimen (Naxian marble is generally coarse grained, Hymettian marble is often grey to blue and banded), but cannot be distinguished with certainty from each other, or from other marbles, in buildings and statuary. Both Pentelic and Hymettian marbles occur on each of these mountains (*1*).

In this initial study a statistical sampling of about 35 percent of the samples was selected for analysis. Further studies, including measurement of trace elements such as Sr and Mg are continuing. However, the isotopic results are so promising that we present them now, in the hope that interested workers will send us marbles from other classical quarry areas and from archeological materials whose place of origin is of interest.

Figure 1 shows the isotopic results on the quarry specimens and some of the archeological samples. The data are given as δ values relative to the PDB isotopic standard (*14*):

$$\delta\,(\text{per mil}) = [(R/R^{+}) - 1] \times 1000$$

where R is the ratio $^{13}C/^{12}C$ or $^{18}O/^{16}O$ and R^{+} is the ratio in the PDB standard. The mass spectrometric methods and calculations have been described (*14*). The analytical precision is $\pm$ 0.05 per mil.

On the ^{13}C-^{18}O diagram, the marbles fall into well-defined groups with the possible exception of certain Naxian and Pentelic varieties. The Parian marbles are unique in having the highest $\delta^{13}C$ values of the Greek specimens and all of the marbles studied by Baertschi (*9*). These marbles resemble algal carbonates and travertines in their high ^{13}C values, and this resemblance together with the high purity leads us to suspect that they originated as a chemical precipitate (*15*).

Pentelic and Naxian marbles are much lower in ^{18}O than Parian and Hymettian marbles, a feature which is generally due to interaction with meteoric waters at elevated temperatures (*9*). The Pentelic marbles are also higher in ^{13}C than almost all of the marbles studied by Baertschi, and the Naxian and Hymettian marbles fall in the upper part of his range. Only the Hymettian marbles fall within the general ^{13}C-^{18}O trend outlined by the marble samples in Baertschi's work. It is noteworthy that the isotopic data clearly confirm Lepsius's conclusion (*1*) that Hymettian and Pentelic marbles ("upper and lower" marbles) are different geological formations.

The Naxian marbles so far studied fall into two groups with respect to $\delta^{18}O$ values. Each of these isotopic subgroups contains samples from both the Naxian localities studied. Lepsius (*1*) noted that there were two types of marble in the vicinity of the Apollon Kouros, one of which closely resembles the roof tiles of the "Old Temple" of the Acropolis and the Temple of Zeus in Olympia. The isotopic data indicate that both these marbles probably outcrop at both Kouros sites on Naxos.

Similar uncertainties in the case of the Attic marbles require further study. Herz and Pritchett (*5*) placed most of the Hymettian quarries in the "lower" or Pentelic formation (which provides the Pentelic marble on Pentelikon). However, the isotopic data show clearly that the two sets of Attic marbles represent quite different formations, and that the quarries we studied on Mount Hymettus are probably in the "upper marble" of Lepsius. The geological relationships at Hymettus are the most complicated of the entire region.

We were unable to obtain permission from U.S. authorities to use the most detailed U.S. Army Map Service maps; thus, we could not resolve this question in the time available.

In Table 1 we list the archeological samples collected for comparison with the quarry results. Figure 1 shows that some success was obtained on these first "unknowns." The "Theseion" of the Athenian Agora (about 450 B.C.) is almost certainly Pentelic marble, at least on the north and south sides. The carved blocks inside the Treasury of Siphnos at Delphi are quite clearly of Parian marble. (The Treasury itself is reputed to be of Siphnian marble.) The isotopic compositions of the rest of these samples do not correspond to any of the ranges so far established for the four areas studied. It is worth noting that two quite different marbles are lying in close proximity to the Tholos (or labyrinth) of Epidaurus.

(In this connection it should be pointed out that the Athenians scatter fragments of Pentelic marble around the Parthenon each winter, in order to provide material for the insatiable pillage by tourists. This marble is from modern quarries and is isotopically distinct from that of the classical quarries. All of the samples in Table 1 are definitely ancient artifacts.)

A single sample of grey marble was collected at Caesarea, Israel, in the belief that it might be Hymettian marble imported by the Romans. However, this appears not to be the case (Table 1).

It appears that the isotopic method for determining the origin of Greek marbles will probably be the most useful of the tests so far devised, especially if used in conjunction with other techniques. Some of the archeological samples in Table 1 fall outside of the isotopic provenances so far delineated, and it is clear that other quarrying areas were used. Thus, coincidence of a sample with one of the isotopic clusters in Fig. 1 is not, in itself, a unique indication of provenance. We hope to establish a variety of geochemical characteristics of these and other marbles. We will welcome samples from areas in which other marbles used by the ancient Greeks were quarried, in order to extend the isotopic method to as many localities as possible (*16*).

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References and Notes

1. R. Lepsius, *Abh. Akad. Wiss. Berlin* (1890); H. S. Washington, *Amer. J. Archaeol.* **11**, 71 (1898).
2. G. M. A. Richter, *The Sculpture and Sculptors of the Greeks* (Yale Univ. Press, New Haven, Conn., 1950).
3. N. Herz, *Trans. N.Y. Acad. Sci. Ser. 2* **17**, 499 (1955); *Amer. J. Sci.* **253**, 299 (1955).
4. Naxian marble (the earliest quarried) could have been used in later times, but Pentelic marble is of better quality and was much more accessible to Athens. Parian marble was always in demand because of its superior luster and grain, but our studies of the underground mine from which the Lychnites marble of Paros was obtained showed that mining stopped because the unfractured Lychnites was totally removed. About 50,000 tons of this beautiful marble was ramped up two narrow shafts dipping 35° before the bed was abandoned.

N. Herz and W. K. Pritchett, *Amer. J. Archaeol.* **57**, 71 (1953). The geology of the Attic marbles is reviewed in this paper.

6. L. E. Weiss, *Amer. J. Sci.* **252**, 641 (1954).
7. L. Rybach and H. U. Nissen, *Radiochem. Methods Anal. Proc. Symp. 1964* **1**, 105 (1965).
8. N. Herz has pointed out to us that most of these studies simply confirm that the Greeks used the purest and most isotopic marbles that could be obtained.
9. P. Baertschi. *Schweiz. Mineral. Petrogr. Mitt.* **37**, 73 (195 H. Craig, *Geochim. Cosmochim. Acta* **3**, 53 (1953).
10. Fieldwork was done during the fall of 1968, supported by a research grant from the University of California at San Diego. We gratefully acknowledge the many kindnesses of the following: Dr. A. Panagos of the University of Athens for many helpful discussions; Dr. E. Vanderpool of the American School of Classical Studies who led us to the Hymettian quarries; and H. Alt, F. Tsanos, and the officers of the Societé Anonyme des Carrieres du Marbre Dionyssos–Pendelis, for most helpful assistance on Mount Pentelikon.
11. A geological map of Naxos is given by I. Papastamatiou, *The Emery of Naxos* (Geological and Geophysical Surveys, Athens, 1951).
12. J. Anastopoulos, "Geological Survey of Lychnites, Paros," stencil report (Institute of Geological Subsurface Research, Athens, 1962). The name "Lychnites" refers to the lamps used underground by the ancient quarry workers.
13. The ancient quarries are on the north bank of Kakorhevma gorge, and are difficult to locate. The gorge runs east to west at the site of the quarries, which are indicated on U.S. Army Map Service Sheet NJ 34-12 (Athinai) at coordinate reference GH 4505. The Acropolis bears N67°W from the easternmost ancient quarry; the radar dome on the opposite bank is S85°E.

H. Craig, *Geochim. Cosmochim. Acta* **12**, 133 (1957). The PDB is a Cretaceous belemnite.

15. The ^{13}C is enriched in carbonate precipitating from solution by escape of CO_2 which is depleted in ^{13}C.
16. A great advantage of the isotopic method is that only 10 to 20 mg of $CaCO_3$ are required for both analyses. We prefer to receive larger samples in order to ensure obtaining a clean unaltered portion for analysis.
17. We thank K. Podvin and J. Brown for performing the isotopic analyses and Professor N. Herz for many helpful discussions. Dr. H. U. Nissen in Zurich was also most helpful. The laboratory work was supported by the National Science Foundation.

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Electrical Conductivity and the Red Shift of Absorption in Olivine and Spinel at High Pressure

Abstract. *Above 100 kilobars the apparent absorption edges (approximately 3 electron volts) of single-crystal and polycrystalline samples of the metastable olivine and stable spinel forms of Fe_2SiO_4 shift rapidly with pressure from the near-ultraviolet into the lower-energy infrared region. Simultaneously, an exponential increase in electrical conductivity occurs. These effects are reversible as pressure is reduced or reapplied and are not accompanied by a first-order phase change in olivine or spinel. These observations relate to fundamental concepts of electrical conductivity and photon absorption in complex transition-metal silicates in that they cannot be readily interpreted in terms of an intrinsic band-gap model. The intensity and energy changes are too great and the effect occurs at too low a pressure to be explained by processes such as spin-pairing and other crystal-field effects. The results suggest that a new mechanism of conduction, perhaps symbiotic and employing an efficient charge-transfer process, is induced at high pressure.*

Measurements of the optical and electrical properties of fayalite (olivine, orthorhombic) and spinel (cubic) forms of Fe_2SiO_4 have been made at pressures in the range from 45 to 300 kb. The experimental apparatus is a modification of the design employed in an earlier study (*1, 2*) in which the effects described herein were first discovered. Optical absorption, electrical conductivity, and x-ray diffraction are measured simultaneously with a diamond-windowed cell in single crystals and polycrystalline powders under pressure (*3*).

Earlier definitive studies of the optical absorption properties of olivine at 1 atm (*4, 5*) dealt mostly with crystals having magnesium-rich compositions in the olivine series. High-resolution polarized spectra for iron-rich olivines at 1 atm have been reported by Burns (*6*) and Mao and Bell (*3*). Several investigators (*7*) have measured olivine spectra at high pressure, but curiously, as in the investigations of electrical conductivity mentioned below, they did not explore pressures high enough in combination with sufficiently iron-rich olivine to observe the major effects.

Properties of both natural (Inyo County, California) and pure synthetic fayalite (Fe_2SiO_4) were measured. The synthetic crystals of olivine were pre-