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WHITE MARBLE FROM ITALY AND TURKEY: AN ARCHAEOMETRIC STUDY BASED ON MINOR- AND TRACE-ELEMENT ANALYSIS AND PETROGRAPHY

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In 94 marble samples from 4 quarry districts in Italy (Carrara) and Turkey (Proconnesus, Dokimeion, Uşak), minor and trace elements were determined by instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS). The maximum size of the calcite grains (MGS) of the rocks was measured in thin section. For 16 elements considered in this work, the concentration ranges show important inter-district overlaps; this also applies to the maximum grain size. However, the application of cluster analysis, using selected attributes, allows one to discriminate every pair of districts; 90 samples are classified correctly in all classification dendrograms.

Introduction

A major topic in archaeometry is the provenance determination of artifacts. When speaking about white marble - one of the most common building and sculptural stones - the problem to be solved mostly concerns the origin of the raw material. This information is used in archaeology to reveal trade patterns and economical organisation, as well as in art historical studies and for restoration purposes.

It is a favourable circumstance that the location of the major classic Greek and Roman quarries is known. The partial or complete destruction of many ancient quarries, generally by modern exploitation, does not prevent a representative sam-

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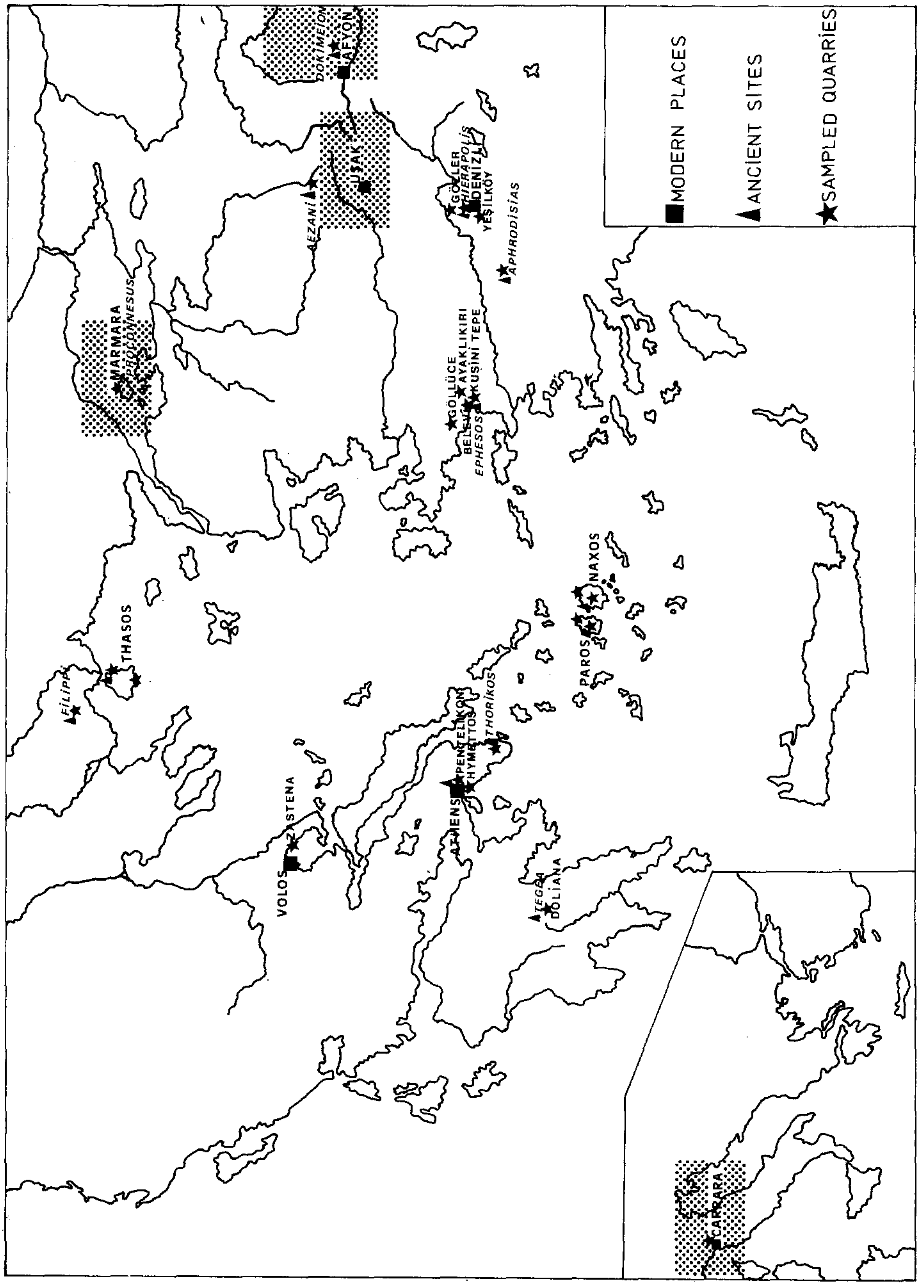


Fig. 1. Location of the major ancient quarry districts of the Mediterranean area. The four districts discussed in this paper are highlighted

pling of the extraction zone in which the antique quarries are situated.

Petrographical, chemical and physical methods were applied in trying to offer objective criteria to characterize the white marble from the different ancient quarries; the subject was recently reviewed by Herz[1]. Chemical analysis, performed in the sixties and the seventies, by INAA[2], and by optical emission spectrometry and X-ray fluorescence[3], yielded concentration data for a limited number of elements in samples from several major quarries. A large within-quarry variability and substantial inter-district overlaps were found for virtually all elements, leading to the widely accepted idea that chemical data are of little use in characterizing white marble[1,4].

None of the hitherto proposed techniques being entirely successful, an interdisciplinary approach, combining the information of isotopic analysis (C and O isotopes), minor- and trace- element determination, microprobe analysis, and thin-section microscopy, was set up at the State University of Gent. The major ancient quarry districts in Italy, Greece, and Turkey were sampled (Fig.1), and analytical work is in progress. The final results will be used as a basis for comparison when in the near future artifacts will be available for analysis.

The present paper is focused on the chemical composition of 27 samples from Carrara (Italy), 27 samples from Dokimeion (Turkey), 24 samples from the Proconnesus (Turkey), and 16 samples from Uşak (Turkey). In addition, some petrographical data are presented.

Experimental

Field sampling

The location of the antique quarry districts considered in this work is highlighted in Fig.1. At Carrara, Dokimeion, and the Proconnesus, the studied quarries are distributed all over the extraction zone (see e.g., Fig.2). The district of Uşak, however, consists of separated quarry areas containing only a few quarries each (Fig.3).

By preference, sampling was performed on modern walls. Using a geological hammer, unaltered hand specimens of 0.5 to 1 kg were extracted. Occasionally, weathered surfaces (near antique walls) were also sampled to study the effect of long-

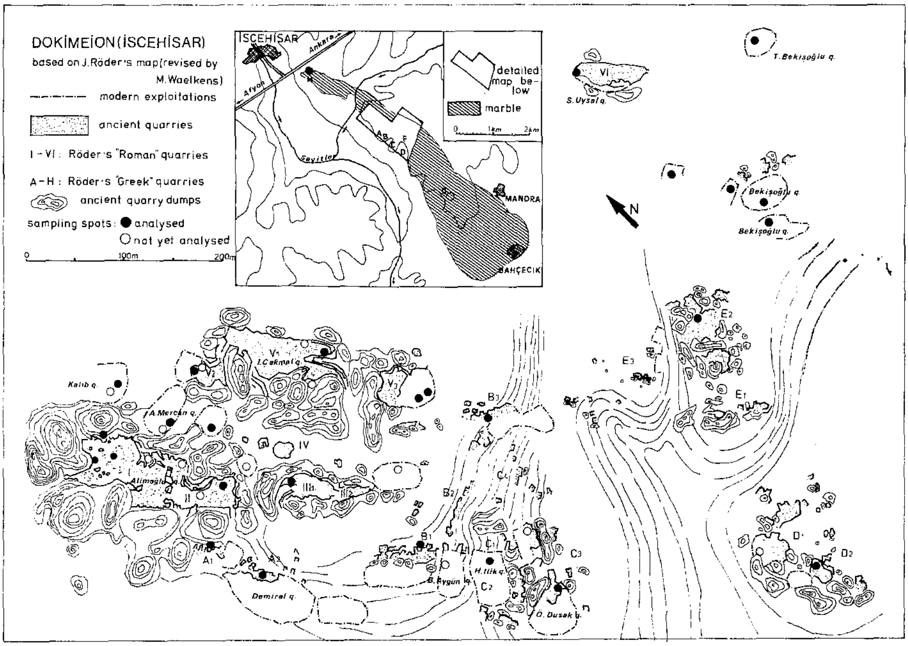


Fig. 2. The quarry region of Dokimeion [after J. RÖDER, JDAI, 86 (1971) 253]. Sampling spots are indicated by open circles or black dots (= samples included in this work)

lasting exposure. From previous work[5] it was concluded that weathering has only little effect on the minor- and trace-element contents. It was found to be sufficient to take the samples at 1 to 2 cm below the exposed surface. Complementary analyses are in progress to verify these preliminary conclusions.

For the present study, coloured and weathered stones were discarded, and a geographically representative selection was made.

Laboratory sampling

Cylinders of about 9.5 g (height = 20 mm; diameter = 15 mm) were taken from the hand specimens using a diamond tipped core

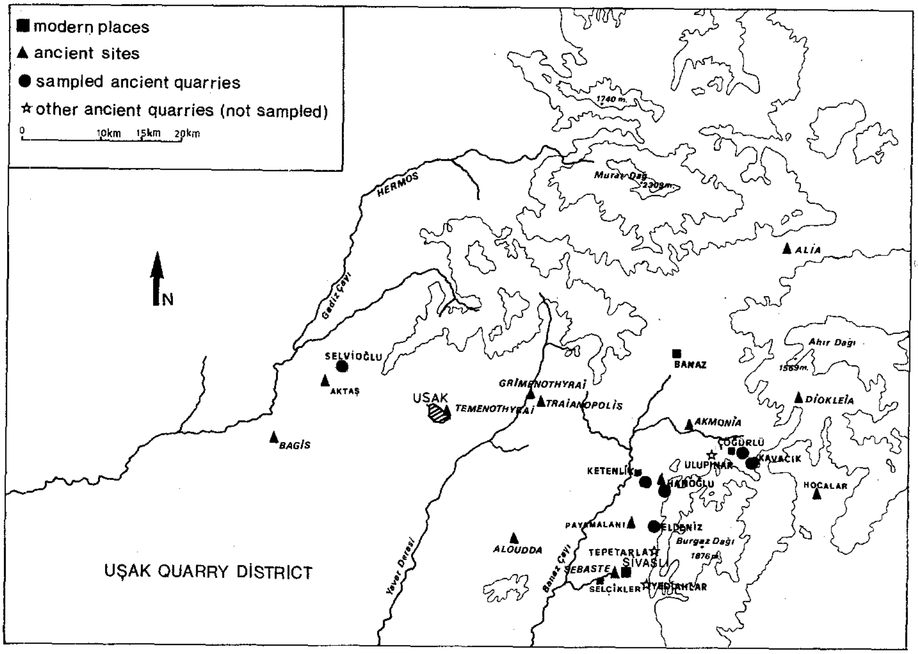


Fig. 3. The quarry areas of the Usak district. In the present study, the quarries at Kavacik (7 samples), Selvioğlu (4 samples), and at Hanoğlu-Eldeniz (5 samples) were considered

drill and a diamond saw. This process introduces substantial contamination for several elements present at low concentrations. The Co contamination, for instance, would yield an apparent Co content of about 0.5 ppm, whereas in the hitherto analysed marbles the actual concentrations range from 1.34 to 325 ppb. Therefore, a procedure was developed to obliterate the contamination resulting from drilling and sawing; a full report is given elsewhere[6].

The laboratory sampling mimiced the sampling of artifacts, the size of the actually analysed quarry samples being determined by the maximum amount of material expected to be obtainable from museum pieces.

Methods

Chemical analysis

For INAA, samples were irradiated for about 7 hours in the reactor Thetis of the Institute for Nuclear Sciences (Gent), at a thermal-neutron flux of 1.5×10^{12} $n.cm^{-2}.s^{-1}$, a thermal-to-epithermal flux ratio (f) of 28.5, and a non-ideality of the epithermal spectrum (α) of 0.03. The k_o-standardization method[7,8] was applied, requiring the co-irradiation of a comparator; a Au (0.1%)-Al alloy wire was used for this purpose. At 3 to 6 months intervals, f and α were instantaneously determined by irradiating a Zr foil together with the sample and the Au comparator[9,10]. In the reactor Thetis, f and α were found to be sufficiently constant over long periods. Gamma-spectrometry on a high-purity Ge detector was performed after 1 day (measuring time, t_m = 15 h), 1 week (t_m = 24 h), and 5 weeks decay (t_m = 24 h). Application of the k_o-standardization method allows one to use the available counting time am-most entirely for sample measurements.

The ^{47}Ca (T = 4.54 d) and ^{47}Sc (T = 3.34 d) matrix activity was moderate, and posed no obstacle for the measurement of isotopes with medium and long half-lives. Determinations via short-lived isotopes were hampered by the high ^{49}Ca activity

Table I

Minor- and trace-element concentrations in a white marble sample from Carrara (Italy); results of INAA, except for Si (colorimetry), Mg (FAAS), Al and V (EAAS)

Element (units)	Concentration ± uncertainty	Element (units)	Concentration ± uncertainty
Na (ppm)	9.5 ± 0.3	Sr (ppm)	174. ± 5.
Mg (%)	0.48 ± 0.01	Sb (ppb)	43. ± 2.
Al (ppm)	260. ± 10.	Cs (ppb)	5.7 ± 0.7
Si (ppm)	291. ± 1.	Ba (ppm)	1.4 ± 0.3
K (ppm)	127. ± 4.	La (ppb)	580. ± 20.
Sc (ppb)	80. ± 2.	Ce (ppb)	640. ± 20.
V (ppb)	430. ± 40.	Sm (ppb)	102. ± 3.
Cr (ppm)	1.12 ± 0.04	Eu (ppb)	23.7 ± 0.7
Mn (ppm)	19.9 ± 0.6	Tb (ppb)	19.0 ± 0.6
Fe (ppm)	109. ± 4.	Ho (ppb)	30. ± 2.
Co (ppb)	46. ± 2.	Yb (ppb)	84. ± 4.
Zn (ppm)	1.84 ± 0.06	Hf (ppb)	15. ± 1.
Ga (ppb)	40. ± 3.	Ta (ppb)	2.9 ± 0.3
As (ppb)	45. ± 2.	Th (ppb)	40. ± 2.
Br (ppb)	17. ± 3.	U (ppb)	134. ± 6.

(T = 8.72 min.). Though Al, Mg, and V could be determined with good (Al) or acceptable (Mg, V) precision, it was decided to apply AAS for these elements (flame AAS for Mg; electrothermal AAS for Al and V). Si was determined using colorimetry.

It was thus possible to determine 30 elements in white marbles with relatively high trace-element contents (Table I); for much purer samples, precisions will be worse, and for some elements the concentration will drop below the detection limit.

Thin-section microscopy

The main and accessory constituents of the rocks were identified with the help of a polarizing microscope. The same equipment was used for studying the texture, and for determining the maximum grain size (MGS) of the calcite crystals. A staining technique was applied to the thin sections to distinguish calcite from dolomite. For this purpose, alizarin red S was used. The present paper is only concerned with rocks containing less than 10 % dolomite.

Results and discussion

Chemical data

For the present study the concentrations of 16 elements were considered. In Table II, concentration ranges and medians are listed for the four districts under study. It is clearly shown that, although medians for the different regions are often distinct, within-district ranges are wide, causing inter-district overlaps for all elements, with only a few excep-

Table II
Concentration ranges and medians for the quarry districts under consideration

Element	Carrara (27 samples)		Proconnesus (24 samples)		Dokimeion (27 samples)		Uşak (16 samples)	
	Range	Median	Range	Median	Range	Median	Range	Median
Na(ppm)	7.3 - 100.	20.4	2.07 - 43.8	7.1	3.03 - 63.	6.1	2.06 - 142.	11.9
Mg(%)	0.36 - 0.81	0.43	0.24 - 0.90	0.30	0.054 - 0.53	0.11	0.15 - 1.7	0.27
Al(ppm)	36.0 - 340.	167.	16.0 - 85.0	32.0	22.0 - 530.	70.	9.0 - 340.	82.5
K(ppm)	18.3 - 276.	95.	0.70 - 16.0	2.66	1.82 - 291.	18.2	0.0185 - 154.	4.36
Sc(ppb)	12.9 - 247.	71.	0.310 - 84.	15.1	7.4 - 208.	20.5	0.80 - 398.	24.9
V(ppb)	220. - 3650.	660.	90. - 2010.	480.	60. - 1140.	480.	200. - 3870.	410.
Cr(ppm)	0.215 - 2.87	1.97	0.230 - 3.97	1.85	0.0230 - 2.85	0.233	0.270 - 3.13	0.71
Mn(ppm)	11.1 - 73.	21.8	0.487 - 9.1	0.85	5.70 - 141.	25.5	1.52 - 51.0	14.6
Fe(ppm)	20.4 - 286.	98.	4.47 - 54.	16.8	15.9 - 500.	100.	13.0 - 450.	101.
Co(ppb)	17.3 - 124.	57.	1.34 - 49.	2.76	9.2 - 325.	37.3	3.86 - 278.	38.3
Zn(ppm)	0.76 - 5.22	1.83	0.260 - 6.00	2.09	0.356 - 5.74	0.91	0.299 - 14.2	0.67
Sr(ppm)	147. - 225.	170.	124. - 254.	165.	48.9 - 200.	95.	113. - 410.	210.
La(ppb)	231. - 1060.	430.	<1.9 - 1070.	28.5	36.4 - 860.	118.	32.5 - 2330.	94.
Hf(ppb)	5.3 - 30.	12.4	<1.3 - 5.0	2.8	1.7 - 44.	4.5	0.51 - 25.	4.2
Th(ppb)	9.5 - 101.	30.5	1.0 - 19.8	2.61	1.56 - 126.	10.3	<1.3 - 48.	9.9
U(ppb)	45.0 - 660.	127.	38.0 - 830.	212.	23.5 - 151.	53.	8.4 - 940.	102.

tions (e.g., Carrara and Proconnesus show separated ranges for K, Mn, and Hf). As demonstrated in previous papers[5,11], for each region the frequency distribution of the concentrations is non-Gaussian for virtually all elements ; the log-normal empiricism was found to be a better approximation.

Petrographical data

All the investigated rocks are rather pure calcite-marbles, as the total amount of accessory minerals (dolomite included) never exceeded 10%, and usually was less than 1 % of the rock volume. The nature and the content of accessories are highly variable, depending on secondary processes (dolomitization), the place of sampling in the quarry, the location of the quarry, the geographical position of the quarry district, etc. Except dolomite, the accessories include plagioclase, muscovite, opaque minerals (pyrite, chalcopyrite, etc.), potash feldspars, quartz, epidote minerals, and carbonaceous inclusions. If the dolomite content is disregarded, it appears that the Proconnesian marbles and those collected at Dokimeion have the lowest accessory mineral content.

Textural differences also occur. While the rocks from Carrara and Dokimeion generally have a well-developed homeoblastic texture, one notes that the specimens from the Proconnesus and from the Uşak province have in most cases a heteroblastic and a mortar texture, respectively.

Table III gives the range of the maximum size of the calcite grains (MGS) in rocks coming from the different quarry districts. For most areas, the ranges are overlapping, although

Table III
Ranges of the maximum size of the calcite grains (MGS) in marbles from the quarry districts under consideration

Quarry district	MGS
Carrara	0.6 - 1.3 mm
Proconnesus	2.2 - 3.6 mm
Dokimeion	0.8 - 1.8 mm
Uşak	1.2 - 3.4 mm

this parameter is useful to discriminate, e.g., material from Carrara and Marmara[12].

Inter-quarry discrimination

The former paragraphs clearly show that the ranges found for the maximum grain size and for the concentrations of all elements are overlapping, making direct discrimination based on single parameters impossible. As a consequence, multi-variate methods are needed to reveal the discriminative information expected to be present in the data set. For this study, data analysis was performed using the DPP program[13], including a.o. hierarchical clustering methods ; a pragmatic choice was made for the furthest-neighbour strategy. A logarithmic transformation was applied to the elemental concentrations, according to the adopted log-normal empiricism.

Running the program for different sets of attributes allows one to select the discriminative ones. As no common set of attributes was found to separate the four districts in a single dendrogram, a set of discriminants was selected for each pair of districts. This is schematically shown in Fig.4, where the number of misclassified samples and the number of samples involved in the comparison are also indicated. In two out of the six two-by-two comparisons, the discrimination is incomplete, but 95% or more of the samples are classified correctly; in the other cases the districts are completely separated. As an example, the classification dendrograms comparing Dokimeion to the Proconnesus, and Uşak to Carrara, are shown in Figs. 5 and 6, respectively. In Fig.5, the Dokimeion and Proconnesus samples are exclusively grouped together. The subgroups existing in both clusters at present can be correlated neither with the stratigraphical position nor with mineralogical properties. Fig. 6 shows the presence of two Uşak subgroups ; the first subgroup, which is directly fused with the Carrara cluster, contains the samples from the Selvioğlu, Hanoğlu, and Eldeniz quarries, whereas in the other subgroup the samples from the quarries at Kavacık are found. The particular position of

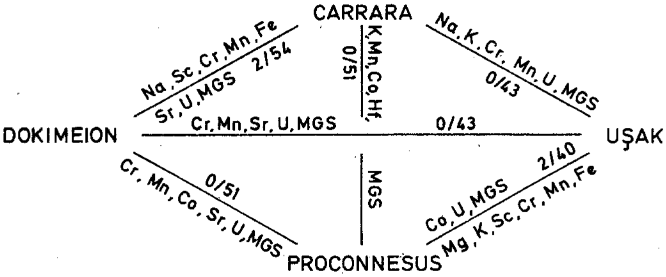


Fig. 4. Schematic representation of the two-by-two discrimination between the quarry districts considered in this work; the selected discriminants and the ratio of the misclassified samples to the total number of samples involved are indicated

```
  Classification dendrogram  :  Proconnesus - Dokimeion
=========================================================

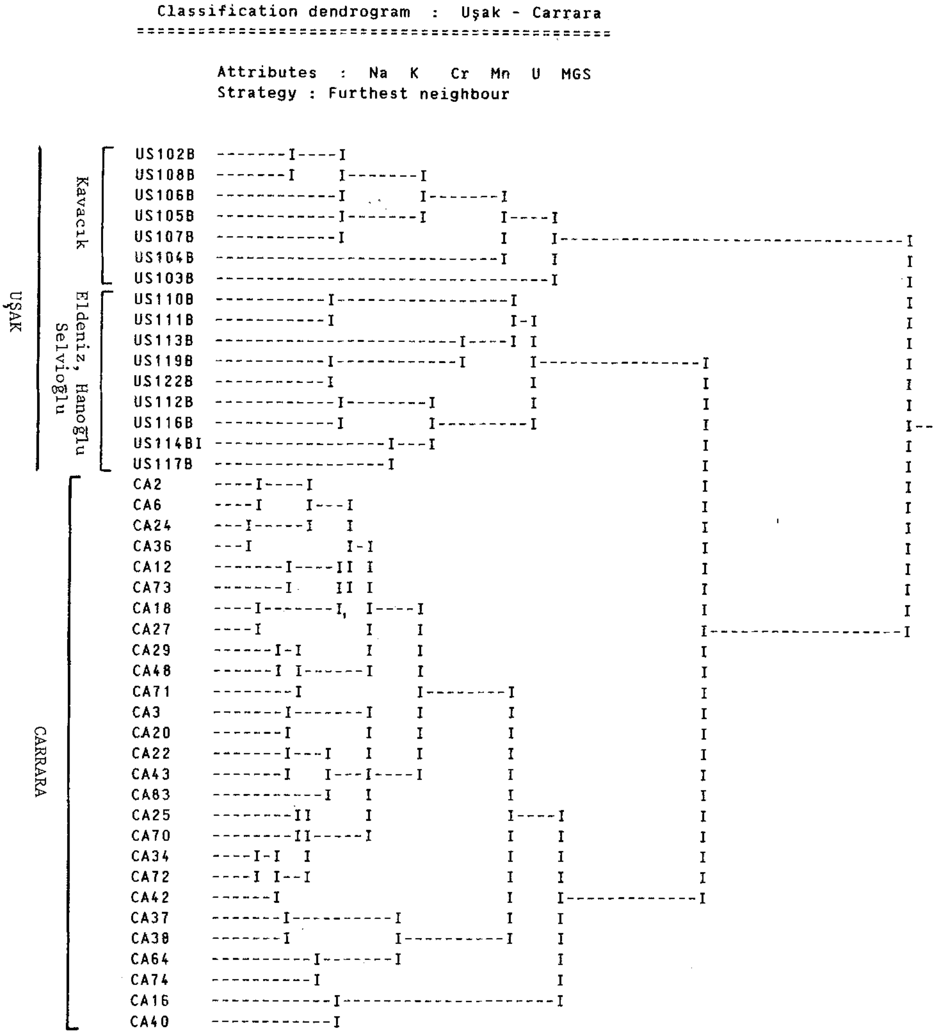
        Attributes  :  Cr  Mn  Co  Sr  U   MGS
        Strategy : Furthest neighbour

PR56    ---I---I
PR75    ---I   I-I
PR76    -------I I--------I
PR65    ---------I        I------------I
PR58    -----I--------I   I            I
PR99    -----I        I---I            I
PR59    ----------I---I                I
PR93    ----------I                    I
PR62    -------I------I                I-------------I
PR64    -------I      I-----I          I             I
PR70    -----I-I      I     I          I             I
PR96    -----I I------I     I          I             I
PR72    -------I            I--------I I             I
PR63    -----I----I         I        I I             I
PR77    -----I    I---I     I        I-I             I----------------------I
PR94    ----------I   I-----I        I               I                      I
PR98    --------------I              I               I                      I
PR66    -----------------------------I               I                      I
PR67    --------------I---------------I              I                      I
PR68    --------------I               I              I                      I
PR73    ---II                         I--------------I                      I
PR86    ---II----------I              I                                     I
PR87    ----I          I--------------I                                     I
PR82    ---------------I                                                    I
D01B    ----------------I--I                                                I
D042B   ---------I------I  I-----------------------I                        I--
D048B   ---------I         I                       I                        I
D025B   -------------------I                       I                        I
D02B    --------I-------I                          I                        I
D021BI  --------I       I-----I                    I-I                      I
D010B   ------------I---I     I                    I I                      I
D045B   ------------I         I----I               I I                      I
D013B   -------I----I         I    I               I I                      I
D014B   -------I    I---------I    I---------------I I                      I
D031B   ------------I              I                 I                      I
D024B   --------------I----I       I                 I                      I
D050B   --------------I    I-------I                 I                      I
D032B   ------I---I        I                         I----------------------I
D046B   ------I   I--------I                         I
D044B   ----------I                                  I
D06B    -------I---------I                           I
D011B   -------I         I--------I                  I
D08B    -----------------I        I                  I
D017B   --------I-I               I--------I         I
D018B   --------I I----I          I        I         I
D017B2  ----------I    I----------I        I         I
D022B   -------I-------I                   I---------I
D047B   -------I                           I
D026B   ---------I---I                     I
D030B   ---------I   I---------------------I
D027B   -------------I
```

PROCONNESUS

DOKIMEION

Fig. 5. Classification dendrogram for 51 samples from Dokimeion and the Proconnesus; hierarchical cluster analysis (Euclidean distance, furthest-neighbour strategy, data normalised, relative dissimilarity scale)



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     Classification dendrogram  :  Uşak - Carrara
==========================================

        Attributes  :  Na  K   Cr  Mn  U  MGS
        Strategy : Furthest neighbour

US102B  -------I----I
US108B  -------I    I-------I
US106B  ------------I       I-------I
US105B  ------------I-------I       I----I
US107B  ------------I               I    I---------------------------------I
US104B  ----------------------------I    I                                 I
US103B  ---------------------------------I                                 I
US110B  -----------I-----------------I                                     I
US111B  -----------I                 I-I                                   I
US113B  ------------------------I----I I                                   I
US119B  -----------I------------I      I---------------I                   I
US122B  -----------I                   I               I                   I
US112B  ------------I--------I         I               I                   I
US116B  ------------I        I---------I               I                   I--
US114BI -----------------I---I                         I                   I
US117B  -----------------I                             I                   I
CA2     ----I----I                                     I                   I
CA6     ----I    I---I                                 I                   I
CA24    ---I-----I   I                                 I                   I
CA36    ---I         I-I                               I                   I
CA12    -------I----II I                               I                   I
CA73    -------I    II I                               I                   I
CA18    ----I-------I, I----I                          I                   I
CA27    ----I          I    I                          I-------------------I
CA29    ------I-I      I    I                          I
CA48    ------I I------I    I                          I
CA71    --------I           I-------I                  I
CA3     -------I-------I    I       I                  I
CA20    -------I       I    I       I                  I
CA22    -------I---I   I    I       I                  I
CA43    -------I   I---I----I       I                  I
CA83    -----------I   I            I                  I
CA25    --------II     I            I----I             I
CA70    --------II-----I            I    I             I
CA34    ----I-I  I                  I    I             I
CA72    ----I I--I                  I    I             I
CA42    ------I                     I    I-------------I
CA37    -------I----------I         I    I
CA38    -------I          I---------I    I
CA64    ----------I-------I              I
CA74    ----------I                      I
CA16    ------------I--------------------I
CA40    ------------I
```

Fig. 6. Classification dendrogram for 43 samples from Uşak and Carrara; hierarchical cluster analysis (Euclidean distance, furthest- neighbour strategy, data normalised, relative dissimilarity scale)

the Kavacik marble can be correlated with field observations showing its exceptional purity and brightness.

The described two-by-two discrimination could also be used for provenancing artifacts. Indeed, using the parameters found to be discriminative for a given pair of quarry districts, cluster analysis can be applied to the samples from these districts plus those from the artifact. Repeating this procedure for each pair of quarry regions, in principle, allows one to determine the most probable origin of the artifact by successive elimination. This approach was successfully applied to quarry samples taken from hand specimens which were not included in the present work. However, as the number of quarry districts to be considered will increase in the future, cluster analysis using a two-by-two approach will become tedious. Therefore other methods, such as supervised discriminant development techniques, will be investigated in future work.

Conclusions

It was shown that white marble samples from the quarry districts of Carrara, Proconnesus, Dokimeion, and Uşak can be discriminated by applying cluster analysis, using selected petrographical and chemical data as attributes. Different sets of discriminants are found for each pair of regions. The inter-district separation is complete, except for Dokimeion vs. Carrara, and Uşak vs. Proconnesus, where two samples (out of 54 and 40, respectively) are misclassified.

In general, the present study shows that minor- and trace-element concentations and granulometrical data can contribute substantially to inter-quarry-district discrimination, in spite of overlapping ranges. This, however, requires the use of multi-variate methods.

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