Chapter 8.4

DISCRIMINATION OF GREEK MARBLES BY TRACE-, ISOTOPE- AND MINERALOGICAL ANALYSIS

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Abstract: Petrographically marbles are crystalline carbonate rocks with main mineral phases Calcite ($CaCO_3$), Calcitic marbles or dolomite ($CaMg(CO_3)_2$), dolomitic marbles. The commercial and archaeological interest for the characterization of provenance of marbles from specific marble quarries is great. Within this aim several studies have been carried out in the past, which referred to the petrographic characterization as well as to trace element analysis. In the present work a farther attempt is made for the discrimination of the origin of marbles, based on their mineralogical characterization and analysis of major and trace elements as well as isotopes analyses. In particular, 8 major elements (Si, Al, Fe, Mn, Mg, K, Ca, Na), 27 trace elements: (Li, Be, B, Sc, B, Cr, Co, Ni, Cu, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Sn Sb, Cs, Ba, Hf, Pb, Bi, Th, U), 14 REE (Rare Earth Elements): (La, Ce, Pr, Nd, Sm, Eu, Tb, Gd, Dy, Ho, Er, Tm, Yb, Lu) and the ratio of isotopes: Pb, Sr und Rb (204/206Pb, 207/206Pb, 208/206Pb, 207/204Pb; (85/87Rb); (84/86Sr, 87/86Sr, 88/86Sr87/86Sr) have been measured. Eleven different Greek marbles have been analyzed from various marble regions. The study of the analytical results shows that the discrimination of marbles is possible based on the trace elements in combination with the isotope analysis. Binary and ternary chemographic diagrams like 207Pb/206 Pb-208Pb/206Pb, 87Rb/86Sr-206Pb/204Pb, Ti-B-Be, (Sn+Pb)-(V+Cr)-(Sc+Y) and the ratio 147Sm/146Nd contribute to, more or less, a clear group discrimination of the Greek marbles. This discrimination is significantly improved involving the mineralogical analysis combined with Image Analysis Techniques. By the ternary diagrams Pr-Nd-Sm, Tb-Gd-Dy and Tm-Yb-Lu a discrete and significant grouping of all examined Greek marbles is achieved, which could be probably used for the discrimination of the Greek marbles from other localities of the Mediterranean area.

Key words: marbles; trace elements; isotope analyses; X-ray diffraction; image analysis.

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1. INTRODUCTION

Marble is the most important decorative building stone in the human history. Buildings of marbles, predominantly from the Hellenistic, Hellenistic - Roman and later period, can be regarded as indicators for the culture-historical development of the European settlement area. The provenance allocation of the marbles, which were used for monuments, sculptures, buildings and other historical culture objects, is very important for the archaeological study and give interesting information about the culture and the trade relations within Europe and the neighboring regions. Even for modern buildings of marbles, if restoration is required, the knowledge of the provenance of the marbles is very important.

The archaeological interest for the regional allocation of marble artifacts at certain marble occurrences of the Mediterranean area began relatively early. By the material allocation of marble artifacts to certain delivery areas (quarries) possible historical cultural and trade relations could be archaeologically reconstructed within Europe. As it was shown in the case of ceramic artifacts, (Kritsotakis, 1994; Schneider and Rother, 1991), it should be possible, due to mineralogical and geochemical criteria, to locate historical marble objects with probably good safety. This can be done by comparative mineralogical-geochemical investigations with "groups of reference marbles" from different historical settlement regions of Europe. In addition marble fragments, belonging together as well as replicates could be more easily recognizable with the help of the groups of reference marbles.

A condition for a Data Bank of groups of marble references is a systematic sampling of historical and recent marble occurrences within the regions of interest. Furthermore it is necessary that from each sampled marble occurrence (quarry) a large number of samples is collected, representative of the occurrence, and examined mineralogically as well as geochemically.

Lepsius (1890) described marble occurrences and artifacts from different regions of Greece in detail and tried to differentiate chemically the Penteli marble from the cycladic marbles. He compared thereby the Fe_2O_3 contents of these marbles and found for the Penteli marble a Fe_2O_3 content of 0.2 %, while in the cycladic marbles no Fe_2O_3 was detected, obviously because at that time the Fe_2O_3 content laid below the analytical detection limit.

The first scientifically documented publications, which were concerned comprehensively with the geostructural and stratigraphical situation of the marble occurrences in the Aegean area, appeared during the late ’40s. Marinos (1948) examined the Aegean marbles petrographically and showed that their texture, crystalinity, twinning, weathering and roughness as well as some further mechanical properties depend on the geostructural position of the marbles. The more deeply their geotectonic position is, the larger, more uniform and clear (high P-T conditions) their calcite crystals are, and therefore they are suitable for sculpture work.

Martin (1965) and Papagiorgakis (1963, 1967) described in detail the geotectonic and petrographic environment of the marbles, which were found in antique Greek architecture, while Dworakowska (1975) gave a broad overview of the localities of some historical quarries. The classical marble occurrences of Asia Minor were described likewise in detail by Monna and Pensabene (1977). In the meantime a large number of works were concerned with the mineralogical petrographic and/or geochemical characterization (main and trace elements, carbon-, oxygen and Sr-Isotopes) of marble artifacts and marble occurrences from the Mediterranean area. A large part of these contributions is coherently discussed in the Monograph by Kempe and Harvey (1983), while in the Monograph by Herz and Waelkes (1988) many relevant research papers are presented in detail. Interesting abstracts with the same topic are also found in the proceedings of ASMOSIA. Two interesting contributions of Moens et al. (1987, 1988) are concerned with the investigation and characterisation of the Asia Minor marble occurrences.

Lately for the characterisation of the Mediterranean marbles and/or marble artifacts spectroscopic methods were used. Thus, the cathode luminescence was used in connection with petrographic-geochemical investigations (Barbin et al., 1992a; Schmid et al., 1999) as well as the electron paramagnetic resonance spectroscopy (Baietto et al., 1999) for the discrimination of white marbles of the cycladic islands and the Greek mainland (Vakulis et al., 2000).

Studying the literature, it was shown that most investigations considered only a few regional marble occurrences of the Mediterranean area. Besides, the number of examined samples cannot be regarded as representative. Furthermore the obtained results for the same marble, with different research methods, are partly contradictory and in themselves not consistent.

Petrographic and textural studies, (Weiss, 1954; Herz, 1955b; Renfrew and Peacey, 1968; Germann, 1978), supplied partial useful results but the investigations are very time consuming, partly subjective, not always reproducible and require a large experience from the scientist. Although the numerous chemical analyses of main- and trace- elements - of marbles from different Mediterranean Localities, (Rybach and Nissen, 1965; Renfrew and Peacey, 1968; Andreae et al., 1972; Conforto et al., 1975; Germann, 1978; Lazzarini et al., 1980), are well reproducible, they brought no satisfying significant discriminations. The reason for this lies obviously in involving only few main- and trace-elements for the discrimination.

In recent time an attempt was often undertaken to discriminate Hellenistic and Roman marble artifacts by involving the stable isotopes ($^{13}C/^{12}C$, $^{18}O/^{16}O$), Lazarini (1995, 2000, 2002), and the Sr isotope ratios (Craig and Craig, 1972; Manfra et al., 1975; Herz and Wenner, 1978; Coleman and Walker, 1979; Gale, 1979; Gast et al., 1979; Germann et al., 1980; Herz, 1987). Although at the beginning a very good discrimination of some Greek marble occurrences could be achieved, by the data of Craig and Craig (1972), the discrimination of the groups became more unclear by plotting data from further localities into this diagram, and therefore is useless as a group discrimination tool.

The stated difficulties arouse the impression that the Mediterranean marble occurrences are neither with petrographic nor with chemical methods reliably discriminable. It should however be possible, due to geochemical considerations, by involving additional trace elements, e.g. the Rare Earth Elements (REE), as well as the Rb-Sr and Pb-Isotopes to receive more effective discrimination for these marbles. Today it is possible, by the means of solution and Laser Ablation - ICP MS, to receive very fast precise analytical data for a large number of elements.

In the context of a pilot project, between the Institute for Geology and Mineral Exploration (IGME) in Athens, the Technical University of Crete (Mineral resources department) and the Institute fuer Geowissenschasften, Universitaet Mainz, only a limited number of marble samples from different occurrences in Greece was analyzed for their chemical and isotope composition. In this project as many as possible chemical elements and isotope rations from different marble occurrences have been analyzed, to test whether it is at all possible to achieve a clear discrimination from each other. In case of a clear discrimination of the marble occurrences, the project should be extended to the systematic investigation of all well-known historical and recent marble occurrences of Greece. The data obtained and chemographic discriminants are to be summarized afterwards in the form of a geochemical Atlas. These data should serve to the characterization of marble artifacts regarding their origin. In a long-term project it is intended to work on all well-known marble occurrences of the Mediterranean area.

2. MARBLE: DEFINITION AND MINERALOGY

Petrographically marbles are crystalline carbonate rocks with main mineral phases Calcite ($CaCO_3$), Calcitic marble or dolomite ($CaMg(CO_3)_2$), dolomitic marble. Contrary to this petrographic definition in the decorative stone industry, marbles are, generally, all easily machinable rocks, i.e. sharpen and polishing. Therefore in the stone-processing industry not metamorphic rocks and fine-grained limestones are also called "marbles".

Marbles are from the petrographic point of view, recrystallized carbonate rocks, named also crystalline limestones, where the recrystallisation takes place via the thermal stress of sedimentary carbonates. Pure limestones are converted by thermal metamorphose to fine up to coarse crystalline Calcitic marbles. From silica and/or clay containing carbonate rocks, depending on metamorphose degree, additionally mineral phases can occur as accessory minerals in the marble, like: Quartz, Chlorite, Epidote, Zoisite, amphibole, Clinopyroxene, garnet, plagioclase, light and dark mica. From these, marble designations result, like Zoisit-, or Chlorite-marble.

Table 1. Analysed marbles from different localities in Greece.

Sample Number	Locality	Mineralogical characterization
M 1	Crystalline, Thassos	Calcitic marble
M 2	White, Prinos, Thassos	Dolomitic marble
M 3	Yellowish-white, Platanotopos, Kavala	Dolomitic marble
M 4	Black, Vathylakos, Drama	Calcitic marble
M 5	White, Volakas, Drama	Dolomitic marble
M 6	White, Menikion, Serres	Calcitic marble
M 7	Roditis, Kozani	Calcitic marble
M 8	Grey, Tranovaltos, Kozani	Calcitic marble
M 9	White, Tranovaltos, Kozani	Calcitic marble
M 10	Crystalline, Naxos	Calcitic marble
M 11	White, Dionyssos, Penteli (Attica)	Calcitic marble

The frequently arising clay parts in the primary limestones are converted by the metamorphic processes to mineral associations of the green and/or Amphibole fazies and form the well-known banded marbles, or by syn- or post-metamorphic tectonic processes, irregularly distributed, darkly colored engagements. Such a different colour veining, lend a decorative effect, particularly if, as in some crystalline limestones, the differences in color are intensive. The color of crystalline limestones is not definable, since nearly all color nuances and color combinations can occur, from pure white up to deeply black varieties. The frequently occurring colors form a white to light-grey carbonate matrix with gray-green to black veins.

The structure of the marbles is massive. Banded types arise only if the marbles contain larger quantities of phyllosilicates or needleform minerals (mica, graphite, needleform amphiboles). In consequence of the crystallization friendliness of the carbonate minerals, granoplastische (coarse grained) Calcitic and dolomitic structures arise in tectonically strongly stressed areas, which show a close interconnection of the crystallites, where the pore area of the marbles becomes extraordinarily small (up to 0.01 volume per cent). The grain structure analysis usually shows no uniformed orientation of the carbonate minerals.

Marbles occur in all crystalline areas, where they are most strongly represented in low metamorphic series.

3. SAMPLING AND ANALYTICAL TECHNIQUES

For the present investigation marble samples from 11 different marble occurrences from Greece were analysed. In Table 1 the localities and the mineralogical characterisation of the samples are given.

The geographic localities of the occurrences indicated in Table 1 are registered in the map of Greece (Figure 1) as well as the localities of well-known marble occurrences. With the exception of Penteli (Attica), Thassos and Naxos, the examined marble occurrences originate from north Greece.

Table 1. Analysed marbles from different localities in Greece.

Sample Number	Locality	Mineralogical characterization
M 1	Crystalline, Thassos	Calcitic marble
M 2	White, Prinos, Thassos	Dolomitc marble
M 3	Yellowish-white, Platanotopos, Kavala	Dolomitic marble
M 4	Black, Vathylakos, Drama	Calcitic marble
M 5	White, Volakas, Drama	Dolomitc marble
M 6	White, Menikion, Serres	Calcitic marble
M 7	Roditis, Kozani	Calcitic marble
M 8	Grey, Tranovaltos, Kozani	Calcitic marble
M 9	White, Tranovaltos, Kozani	Calcitic marble
M 10	Crystalline, Naxos	Calcitic marble
M 11	White, Dionyssos, Penteli (Attica)	Calcitic marble

The mineralogical analysis was performed by X-ray powder diffraction techniques. A Siemens D500 diffractometer was used with copper radiation and graphite monochromator. The qualitative evaluation was carried out by the Diffrac Plus software and the PDF (Powder Diffraction File) data base. The quantitative analysis was performed by Rietveld refinement technique. This method gives the most accurate quantitative analysis, which can be achieved by X-ray diffraction analysis.

Figure 1. Distribution of the most important marble occurrences in Greece.

Thin sections were prepared and photos were taken with a digital photo camera. The photos were taken from a stereo transmission microscope, which was converted to a simple polarizing microscope, adding two commercial polarizing filters. In this way the optical field was >1 cm, instead of a few millimeters in a normal polarizing microscope, even in low magnification. This arrangement allows to measure coarse crystalline marbles, with grains >2 mm. The grain size of the analysed marbles was determined by image processing techniques followed by statistical evaluation.

For the chemical analysis, about 10 g of each sample were grounded, in an agate mortar, and twice 0.1 g sample material were dissolved with 10 ml 1n HNO_3 ultrapure in Teflon bottle. Not dissolved portions were filtered and the solutions were diluted with ultrapure H_2O into a Teflon bottle to a final dilution 1000. With these solutions all further analytical work was carried out. The sample solutions were analyzed with a PQ3 S Quadrupole ICP MS of the company VG-Instruments. For the analyses the element In with a concentration of 10 ppb was used as internal standard. The optimization work of the system took place with the necessary reference solutions. The reproducibility and accuracy of the measuring data were tested with the help of synthetic solutions and international rock and isotope reference standards. Isobar mass interferences were corrected by optimized correction factors as far as possible.

Quantitatively 8 main elements (Si, Al, Fe, Mn, Mg, K, Ca, Na) and 27 trace elements: (Li, Be B, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, Hf, Ta, Pb, Bi, Th, U), 14 REE: (La, Ce, Pr, Nd, Sm, Eu, Tb, Gd, Dy, Ho, Er, Tm, Yb, Lu) and the Pb-, Sr- and Rb- isotope ratios: (204/206Pb, 207/206Pb, 208/206Pb, 207/204Pb, 208/204 Pb); (85/87Rb); (84/86Sr, 87/86Sr, 88/86Sr, 87/86Sr) were measured.

4. RESULTS AND DISCUSSION

The discussion and presentation of the extensive analytical data, will be done in form of binary and ternary chemographic diagrams. From a large number of diagrams, there are presented and discussed only those which contribute to more or less clear group discrimination (The analytical data are available on request). The mineralogical composition and the cristallinity of the marbles are given in Table 2. The physical properties and the chemical composition of the examined marbles are given in Table 3 and Table 4.

Based on Table 2, all examined marbles consist mainly of the minerals calcite, dolomite and quartz, with some trace of muscovite in samples M6, M7 and M11. The marbles M2, M3 and M5 are nearly pure dolomitic, the M3-Marble contains 3.5% Calcite while M2 and M5 contain only ~1% calcite. The rest of the marbles are calcitic, which, besides quartz, contain also small amount of dolomite (~3 %).

Table 2. Mineralogical composition, crystallinity and grain size of the marbles samples

Marble Sample	Calcite %	Dolomite %	Muscovite %	Quartz %	Crystallinity	Mean Grain Size (μm)	Std. Ddev.
M1 Kristalin Thassos	100	-	-	<0.1	coarsely crystalline	891	437
M2 White, Prinos Thassos	1.5	98.4	-	<0.1	coarsely crystalline	983	366
M3 Yellowish Platanotopos/Kavala	3.5	96.4	-	<0.1	Medium crystalline	178	69
M4 Black, Vathylakos/ Drama	99.8	-	-	0.2	coarsely crystalline	509	163
M5 White, Volakas/Drama	1	99	-	<0.1	Medium crystalline	190	53
M6 White Menikion/Serres	99.5	0.5	Trace	<0.1	coarsely crystalline	522	200
M7 Roditis/Kozani	97.6	2	Trace	0.4	coarsely crystalline	501	153
M8 Gray, Tranovaltos/ Kozani	99	0.5	-	<0.1	Medium crystalline	171	58
M9 White,Tranovaltos /Kozani	96.5	3	-	<0.1	Medium crystalline	240	72
M10 Kristalin, Naxos	99	0.5	-	0.5	coarsely crystalline	1028	506
M11 White Dionyssos/Penteli	98	0.5	trace	2	Medium crystalline	289	85

Although the grain sizes of the studied marbles have a relative big standard deviation, we can recognize differences between the different marble localities. Samples M1, M2 (Thassos) and M10 (Naxos) are characterized as coarsely crystalline while the rest of the marbles are medium crystalline. Among the medium crystalline marbles, the marbles M3 (Kavala), M8 (Gray/Kozani), M9 (White/Kozani) and M11 (Dionyssos) have the lower crystallinity (microscopical pictures and grain size distribution are given in the Appendix).

Combining the mean grain size of the marbles with the physical properties, a relation could be recognized between grain size and compressive strength. The marbles M3, M5 and M8 have the smaller grain sizes and highest compressive strength. The same relation is observed also after freezing and thaw. The concentrations of the elements Si, Al, Fe, Mn, Mg, K, Ca, Na are quite low in all marbles (Table 3). A clear discrimination of these marbles is not easy due to their mineral composition and/or their main element concentrations. It can be differentiated between calcitic and dolomitic marbles, but a clear differentiation within the group of either the calcitic or the dolomitic marbles is not easy too.

Using the Fe-concentration in Table 3 a simple discrimination of the examined marbles is possible in marbles with Fe_2O_3 <0.1% or Fe_2O_3 >0.1%.

Table 3. Physical properties of the marble samples

	Apparent Specific Weight (DIN 52102)	Porosity and Water Acces. (DIN 52102)	Absorption Coefficient (DIN 52103)	Modulus of elasticity (DIN 1048, part 5)	Compressive Strength (dry) (DIN 52105)	Modulus of Rupture (dry) (DIN 52112)	Compressive Strength after freezing and thaw (DIN 52104) and (DIN 52105)	Abrasion Resistance (DIN 52108)	Impact Strength (UNI-U 32.07.248.0)
	Kg/m^3	% vol.	%wt.	GPa	MPa	MPa	MPa	mm	cm
M1	2714	0.14	0.05	18	60	9	64	2.20	38
M2	2846	0.28	0.1	21	80	10	103	2.49	40
M3	2850	0.60	0.21	42	120	11	81.2	2.06	29
M4	2711	0.21	0.08	23	89	18	72	2.26	41
M5	2825	0.54	0.19	35	139	10	103	2.20	59
M6	2712	0.17	0.06	34	77	24	86	2.35	46
M7	2732	0.19	0.07	25	63	20	81	2.28	33
M8	2726	0.29	0.11	24	114	24	104	2.3	53
M9	2719	0.28	0.1	25	90	9	84	2.68	65
M10	2710	n.d	0.09	35.5	89	12.8	n.d	8.56	n.d
M11	2717	n.d	0.11	57.2	111	19.2	n.d	6.7	n.d

Table 4. Concentrations of the main elements in the marble samples

	M 1	M 2	M 3	M 4	M 5	M 6	M 7	M 8	M 9	M 10	M 11
CaO	53.50	30.40	30.0	54.50	30.60	54.00	53.20	53.60	53.30	55.60	54.80
MgO	1.92	21.90	20.8	0.66	21.50	0.7	2.60	0.84	0.84	0.50	1.55
SiO_2	0.50	0.60	1.2	0.20	0.20	0.6	0.65	1.00	0.80	0.07	1.10
Fe_2O_3	0.05	0.07	0.20	<0.05	<0.05	0.08	0.10	0.10	0.15	0.14	0.14
Al_2O_3	0.11	0.08	0.16	<0.05	<0.05	0.04	0.20	0.15	0.20	0.02	0.20
K_2O	<0.01	0.01	0.01	<0.01	<0.01	0.03	0.03	0.02	0.03	0.02	0.09
Na_2O	<0.01	<0.01	0.04	0.01	0.01	0.01	0.01	<0.01	<0.01	0.04	0.04
MnO	0.01	0.01	0.02	<0.01	<0.01	0.01	0.02	0.02	0.02	0.02	0.02
LOI	43.44	46.93	46.1	43.60	47.60	43.50	43.20	43.00	42.80	43.00	43.05

The yellowish white marble from Platanotopos/Kavala (M3) is characterized by a high Fe-concentration. The yellowish colour of this marble is obviously caused by its high iron content. Also the light reddish colour of the Roditis/ Kozani (M7) marble is due to its relatively high Fe-concentration. The Calcitic marble from Dionyssos/Penteli (M11) is likewise iron-rich. Of the examined marbles only the marbles from Vathylakos (calcitic marble) and Volakas (dolomitic marble) near Drama (M4, M5) differ, because they are iron free.

Within the dolomitic marbles the calcite content could possibly serve as discrimination criterion, because, as seen from Table 2, the marble from Platanotopos/Kavala (M3) contains some calcite, higher than in the two other dolomitic marbles (M2, M5) but differs significantly in grain size from M2 (Thassos). However, this is not a safe criterion, because we do not know, the calcite content and the grain distribution in other dolomites, which were not analyzed here. The dolomitic marbles from Prinos/Thassos (M2) and Volakas/ Drama (M5) are not differentiated mineralogically from each other but are clearly differentiated in terms of grain size distribution. The discrimination effectiveness is improved, if apart from the mineralogical analysis, additional criteria are involved, like petrographic (crystalinity, crystall form, crystal/ grain size, crystal orientation) and macroscopical (color, color distribution).

For the discrimination of historical groups of marble objects it is shown that binary and ternary element correlations are particularly well suited. With such representations the concentrations of two or three elements (object-characteristic properties) are correlated to each other. All objects with more or less similar concentrations form discrete point clusters, which are characteristic for the respective group of objects. For a clear and reliable discrimination of the examined marbles several binary and ternary trace element correlations were examined for their discrimination power. The ternary representations Be-B-Ti, (Figure 2) and (Sc+Y)-(V+Cr)-(Sn+Pb), (Figure 3) supplied the best separation.

In the ternary diagram Be-B-Ti the localities and the occurrences within the same locality are quite well separated. In this way, the two samples of Thassos (M1, M2) and the two samples of Drama (M4, M5) are clearly discriminated. On the other hand, the three marble samples of Kozani (M7, M8, M9) though separated, lie not far from each other. The marbles of Naxos (M10) and Dionyssos (M11) are separated too, but the distance of the representing points is not large enough for a reliable discrimination. Additionally, if the grain size distribution is taken into consideration, a better discrimination will be achieved. Furthermore the points of the marble from Serres (M6) and the Roditis Kozani (M7) marbles lie quite close and an overlapping of their ranges is expected.

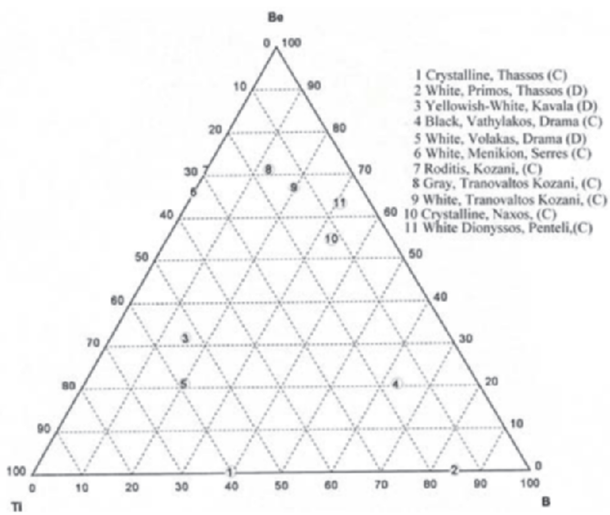


Figure 2. Discrimination of the marbles from Greece in the ternary diagram Be-B-Ti.

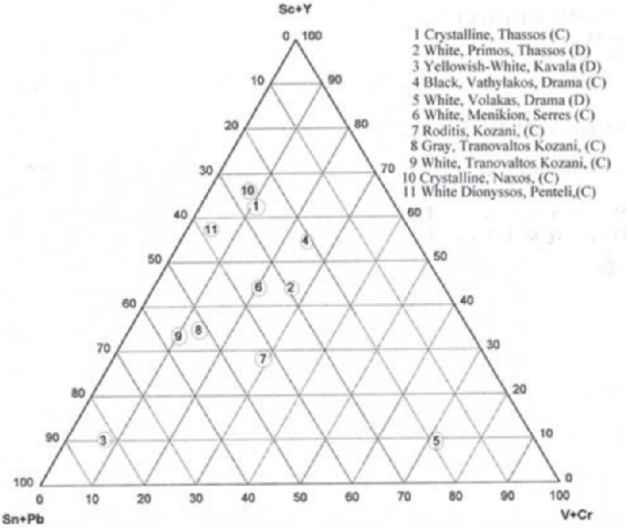


Figure 3. Discrimination of the marbles from Greece in the ternary diagram (Sc+Y)-(V+Cr)-(Sn+Pb).

By the ternary diagram (Sc+Y)-(V+Cr)-(Sn+Pb) (Figure 3) a discrimination of the examined marble occurrences also takes place. In this case the separation distances of the representing points are not so large, so certain partial overlapping of the representing ranges can occur. In the above diagram the two marble samples from Thassos (M1, M2) are clearly separated, as well as the two marbles from Drama (M4, M5). As for the three samples from Kozani the samples M8 and M9 are well together while the sample M7 is separated from the two others, with significantly bigger grain size. Here the point of representing the marble from Naxos (M10) lies quite close to the point representing the marble from Thassos (M1), a fact which is not so favourable but the Naxos marble (M10) is coarser then the Thassos marble (M1). The Rare Earth Elements (REE) were also quantitative analysed and their concentrations were tested for a discrimination.

In Figure 4 the geochemical distribution of the REE in the examined marbles is displayed. The measured concentrations are normalized on the average concentrations of these elements in the Upper Earth Crust. Although such distribution figures do not appear suitable for group discrimination, they supply some geochemically important information. The marbles are relative to the upper earth's crust at REE depleted (Figure 4). It means that the concentrations for all REE in the marbles lie lower than the concentrations of these elements in the Upper Earth Crust. Furthermore the heavy REE are more strongly enriched than the light REE in the marbles, which corresponds to the geochemical behavior of the limestones.

The marbles M4 (Vathylakos/Drama), M1 (crystalline/Thassos), M10 (crystalline/Naxos) and M11 (Dionyssos/Athens) show characteristic distri-

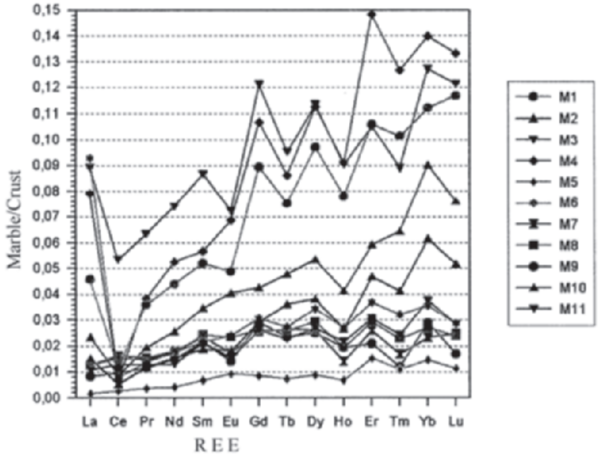


Figure 4. REE distribution of the analyzed marble occurrences from Greece.

bution. These four marbles show a more or less Ce-anomaly and have, with the exception of Ce, higher significant REE concentrations than the remaining marbles. The dolomitic marble of Volakas (M5) has the lowest REE-concentrations. Generally speaking, it can be said that a discrimination of marble occurrences is not to be expected with the help of the REE-distribution.

Using the $^{147}Sm/^{146}Nd$ isotope ratio we achieve a quite good separation of the individual marble samples (Figure 5). The marbles from Thassos (M1, M2) are separated from the others and lie well together. The three samples from Kozani (M7, M8, M9) are split into two groups. The two Calcitic ones, the grey (M8)/ and the white (M9)/(Tranovaltos), lie well together while the reddish Calcitic marble (M7)/(Kozani) separates clearly from the previous two.

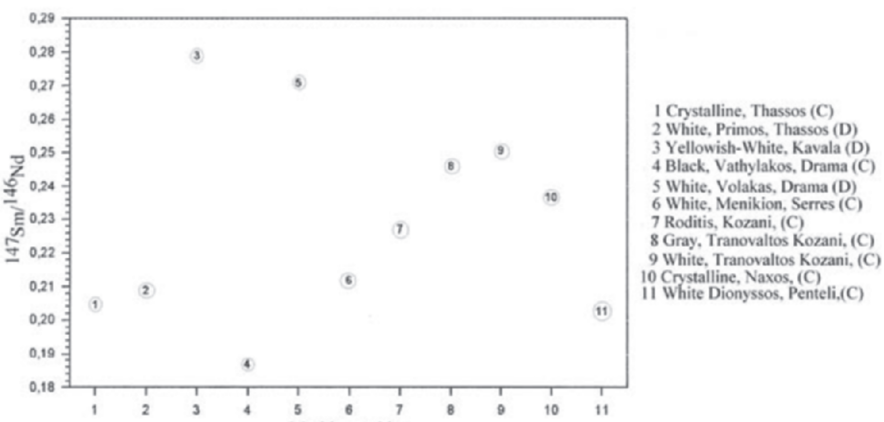


Figure 5. Plotting of the analysed marble occurrences as function of the $^{147}Sm/^{146}Nd$ isotope ratio.

Also the two marble samples from Drama, black Calcitic marble from Vathylakos (M4) and dolomitic marble from Volakas (M5), have a clear separation. The separation of the three specimens from Serres (M3), Naxos (M10) and Dionyssos (M11) is likewise very good.

By the discussed chemographic representation, the discrimination of historical marble objects and their allocation to regional stores seems to be quite possible. The discrimination power of this diagram can be regarded as safe only if it is confirmed without overlapping by additionally analyzed marble occurrences.

Besides, on the search for an efficient discrimination criterion for historical marble objects an attempt was made by using different isotope ratio plots. Two plots (208Pb/206Pb-207Pb/206Pb and 206Pb/204Pb-87Rb 86Sr) which give relatively reasonable results are presented and discussed here. Although the representing points of the analysed marble occurrences are separated for the Pb-Isotopes reasonably well (Figure 6), the separation distances are not large enough, in order to avoid an overlapping with further measuring occurrences. The two marbles from Drama (M4, M5) are also clearly separated by the isotopes and the same applies to the marbles from Thassos (M1, M2). The marbles from Kozani (M7, M6, M9) are also separated in a similar way like the trace elements. The two samples from Tranovaltos/Kozani (M8, M9) have the same isotope ratio, therefore overlap but they differ in their dolomite content and also in grain size, while the sample (M7)/(Roditis) possess a strongly deviating Pb-isotope ratio. The specimens from Kavala (M3), Naxos (M10) and Dionyssos (M11) are also separated clearly by means of the Pb-isotope ratios.

A better separation efficiency of the examined Greek marbles represents the (^{204}Pb/^{206}Pb)- (^{87}Rb/^{86}Sr)- isotope ratios of the samples (Figure 7).

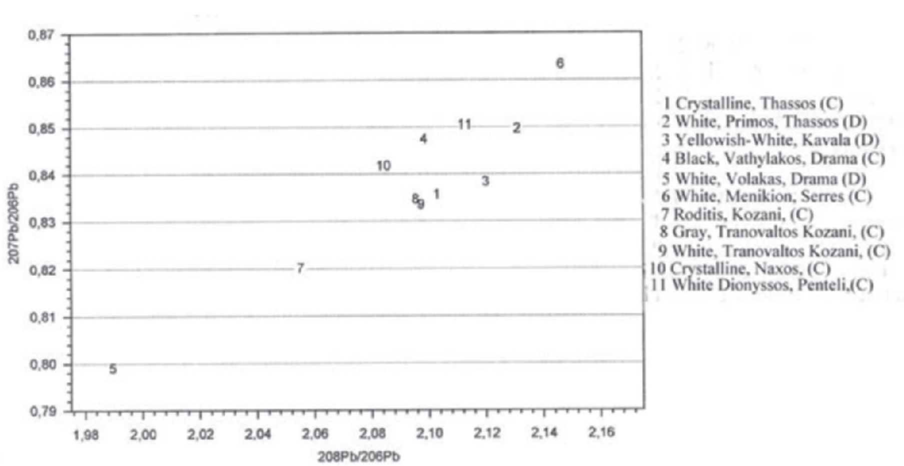


Figure 6. Discrimination of the analysed Greek marble occurrences by means of the Pb-Isotopes.

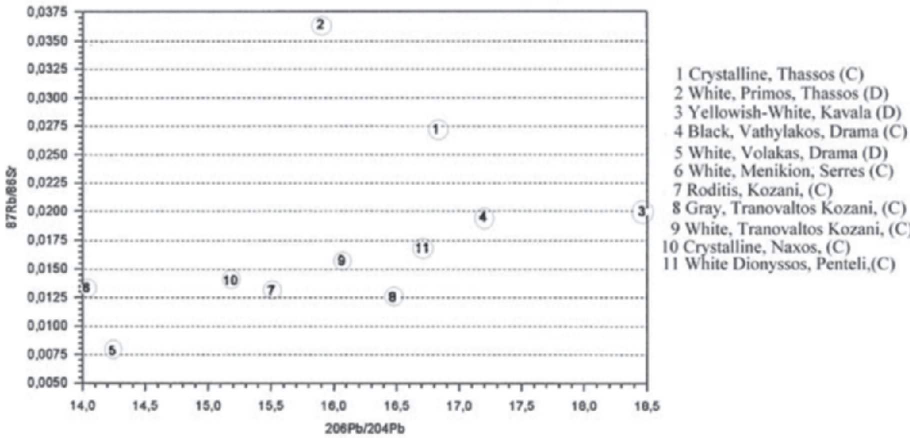


Figure 7. Discrimination of the examined Greek marble occurrences by the means of $^{206}Pb/^{204}Pb$)- ($^{87}Rb/^{86}Sr$)- isotope ratios.

By this representation the different marbles are also separated, but with larger separation distances. The discrimination conditions within the localities remain the same. Here the Thassos marbles (M1, M2) are likewise separated as well as the marbles from Drama (M4, M5). For the marbles from Kozani (M7, M8, M9) the separation is also clearly recognizable. The discrimination of the marbles from Kavala (M3), Naxos (M10) and Dionyssos (M11) is also very good in this representation.

5. CONCLUSIONS, REMARKS

The discussion of the results showed that a more or less clear discrimination, of historical and recent marble objects, can be achieved by using petrological and mineralogical analysis, grain size analysis, trace elements as well as selected isotope ratios. The petrologic and the quantitative mineralogical analysis can classify the marbles regarding their calcitic or dolomitic character. The grain size analysis is a further factor for the characterization of a marble quarry. Trace elements as well as selected isotope analysis can lead to a clear discrimination especially in combination with the above analytical techniques. However, in order to be able to make statistically safe statements regarding the discrimination of the chemographic representations discussed above, substantially more marble samples have to be analyzed, from everyone of the sampled localities. In addition, marble samples from further localities should be analyzed and represented chemographically, in order to confirm the discrimination efficiency of these diagrams.

Furthermore, it is to be examined whether marble occurrences from historically important regions of the Mediterranean area, like Italy, Greece and

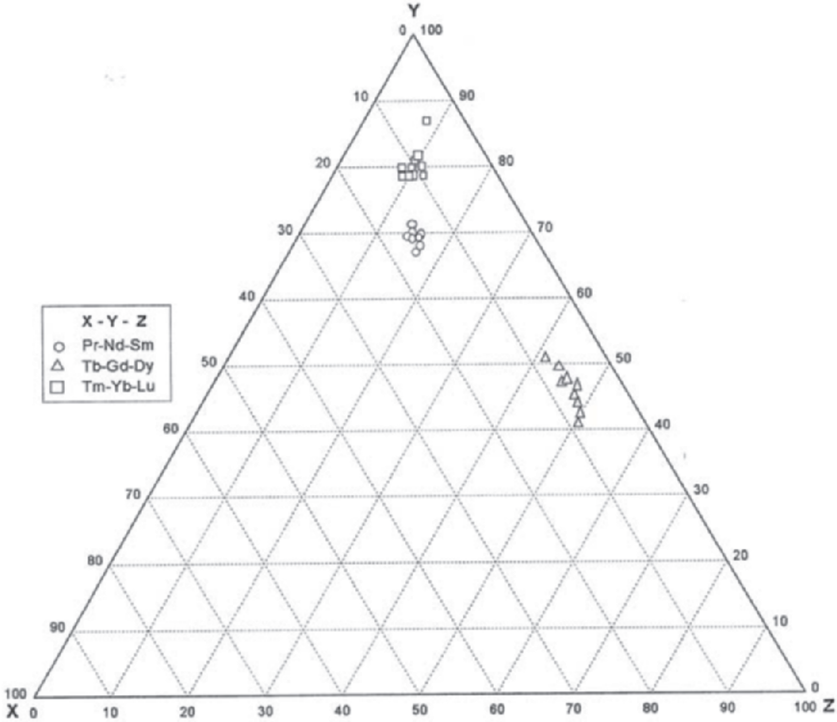


Figure 8. Clusters of the Greek marbles by three different ternary element correlations.

Asia Minor, are separated geochemically. It seems, according to this study, that certain ternary trace element correlations lead to extremely significant groupings of the marbles of Greece (Figure 8). In this ternary diagram, for all examined marble samples, three different REE-correlations were used and graphically projected: Pr-Nd-Sm, Tb-Gd-Dy and Tm-Yb-Lu. It is recognized from this illustration, that all three element correlations gave discrete and significant grouping for the examined Greek marbles.

For the archaeological research it would be therefore interesting to find out, whether marble occurrences from different delivery localities of Mediterranean area, like Italy and Asia Minor, give closed cluster areas, significant and different, as these of Greece. In this case one could use this diagram (Figure 8) to determine and verify first the global delivery region of the marble objects and afterwards by fine solvent diagrams (Figures 5 and 7) to find out the marble queries within the well known large region.

The results of the pilot research project presented here rely only on a small number of samples and are considered therefore as "provisional" and not “representative”. In order to achieve more founded research results, a research project with appropriate financial and personnel resources is to be organized.

REFERENCES

Andreae, B., Oehlschlegel, G., and Weber, K., 1972, Joining the fragments of a Meleagersarkophags in Frankfurt and Kassel, *Yearbook German Archaeological Institut*. **87**: 388-432.

Baietto, V., Villieneuve, G., Schvoerer, M., Bechtel, F., and Heart, N., 1999, Investigation of electron paramagnetic resonance peak into some powdered Greek white marbles, *Archaeometry* **41**(2)**:** 253-265.

Barbin, V., Ramseyer, K., Decrouez, D, Bruns, S. J., Chamay, J., and Maier, J.-l., 1992, Cathodenluminenscence of white marbles: on overview, *Archaeometry* **34:**175-183.

Bruno, M., Lazzarini, L., Soligo, M., Turi B., and Varti-Matarangas, M., 1997, in *Proceedings of the First International Conference on the Archaeology of Paros and the Cyclades*, Paros, 2-5 October 1997.

Coleman, M., and Walker, S., 1979, Stable of isotopes identification of Greek and Turkish of marbles, *Archaeometry* **21:**107-112.

Conforto, L., Felici, M., Monna, D., Serva, L. and Taddeucci, A., 1975, A preliminary evaluation of chemical data (trace of element) from classical marble quarries into the Mediterranean, *Archaeometry* **17:**201-213.

Craig, H., and Craig, V., 1972, Greek of marbles: determination of provenance by isotopic analysis, *Science* **176:**401-403.

Dworakowska, A., 1975, *Quarries of Ancient Greece*, Polish Academy of Sciences, Worclaw.

Gale, N.H., 1979, in *Proceedings of the International Symposium on Archaeometry and Archaeological Prospection*, London, Abstracts 18, 18.

Gast, R., Germann, K., and Eilert, E., 1979, Petrographic and geochemical investigations for the regulation of marbles of brightistic grave places Thessaliens. “La Thessalie, Collection de la Maison de l'Orient Mediterranéen 6, *Série archéologique* **5:**51-62.

Germann, K., 1978, Problems and possibilities, geoscientific certificates of origin for marbles.in: *Minerali raw materials as culture-historical source of information*, edited by H. W. Hennicke, Association of German email specialists. Hagen, 173-190.

Germann, K., Woodman, G., and Winkler, F.J., 1980, Determination of marble provenance: limits of isotopic analysis, *Archaeometry* **22:**99-106.

Gorgoni, C., Lazzarini, L., Pallente, P., and Turi, B., 2002, in *Asmosia 5*, Achetype Publications London.

Herz, N., 1955b, Petrofabrics and classical archaeology, *American journal of Science* **253:**299-305.

Herz, N. and Wenner, D. B., Tracing the Origins of Marble, Archeology **34**: 14-21 (1981).

Herz, N., 1987, Carbon and oxygen isotopic ratios: A data cousin for classical Greek and novel marble, *Archaeometry* **29:**35-43.

Herz, N., and Waelkens, M., Eds., 1988, *Classical marble: geochemistry, technology trade*. NATO ASI Ser. E, 153, Kluwer Academic Publishers, Dordrecht.

Kempe, D.R.C., 1983, in: *The petrology of archaeological artefacts*, 80-153. edited by D. R. C. Kempe, and Harvey, A.P., pp. 374. Clarendon press, Oxford 1983.

Kritsotakis, K., 1994, Mineralogical and geochemical characterisation of the praehistorischen ceramic(s) of Hellbrunnerberg with Salzburg, *Jahrb. RGZM* **41:**145-177.

Lazzarini, L., Moschini, G. and Stievano, B.M., 1980a, A contribution ton the identification of Italian, Greek and Anatolian of marbles through A petrological study and the evaluation of approx./SR ratio, *Archaeometry* **22:**173-182.

Lazzarini, L., Masi, U., and Tucci, P., 1995. *Asmosia III Athens: Petrrographic and geochemical features of the Carystian marble, "Cipollino verde", from the ancient quarries of Southern Euboea (Greece).*

Lazzarini, L., Pensabene, P., and Turi, B., 1995, *Asmosia IV. Isotopic and petrographic characterization of marmor Lesbium, Island of Lesbos, Greece.*

Lazzarini, L, and Cancelliere, S., 2000, Characterization of the white marble of two unpublished ancient Roman quarries on the Islands of Fourni and Skyros (Greece), *Per. Mineral*. **69**(1)**:**49-62.

Lepsius, G.R., 1890, *Greek marble studies*, Papers in Prussian Academy of Sciences to Berlin, Philosophy-historical class, 1-153.

Monna, D., and Pensabene, P., 1977, *Marmi dell'Asia Minore. Consiglio Nazionale della Ricerche*, Rome.

Manfra, L., Masi, A., and Turi, B., 1975, Carbon and oxygen of isotopes ratios of marbles from some ancient quarries of western Anatolia and their archaeological significance *Archaeometry* **17:**215-221.

Marinos, G.P., 1984, Notes on the structure of Greeks of marbles, *American Journal of Science* **246:**386-389.

Martin, R., 1965, *Manuel D ' Architecture Grecque, Volume 1: Matériaux et Tec*hniques. A. and J. Picard, Paris.

Moens, L, Roos, P., and De Rudder, J., 1987, Identification of archaeologically interesting white marbles by instrument valley neutron activation analysis (in a) and petrography: comparison between samples from Afyon to the Usak (Turkey), *J. Trace Microprobe of techniques*, **5**(2/3)**:**101-114.

Moens, L, Roos, P., De Rudder, J., Hoste, J., De Paepe, P., Van Hende, J., Marechal, R. and Waelkens, M., 1988, White marble from Italy and Turkey: on archaeometric study based on minor and of trace element analysis and petrography, *J. Radioanalytical Nuclear Chemistry*, **123**(1)**:**333-348.

Papageorgakis, J.E., 1963, The historical marble quarries of Thessalien, *Praktikà Akadimias Athinon* **38:**564-572 (in Greek).

Papageorgakis, J.E., 1967, The rocks of Greece usable in the marble industry, *Annales Géologiques of the Pays Hélleniques* **18:**193-270.

Renfrew, C. and Peacey, J.S., 1968, Aegean marble, A petrological study, *Annual of the British School RK of Athens* **63:**45-66.

Rybach, L., and Nissen, H.-U., 1965, Neutron activation of Mn and well traces into marbles worked by the ancient Greeks. In: *Radiochemical methods of analysis, Volume I*, Internationally Atomic Energy Commission, Vienna, 105-117.

Schmid, J., Ambuehl, M., Decrouez, D., Mueller, S., and Ramseyer, K., 1999. Quantitative fabric analysis approach ton the discrimination of white marbles, *Archaeometry* **41:**239-252.

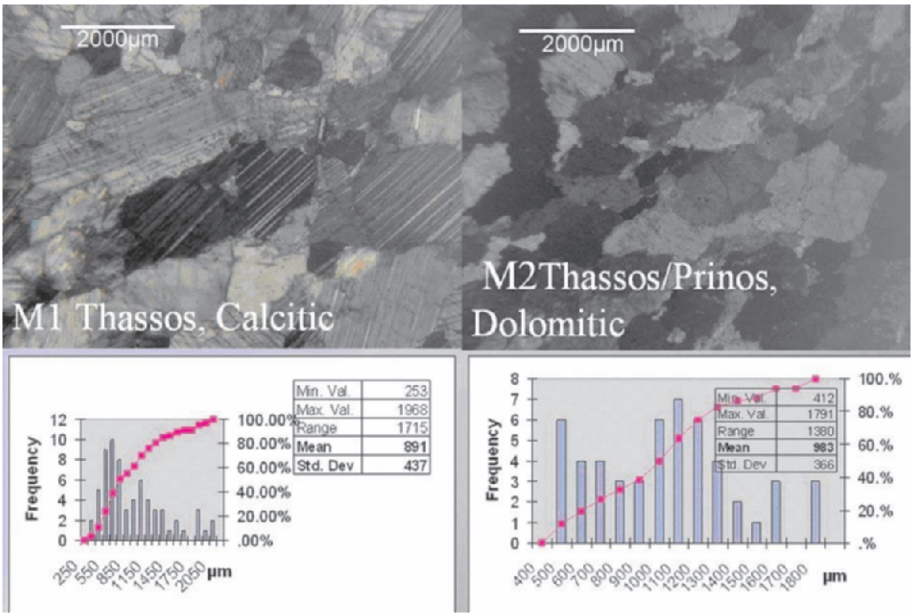
Schneider, G. and Rother, A., 1991, Chemical-mineralogical investigations of people-migration-temporal ceramic(s) of rounding mountain. In, the round mountain of Urach IX., *Heidelberger Acad. Wiss. Schr. Bd.* **15:**190-223.

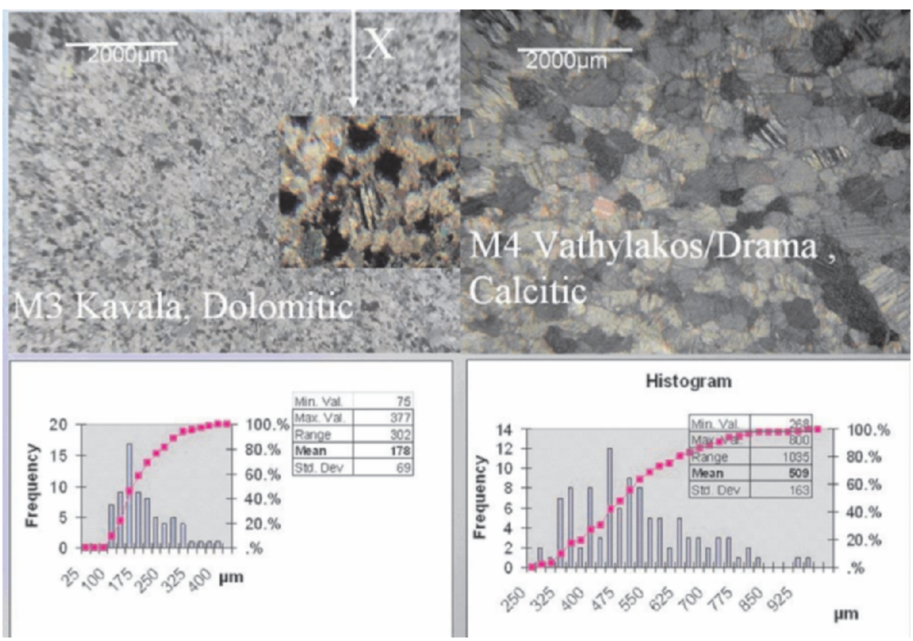
Vakulis, Th., Saatsoglu Paliadeli, Ch., and Maniatis, Y., 2000, in: *Abstracts of the VIth internationally Conference ASMOSIA 2000*, Venice, June 15-18, 2000.

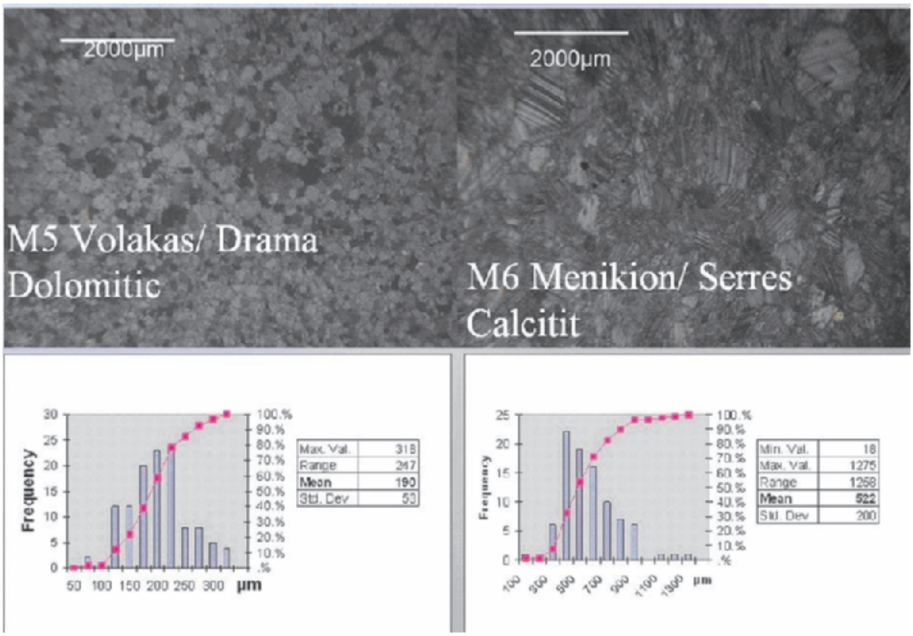
White, L.E., 1954, Fabric analysis of some Greek of marbles and its applications tons archaeology, *American journal of Science* **252:**641-662.

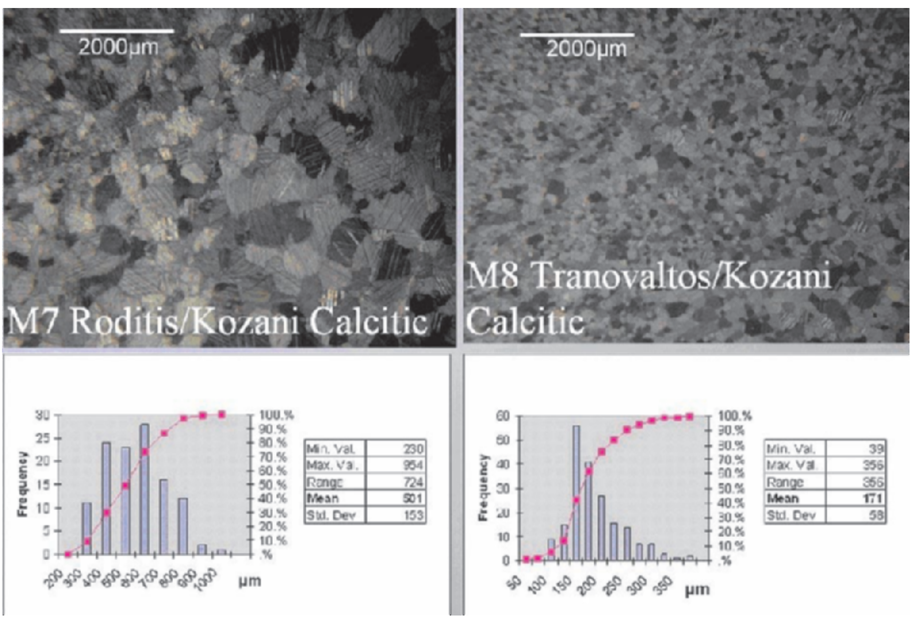
APPENDIX

Microscopic picture of the marble samples and their grain size distribution.






2000µm
M5 Volakas/ Drama
Dolomitic
2000µm
M6 Menikion/ Serres
Calcitit


2000µm
M7 Roditis/Kozani Calcitic
2000µm
M8 Tranovaltos/Kozani
Calcitic