Per. Mineral. (1999), *68*, 2, 145-162

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on *Environmet, Archaeometry* and *Cultural Heritage*

Petrographic and geochemical features of the «Cipollino Verde» marble from the Apuan Alps (northern Tuscany, Italy) and archaeometric implications

CRISTINA NEGRI ARNOLDI[1], ETTORE AZZARO[2], MARIO BARBIERI[3] and PATRIZIA TUCCI[4]*

[1] Via Asiago 8, I-00195 Rome Italy
[2] Dipartimento di Chimica e Fisica della Terra, Università di Palermo, Palermo Italy
[3] Dipartimento di Scienze della Terra, Università di Roma «La Sapienza», P.le Aldo Moro 5, I-00185 Roma, Italy
[4] Centro di Studio per gli Equilibri Sperimentali in minerali e rocce, Dipartimento di Scienze della Terra, Università di Roma «La Sapienza», P.le Aldo Moro 5, I-00185 Roma, Italy

Submitted, November 1998 - Accepted, April 1999

ABSTRACT. — Petrographic and geochemical (major and trace element contents and C, O and Sr isotopic ratios) features of 23 samples of «Cipollino Verde» marbles from the Apuan Alps sectors of Arni, Isola Santa and Monte Corchia (northern Tuscany, Italy) are defined. The results are compared with the «Cipollino Verde» samples quarried, since ancient time, in Euboea (Greece) in order to individualize some discriminating parameters between the Italian and Greek marbles. These would allow to assign archaeological artifacts to their own provenance areas.

The Apuan sectors can be distinguished each other by: the presence of five different lithotypes; the different weight per cent of insoluble residue contents (X_{max}=13.25%, Isola Santa; X_{min}=6.09, Arni); the presence of dolomite. Chemical compositions are homogeneous but Sr and P_2O_5 contents are higher in the Isola Santa and Monte Corchia samples, respectively. Finally, while carbonium (δ^{13}C-PDB=2.16-2.80 ‰) and oxygen (δ^{18}O-PDB=1.6-4.23 ‰) isotopic ratios do not allow any discrimination, strontium isotopic ratios ($^{87}Sr/^{86}Sr$=0.70764-0.71062) make possible to distinguish Arni sector from the others. From the obtained results, the following discriminating parameters can be used: 1) possible presence of dolomite; 2) normalized (5% of insoluble residue) Al_2O_3 *vs* Y; 3) C isotopic ratios only for central and western Euboea; 4) Sr isotopic ratios only for Arni.

RIASSUNTO. — Sono stati caratterizzati dal punto di vista minero-petrografico e geochimico (elementi maggiori ed in traccia, rapporti isotopici del carbonio, ossigeno e stronzio) 23 campioni, rappresentativi del marmo «Cipollino Verde», provenienti dai distretti marmiferi apuani di: Arni, Isola Santa e Monte Corchia (Toscana Settentrionale, Italia). I risultati ottenuti sono stati confrontati con quelli omologhi del marmo «Cipollino Verde» coltivato fin dall'antichità in Eubea (Grecia) al fine di individuare parametri atti a discriminare i marmi italiani da quelli greci. Tali parametri potranno essere utilizzati, in studi archeometrici, per assegnare manufatti archeologici alle loro aree di provenienza.

I tre settori apuani si differenziano tra loro per: presenza di cinque tipi petrografici diversi; differente percentuale in peso del residuo insolubile (Isola Santa, X_{max}= 13,25; Arni, X_{min}= 6,09); partecipazione di dolomite.

La composizione chimica, per contro, risulta omogenea a meno dei contenuti in Sr e P_2O_5 rispettivamente più alti nei campioni di Isola Santa ed in quelli del Monte Corchia. Infine, i valori dei rapporti isotopici del carbonio (δ^{13}C-PDB=2,16-

---

*Corresponding author, E-mail: tuccipa@uniroma1.it
Phone: +39 06 49914912. Fax: +39 06 4454729.

2,80 ‰) e dell'ossigeno (δ^{18}O-PDB=1,6-4,23 ‰) non permettono alcuna discriminazione mentre quelli dello stronzio (0,70764-0,71062) consentono di separare Arni dagli altri due distretti.

Dai risultati ottenuti possono essere considerati parametri discriminanti dei litotipi lapidei apuani e greci: 1) l'eventuale presenza di dolomite; 2) Al_2O_3 contro Y normalizzati al 5% di residuo insolubile; 3) i rapporti isotopici del carbonio limitatamente ai settori dell'Eubea centrale ed orientale; 4) i rapporti isotopici dello stronzio limitatamente al settore apuano di Arni.

KEY WORDS: *«Cipollino Verde», Apuan Alps, petrography, geochemistry, archaeometric implications.*

INTRODUCTION

Petrographic and geochemical features (major and trace elements, δ^{13}C, δ^{18}O and ^{87}Sr/^{86}Sr) of 23 «Cipollino Verde» marbles from Arni, Isola Santa and Monte Corchia, are presented. The results are used to verify if it is possible to distinguish the Apuan marble from the «Cipollino Verde» of the classical greek quarries.

Although it is not clear that the Apuan «Cipollino Verde» was used in antiquity, petrographic and geochemical features of such lithotype can be useful for archaeometric

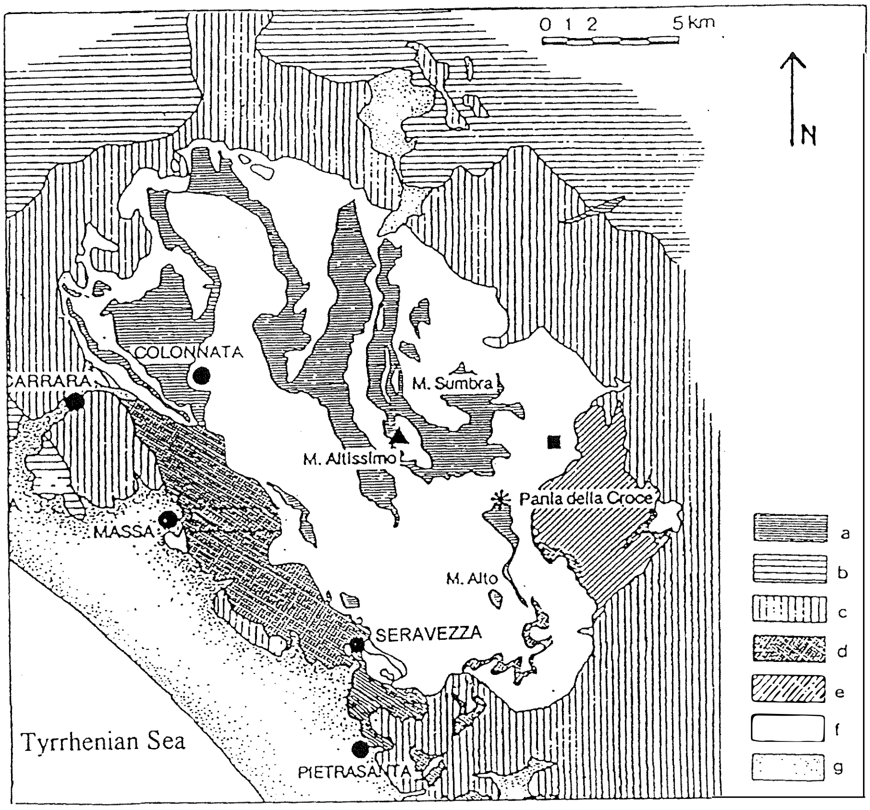

Fig. 1 – Geological sketch map of the Apuan Alps (modified after Carmignani *et al.*, 1993)
▲ = Arni, ■ = Isola Santa, * = M. Corchia
a) marbles; b) Ligurian Complex; c) Tuscan Complex;
d) Parautochthonous Complex; e) Pania Unity; f) autochthonous terranes;
g) alluvial terranes.

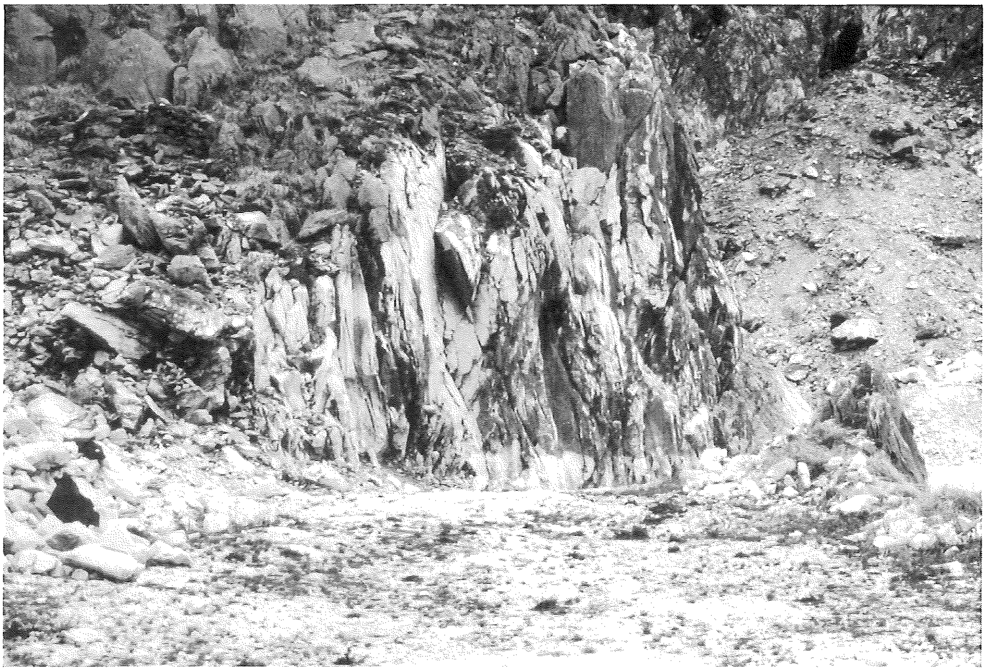

Fig. 2 – The Arni lower quarry.

applications concerning the study of artifacts made of «Cipollino Verde», as it may eventually allow for distinguishing between the Apuan and Euboean lithotypes (Masi *et al.*, 1997). This, in turn, throws light on the provenance of the marble used to make the artifacts and, thus, on marble trade ways.

Taking into account that it is not possible to distinguish «Cipollino Ternario» from «Carystian marble» *via* their isotopic values (Masi *et al.,* 1995; Lazzarini, 1998), in the comparison between Apuan and Greek «Cipollino Verde» the «Cipollino Ternario» from Mani was not considered.

A marble looking quite similar to the «Cipollino Verde» from Euboea crops out in Apuan Alps (northern Tuscany, Italy; fig. 1). Unlike for its classical homologous, petrographic and geochemical characteristics of this lithotype have been studied only marginally (Tucci, 1982); this prompted to undertake the present research.

THE APUAN ALPS AREA AND SAMPLING

The Apuan Alps are located in northern Tuscany (fig. 1). Structurally, they are composed of five thrusted Units, represented by marine sedimentary rocks ranging in age from Cambrian to Tertiary, and named from the bottom to the top: «Unità dell'Autoctono», «Unità di Massa e delle Scaglie di Stazzema», «Unità delle Panie», «Unità Toscana» e «Unità delle Liguridi» (Carmignani *et al.,* 1993). Thrusting responsable for the metamorphic events (T ≅ 450°C, P = 6-8 kbar) of Authochtonous Units took place in middle Miocene during the compressive stage of the Apennine orogenesis. Limestones were changed into marbles: pure limestone into Carrara marble, organic C-rich limestone into Bardiglio marble (Venato and Grigio) and, finally, marly (10-15 % of clay) limestone into «Cipollino Verde» marble.

«Cipollino Verde» occupies the

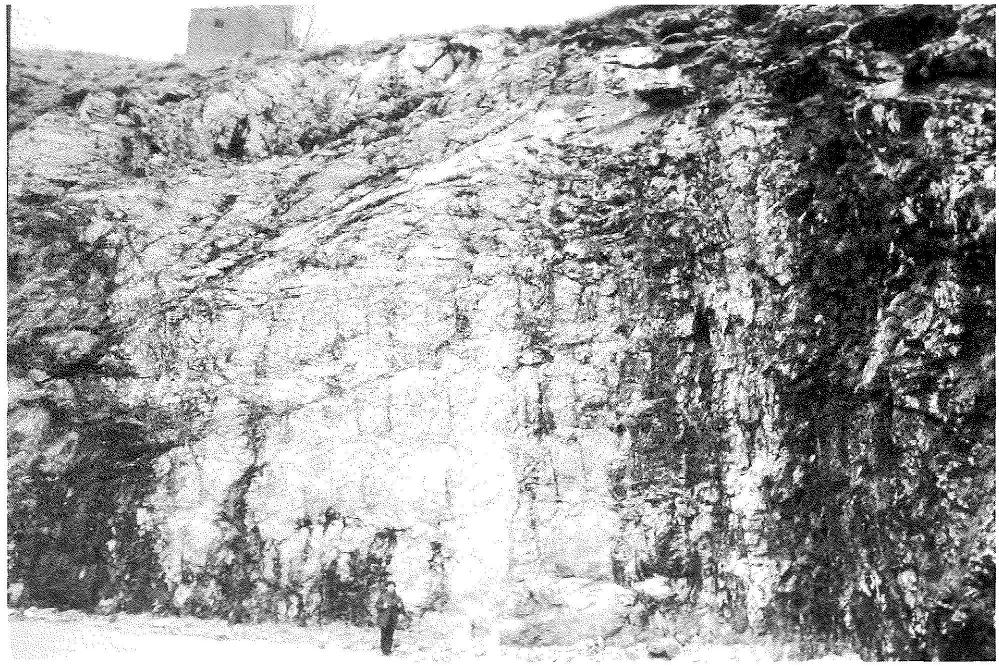

Fig. 3 – The Arni upper quarry showing folded layers.

stratigraphically uppermost position of the Upper Schists within the Marble Suite that includes sericitic schists, cipollins, quartzites and anagenites, crinoid limestones and silex-bearing limestones dated to Lower-Upper Cretaceous (Tucci, 1982; Carmignani *et al.*, 1993).

Studied samples, representatives of all the cropping out lithotypes, were collected from the quarries of the valley of Rio Turrite Secca at Arni and Isola Santa, and from Monte Corchia (fig. 1) along vertical profiles, perpendicularly to rock foliation; these three localities are hereafter referred as A, B and C sectors, respectively. Samples of the sector A belong to two quarries: Lower quarry (Arni-I; 1070 m a.s.l.), not worked since many years, and Upper quarry (Arni-II; located 30 m above the other). Three samples belong to the lower quarry (fig. 2) which has a 3 m-high and very altered front. Ten samples were collected from the Upper quarry which is about 25 m in thickness; it exhibits folded layers and evidents working marks (fig. 3). Seven samples of the B sector come from a quarry located at 575 m a.s.l., where the transition from «Cipollino Verde» to the overlying grey marble is clearly apparent (fig. 4). Finally, three samples of the C sector were collected at 680 m a.s.l. along the muletrail leading from the village of Pruno to that of Foce di Mosceta.

ANALYTICAL PROCEDURE

In order to characterize the collected samples, petrographic, as well as X ray diffraction (XRD), X ray fluorescence (XRF) and isotopic (C, O and Sr) analyses were carried out. XRD analyses were performed on insoluble residue. In this contest, mainly for phyllosilicates study, the powder was oriented and then inserted in the automatic diffractometer (PHILIPS PW 1130/00, CuKα radiation). Major- and trace- element contents

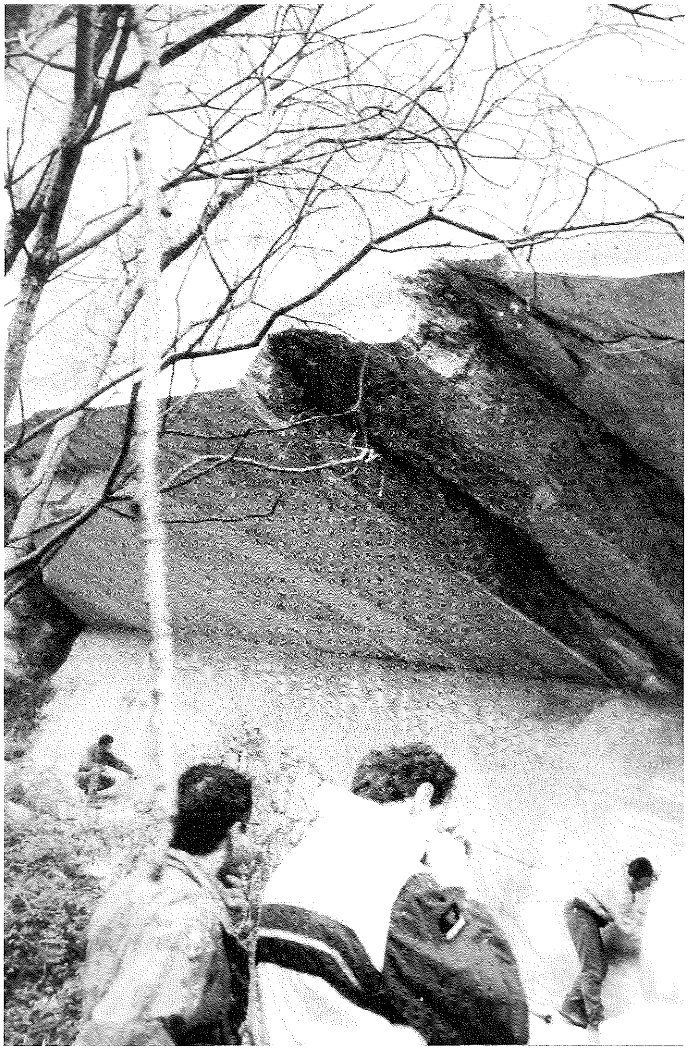

Fig. 4 – Isola Santa quarry with recent working cuts.

were determinated by XRF (SIEMENS spectrometer, Cr anticatode tube). The isotope ratios of the carbonate fraction were determined by mass spectrometry following routine procedure (Mc Crea, 1950; Turi *et al.*, 1976) and the results are reported in per mille against the PDB standard (Craig, 1957). Finally, Sr-isotope ratios were measured on the carbonate fraction obtained by means of a quick dissolution in 2.5 N ultrapure HCl. After centrifugation the solution was passed through a cation exchange column following standard procedures. The isotopic analyses were carried out by means of a VG-54E mass spectrometer; data acquisition and reduction was carried out according to the procedure of Ludwig (1994). Repeated analyses on standards gave averages and errors (2σ) as follow: NBS 987, $^{87}Sr/^{86}Sr$ = 0.710262±15; $^{87}Sr/^{86}Sr$ normalized to 0.1194. Analytical uncertainty is ± 0.00005.

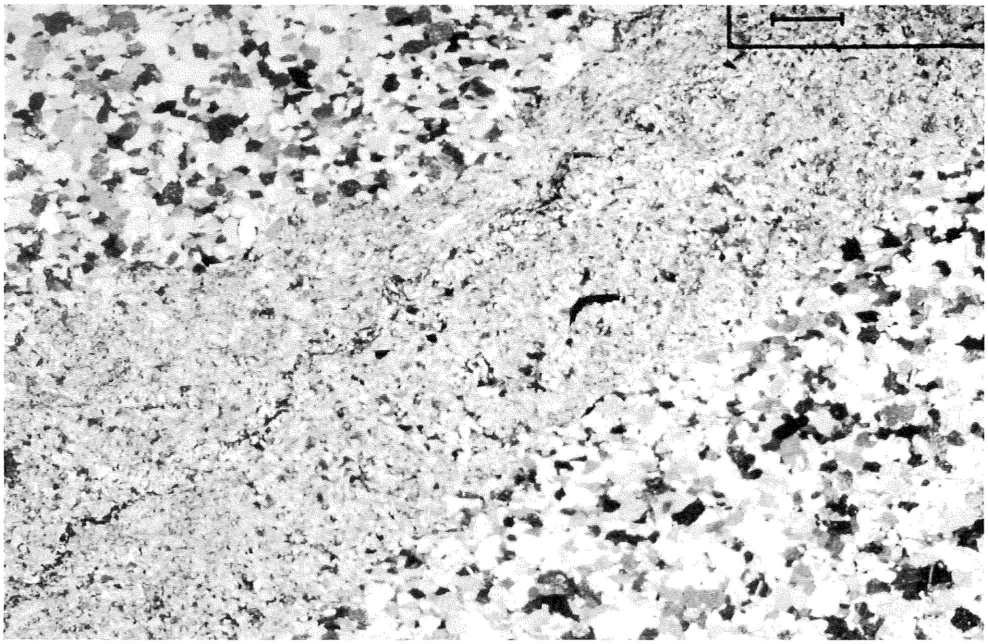

Fig. 5 – Photomicrograph of sample A-I.1 (lithotype I) showing heteroblastic fabric and slightly isotropic texture (crossed polars, 15×).

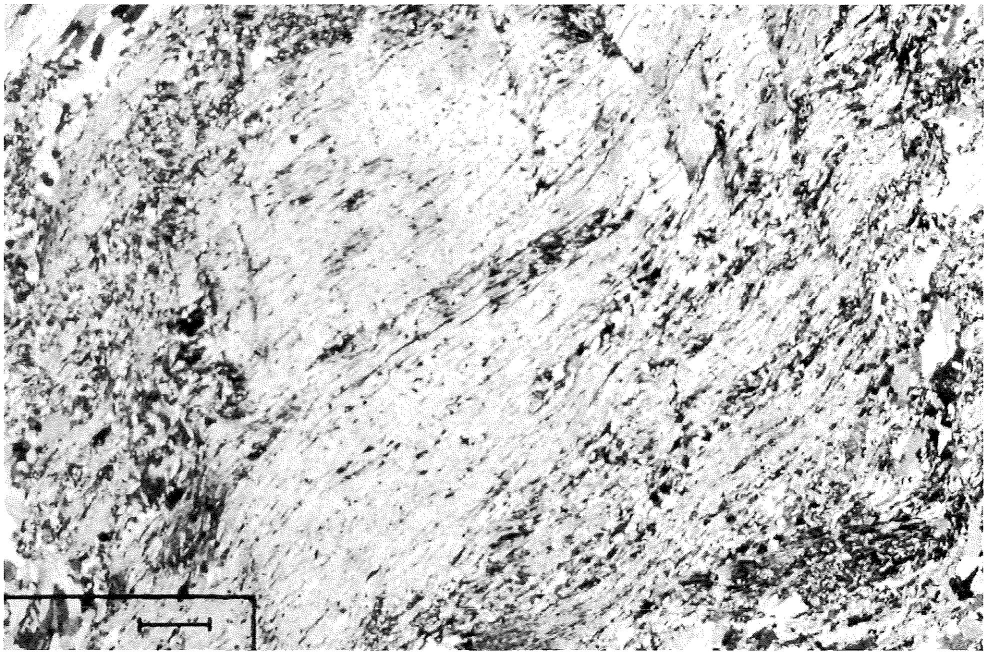

Fig. 6 – Photomicrograph of sample A-II.7 (lithotype II) showing folded phyllosilicates (crossed polars, 2.5×).

EXPERIMENTAL RESULTS

Petrography

Samples of the sector A are composed of dominant calcite; 8 out of 13 samples contain also dolomite.

Two major lithotypes have been identified on the basis of the phyllosilicate abundance.

Lithotype I is phyllosilicate-poor and is characterized by crystalloblastic heteroblastic fabric with slightly isotropic texture (fig. 5). Calcite shows a size ranging between 0.04 and 0.12 mm; larger crystals exhibit polysynthetic twinning and neat cleavage; some samples are characterized by the presence of large overgrown calcite laths. Quartz, albite and phyllosilicates are scarce; the latter (muscovite ($2\theta = 26.90$, Cu kα) and subordinate pennine ($2\theta = 35.00$, Cu kα) occur as thin randomly disseminated needles. Hematite, sphene, ilmenite together with rare pyrite, clinozoisite, rutile and apatite are accessory phases; rutile and apatite are included in quartz.

Lithotype II shows more abundant phyllosilicates, distributed in strongly folded subparallel bands (fig. 6). As results by the microscope identification and by XRD analysis, there are two types of chlorite: pennine ($2\theta = 35.00$ Cu kα) and ripidolite ($2\theta = 25.16$ Cu kα). Growing biotite is less rare than in lithotype I. Ellyptical structures composed of ore minerals, epidote, quartz and chlorites are frequent. Fe-Ti oxides, apatite, rutile, zircon and scarce tourmaline are accessory. Samples of the sector B, that are dolomite-free, show crystalloblastic-lepidoblastic fabric and oriented texture. On the basis of phyllosilicate abundance two major lithotypes are identified.

Lithotype III shows homogeneous grain size (0.30 mm) and is composed of calcite, subordinate quartz, scarce phyllosilicates (chlorite and muscovite) and rare albite (fig. 7); clinozoisite and Fe-Ti oxides (mainly ilmenite) are common accessory minerals.

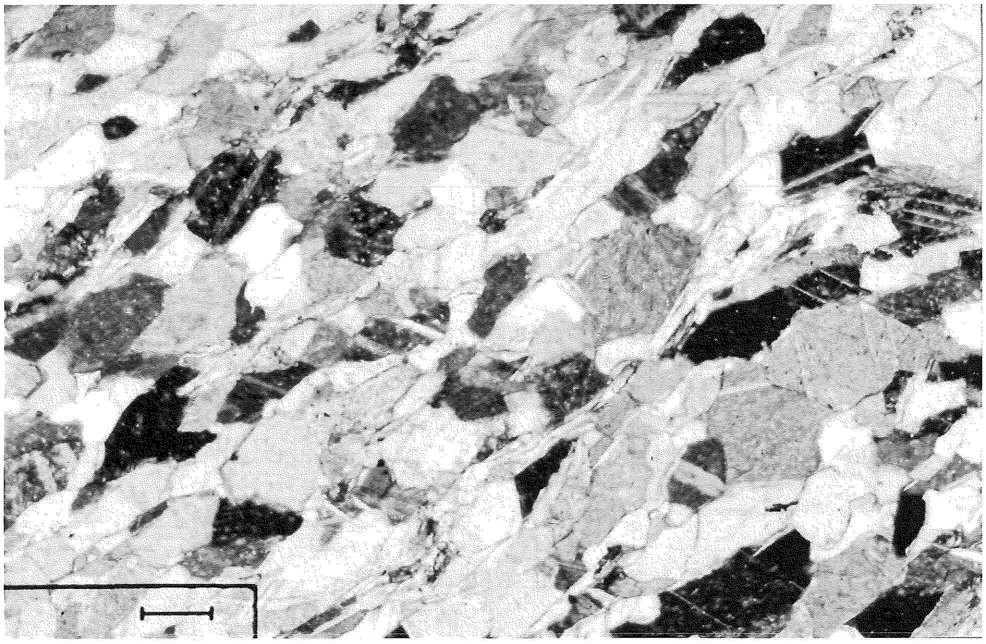

Fig. 7 – Photomicrograph of sample IS-1 (lithotype III) showing isoriented muscovite needles around calcite crystals (crossed polars, 10×).

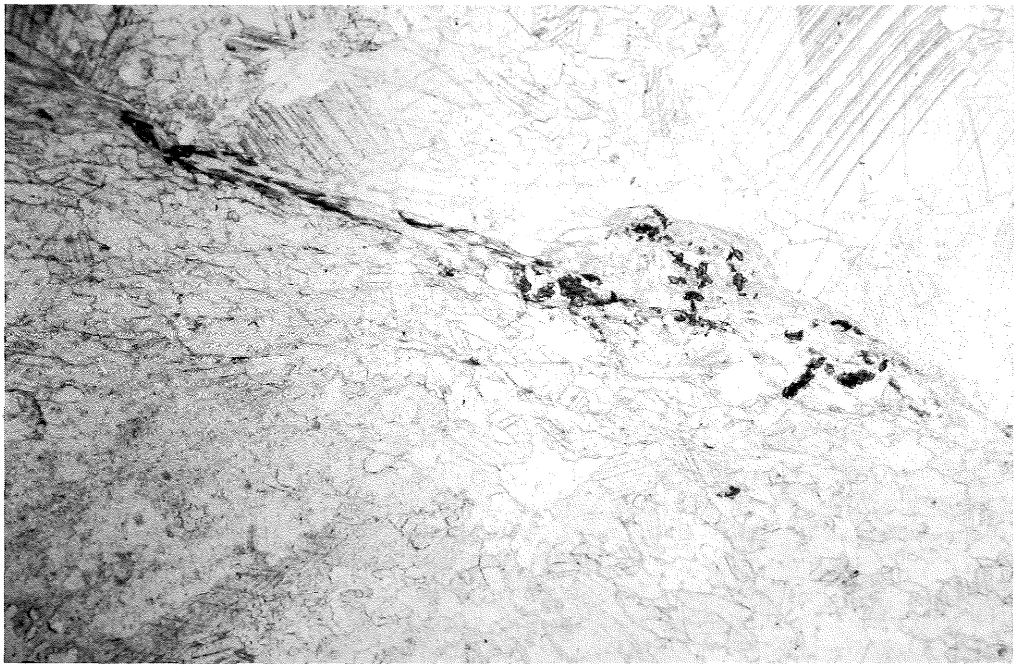

Fig. 8 – Photomicrograph of sample IS-7 (lithotype IV) showing biotite needles bordering chlorite layers (parallel polars, 2.5×).

Lithotype IV shows similar characteristics, but also heterogeneous grain size and abundant phyllosilicates; growing biotite occurs around the chlorite layers (fig. 8); rare hematite crystals, sometimes larger than 0.10 mm, abundant clinozoisite and subordinate zircon and tourmaline are present.

Samples of the sector C (lithotype V) are rather homogeneous, exhibiting saccharoid fabric and wide, slightly ondulated, layers of phyllosilicates. Main minerals are calcite, quartz (xenoblasts), albite, K-mica, chlorite, scarce dolomite and rare growing biotite; disseminated Fe, Ti-oxides, apatite (often included in calcite) and scarce rutile are accessory minerals.

Geochemistry

Major- and trace-element contents are listed in Table 1. C-, O- and Sr-isotope ratios have been carried out on selected samples choosen on the basis of elemental Sr and tickness of outcrops (Table 2).

Samples of the sector A show the largest range of insoluble residue; those of sectors B and C exhibit the highest and lowest contents, respectively. The average composition of the insoluble residue is mainly represented of SiO_2 (46, 50 and 47 wt% for the A, B and C sectors, respectively) and Al_2O_3 (23, 29 and 18 wt%); while MgO (7, 6 and 6 wt%), Fe_2O_3tot (6.6, 8.3 and 6 wt%) and K_2O (4.5, 4.8 and 4.7%) are subordinate. MnO (2.2, 1.0 and 0.6 wt%), TiO_2 (1.3, 0.8 and 0.8 wt%) and P_2O_5 (2, 0.3 and wt 5.6%) are scarce. Na_2O is very low in all samples, especially in those from the A and C sectors. Average values of P_2O_5, also considering the standard deviation values, distinguish the C sector samples from the others.

Among trace elements, Sr is the most abundant; it is mainly contained in the soluble fraction. Its high contents distinguish the B

TABLE 1

Major (wt%) and trace (ppm) element contents of dolomite-bearing (*) and dolomite-free samples of «Cipollino Verde» marble from three sectors of the Apuan Alps. n.d. = below detection limit; IR = insoluble residue.

Samples	**A-I.1***	**A-I.2***	**A-I.3**	**A- I**		**A-II.1***	**A-II.2***	**A-II.3**	**A-II.4***	**A-II.5***	**A-II.6***	**A-II.7**	**A-II.8***	**A-II.9**	**A-II.10**	**A- II**		**Arni**	
				X	±σ											X	±σ	X	±σ
SiO_2	2.10	1.84	1.60	1.85	0.25	0.65	1.78	3.35	0.77	2.71	1.21	13.88	1.89	6.01	2.60	3.49	3.97	3.11	3.51
TiO_2	0.06	0.06	0.04	0.05	0.01	0.03	0.05	0.08	0.03	0.06	0.04	0.20	0.06	0.08	0.07	0.07	0.05	0.07	0.04
Al_2O_3	1.12	1.03	0.72	0.96	0.21	0.38	1.07	1.55	0.45	1.39	0.64	4.98	1.18	1.74	1.34	1.47	1.32	1.35	1.16
Fe_2O_3 tot.	0.30	0.32	0.28	0.30	0.02	0.07	0.25	0.57	0.07	0.46	0.14	1.30	0.20	0.75	0.47	0.43	0.38	0.40	0.34
MnO	0.08	0.08	0.08	0.08	0.00	0.08	0.08	0.13	0.08	0.08	0.09	0.10	0.07	0.14	0.10	0.10	0.02	0.09	0.02
MgO	1.10	0.99	0.76	0.95	0.17	0.62	1.28	0.90	0.45	2.40	0.50	2.51	0.96	1.09	0.96	1.17	0.73	1.12	0.64
CaO	52.88	54.12	54.21	53.74	0.74	54.73	52.71	52.03	54.76	51.04	53.99	42.24	52.97	50.47	53.10	51.80	3.65	52.25	3.29
Na_2O	n.d.	n.d.	n.d.			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				
K_2O	0.23	0.24	0.17	0.21	0.04	0.06	0.19	0.33	0.05	0.30	0.09	0.92	0.21	0.27	0.24	0.27	0.25	0.25	0.22
P_2O_5	0.05	0.06	0.22	0.11	0.10	0.04	0.06	0.05	0.03	0.09	0.04	0.15	0.08	0.04	0.06	0.06	0.04	0.07	0.05
LOI	42.06	42.25	41.91	42.07	0.17	43.33	42.53	41.00	43.30	41.44	42.46	33.70	42.37	39.40	41.66	41.12	2.86	41.34	2.51
Total	99.98	100.99	99.99	100.32	0.58	99.99	100.00	99.99	99.99	99.97	99.20	99.98	99.99	99.99	100.60	99.98	0.33	100.05	0.40
Rb	15	11	15	13.67	2.31	13	11	17	8	17	9	39	14	14	10	15.20	8.92	14.85	7.81
Sr	146	121	120	129.00	14.73	150	124	228	125	121	144	188	137	227	169	161.30	40.67	153.85	38.44
Ba	44	32	38	38.00	6.00	32	30	75	19	73	18	303	37	86	66	73.90	84.25	65.62	74.68
La	11	n.d.	11	7.33	6.35	n.d.	n.d.	6	5	6	n.d.	10	6	11	10	5.40	4.25	5.85	4.58
Ce	6	24	n.d.	10.00	12.49	n.d.	n.d.	18	n.d.	17	6	32	6	n.d.	18	9.70	11.02	9.77	10.82
Y	25	26	40	30.33	8.39	25	29	26	26	25	25	39	31	26	29	28.10	4.36	28.62	5.19
Zr	12	8	9	9.67	2.08	4	6	9	4	11	n.d.	41	8	11	12	10.60	11.34	10.38	9.86
Ni	20	15	10	15.00	5.00	5	7	28	5	14	6	71	8	27	17	18.80	20.29	17.92	17.76
Cr	10	5	12	9.00	3.61	3	5	11	n.d.	6	4	30	4	12	8	8.30	8.45	8.46	7.47
V	9	9	n.d.	6.00	5.20	n.d.	5	15	3	17	3	28	3	6	9	8.90	8.66	8.23	7.90
IR	4.52	4.61	3.87	4.33	0.40	1.50	3.92	6.90	1.48	5.92	2.61	24.00	3.90	10.12	5.84	6.62	6.66	6.09	5.85

TABLE 1: *Continued*

B Sector (Isola Santa)

Samples	IS-1	IS-2	IS-3	IS-4	IS-5	IS-6	IS-7	IS	
								X	±σ
SiO_2	6.64	5.87	6.26	4.98	5.10	7.82	9.10	6.54	1.49
TiO_2	0.11	0.11	0.11	0.09	0.10	0.12	0.12	0.11	0.01
Al_2O_3	3.70	3.71	3.42	3.05	3.01	4.69	5.37	3.85	0.87
Fe_2O_3 tot.	0.97	1.00	0.88	0.88	0.79	1.65	1.59	1.11	0.36
MnO	0.13	0.13	0.12	0.14	0.14	0.14	0.13	0.13	0.01
MgO	0.65	0.81	0.61	0.70	0.60	0.77	0.92	0.72	0.12
CaO	47.94	48.07	48.26	49.51	49.95	46.44	44.25	47.77	1.93
Na_2O	0.13	0.13	0.15	0.04	0.14	0.05	0.12	0.11	0.04
K_2O	0.63	0.60	0.53	0.46	0.48	0.92	0.85	0.64	0.18
P_2O_5	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.00
LOI	39 06	39.53	39.61	40.10	39.65	37.38	37.49	38.97	1.09
Total	100.00	100.00	99.99	99.99	100.00	100.02	99.98	99.99	0.01
Rb	31	26	29	21	23	42	37	29.86	7.54
Sr	787	830	816	832	848	779	779	810.14	28.33
Ba	156	162	163	147	111	221	207	166.71	37.00
La	15	15	10	15	15	15	14	14.14	1.86
Ce	6	11	6	23	12	28	22	15.43	8.83
Y	27	36	34	27	31	27	34	30.86	3.89
Zr	35	40	38	32	36	44	41	38.00	4.04
Ni	24	29	26	24	21	25	27	25.14	2.54
Cr	23	19	17	16	18	35	28	22.29	6.97
V	23	23	28	22	26	34	40	28.00	6.71
IR	13.00	12.40	12.12	10.38	10.40	16.20	18.24	13.25	2.94

C Sector (monte Corchia)

Samples	MC-1	MC-2	MC-3	M C	
				X	±σ
SiO_2	3.25	2.25	6.79	4.10	2.39
TiO_2	0.08	0.07	0.07	0.07	0.01
Al_2O_3	1.67	1.23	1.79	1.56	0.29
Fe_2O_3 tot	0.42	0.32	0.75	0.50	0.23
MnO	0.05	0.03	0.06	0.05	0.02
MgO	2.53	1.23	0.67	1.48	0.95
CaO	50.06	52.86	49.60	50.84	1.76
Na_2O	0.28	0.01	0.12	0.14	0.14
K_2O	0.37	0.32	0.51	0.40	0.10
P_2O_5	0.43	0.8	0.21	0.48	0.30
LOI	41.17	40.89	39.58	40.55	0.85
Total	100.31	100.01	100.15	100.17	0.16
Rb	12	20	15	15.67	4.04
Sr	155	158	846	386.33	398.09
Ba	14	29	30	24.33	8.96
La	8	8	7	7.67	0.58
Ce	2	8	7	5.67	3.21
Y	17	42	30	29.67	12.50
Zr	4	9	7	6.67	2.52
Ni	21	10	15	15.33	5.51
Cr	12	12	10	11.33	1.15
V	16	9	10	11.67	3.79
IR	7.01	5.99	10.37	7.79	2.29

TABLE 2

Carbon, oxygen and strontium isotopic compositions of selected samples of «Cipollino Verde» from the Apuan Alps.

		Samples	$\delta^{13}C$ (PDB)	$\delta^{18}O$ (PDB)	$^{87}Sr/^{86}Sr$
SECTORS	**A**	**A-I.1***	2.70	-2.67	0.70852
		A-I.2*	2.60	-3.16	0.70794
		A-I.3	2.80	-1.61	0.70786
		X ±σ	2.70±0.10	-2.48±0.79	0.70811
		A-II.1*	2.70	-2.29	
		A-II.2*	2.60	-2.48	
		A-II.3	2.50	-3.55	0.70894
		A-II4*	2.70	-2.77	
		A-II.5*	2.60	-3.16	
		A-II.6*	2.50	-3.26	0.70817
		A-II.7	2.60	-4.13	
		A-II.8*	2.50	-2.67	0.70822
		A-II.9	2.60	-4.23	0.71002
		A-II.10	2.60	-3.06	
		$\overline{X}$ ±σ	2.60±0.07	-3.16±0.66	0.70948
	B	**IS-1**	2.50	-3.16	
		IS-2	2.50	-3.26	0.70794
		IS-3	2.60	-3.06	
		IS-4	2.40	-3.26	0.70792
		IS-5	2.30	-3.26	0.70789
		IS-6	2.40	-3.45	
		IS-7	2.50	-3.35	0.70793
		X ±σ	2.46±0.10	-3.26±0.13	0.70794
	C	**MC-1***	2.54	-2.14	0.70804
		MC-2*	2.65	-2.09	0.70764
		MC-3*	2.16	-2.17	
		X ±σ	2.45±0.26	-2.13±0.04	0.70784

sector samples from the others. Ba, that is the second most abundant trace element, is essentially contained in the insoluble residue, of which it (on average) represents 35, 45 and 13.6 ppm, respectively for the A, B and C sectors. Ba can be discriminant among the samples from the three sectors The distinction fails if the A sector samples are disaggregated into the Arni-I and Arni-II groups and only dolomitic samples are considered. Among the other trace elements of the insoluble residue, Y is more abundant in the A and C sectors (average values = 18.4 and 16.5 ppm, respectively) than in B sector (average value = 8.3 ppm), whereas Zr is lower (average values = 6.4, 3.7 and 10.3 ppm, respectively). However, considering the entire range, Zr is not discriminant between the A and B sectors. Moreover, separating the A sector into the Arni-I and Arni-II groups and taking only

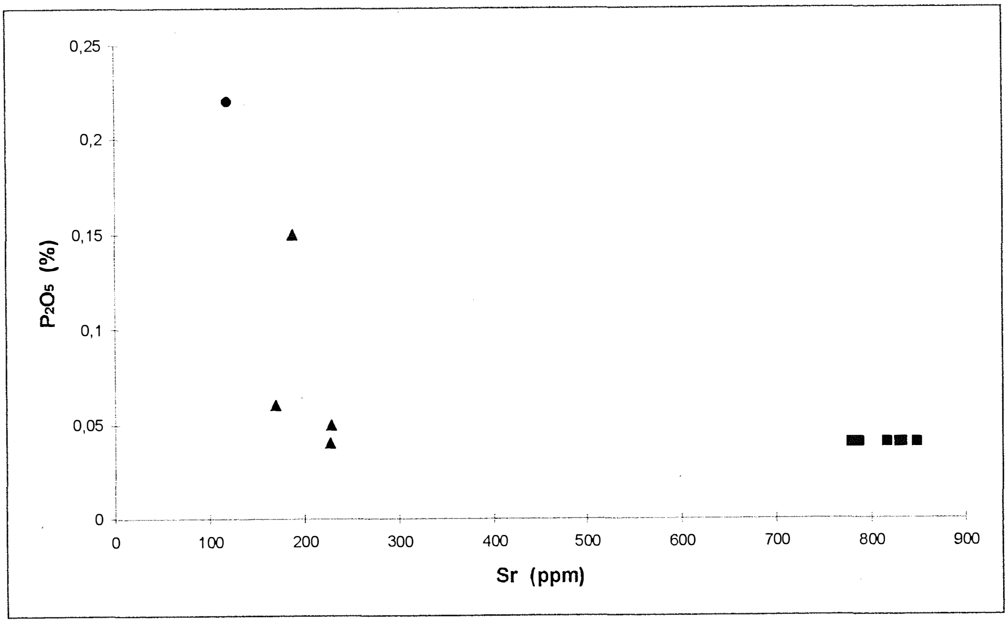

Fig. 9 – P_2O_5 *vs* Sr diagram for dolomite-free samples of «Cipollino Verde» from the Apuan quarries (● = Arni I, ▲ = Arni II, ■ = Isola Santa).

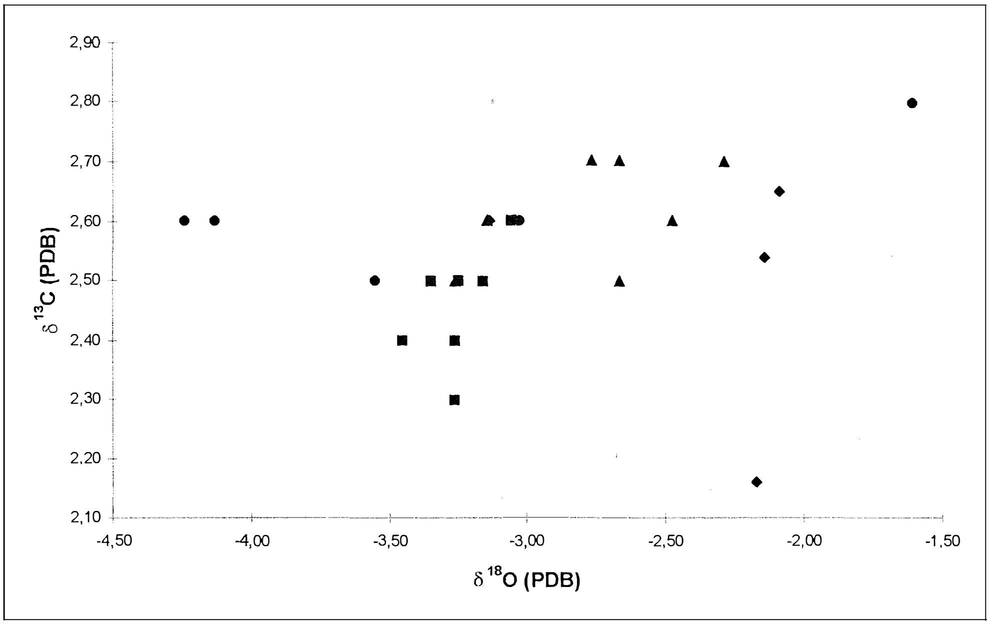

Fig. 10 – Plot of carbon and oxygen isotopic ratios for samples of «Cipollino Verde» from the Apuan Alps. (▲ = Arni with dolomite, ● = Arni dolomite-free, ■ = Isola Santa, ◆ = Mt. Corchia).

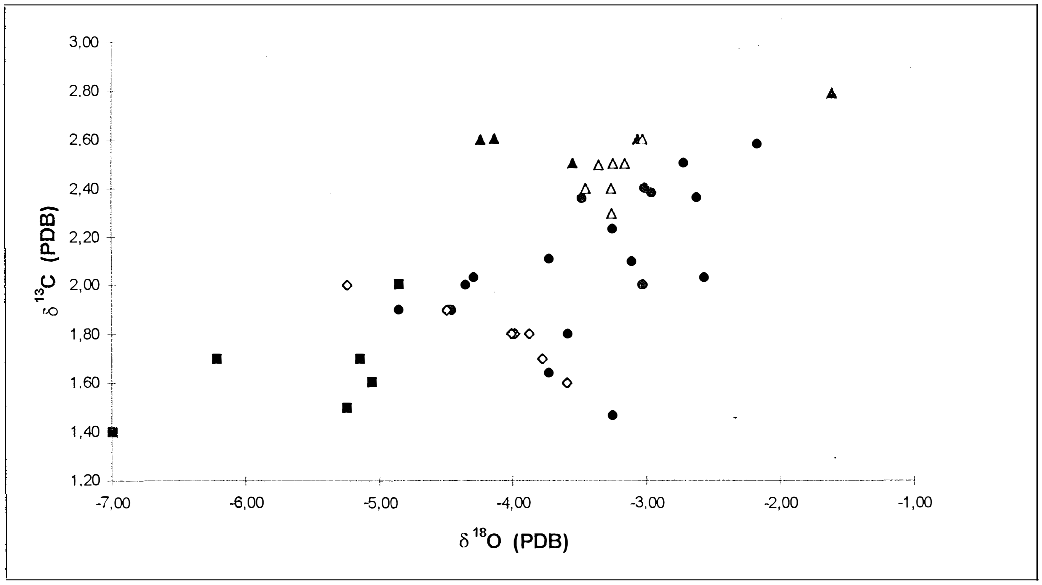

Fig. 11 – Isotopic composition of the carbonate of «Cipollino verde» marble from the Apuan Alps and Euboea (▲ = Arni, Δ = Isola Santa, ■ = eastern Euboea, ◇ = central Euboea, ● = western Euboea).

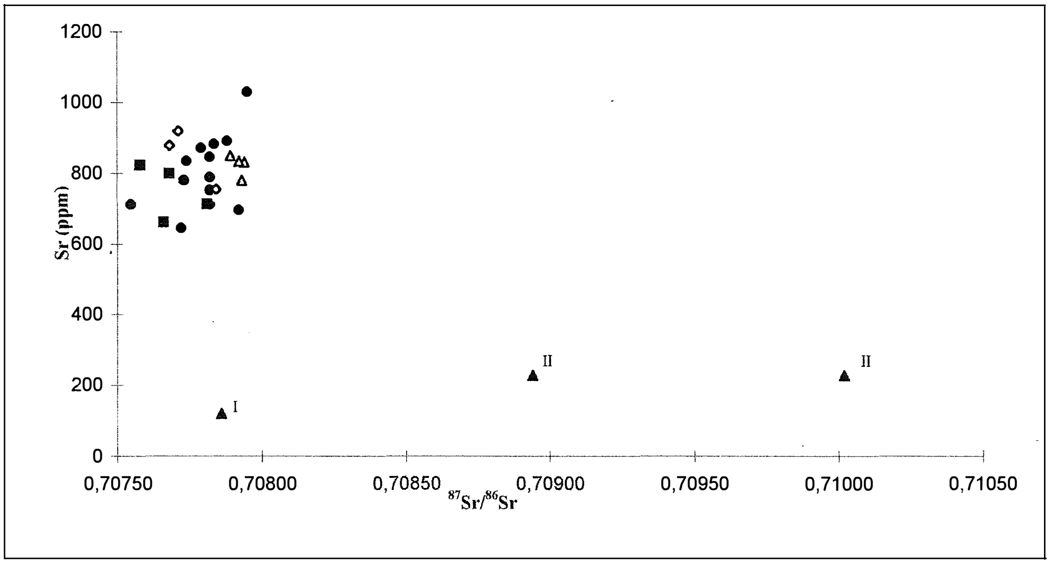

Fig. 12 – Plot of elemental Sr and Sr isotopic composition in the «Cipollino Verde» from the Apuan Alps (only dolomite-free samples) and southern Euboea. (▲ = Arni, Δ = Isola Santa, ■ = eastern Euboea, ◇ = central Euboea, ● = western Euboea).

dolomite-free samples, also Y is not a reliable discriminating element. Finally, Rb, Ni, V, Cr, Ce and La do not discriminate the samples from the three sectors.

Fig. 9 shows the P_2O_5 *vs* Sr diagrams for dolomite-free samples with respect to the sector of provenance.

Finally, considering isotopic ratios, the samples show a narrow range of $\delta^{13}C$ values (2.16 to 2.80‰, Table 2), while the ranges of $\delta^{18}O$ and Sr-isotopes are larger (-1.61 to -4.23 and 0.70764 to 0.71002, Table 2). The isotopic ratios do not distinguish among the samples from the three sectors (fig. 10).

COMPARISON WITH THE «CIPOLLINO VERDE» MARBLE FORM EUBOEA

From a petrographic point of view, the Apuan and Euboean marbles are quite similar. The presence of dolomite in several Apuan and its absence in all Euboean samples may represent a diagnostic feature; on these basis, dolomite in archaeological artifacts made up of «Cipollino Verde» marble excludes their provenance from the Greek quarries.

Average chemical compositions of dolomite-free samples of both Apuan and Euboean «Cipollino Verde» (Lazzarini *et al.*, 1995; Masi *et al.*, 1996, 1999) are reported in Table 3. It is apparent that the Apuan samples cannot be chemically distinguished from the Euboean samples. Apuan samples can be distinguished from those of central and eastern Euboea taking into account their higher C isotope ratios, while some overlap between western Euboea and Apuan Alps exists (Tables 2 and 4, fig. 11). Finally Sr isotope ratios of the Apuan samples overlap those of the Euboean samples with the exception of those from the Arni-II ones, that exhibit higher values (Tables 2 and 5, fig. 12).

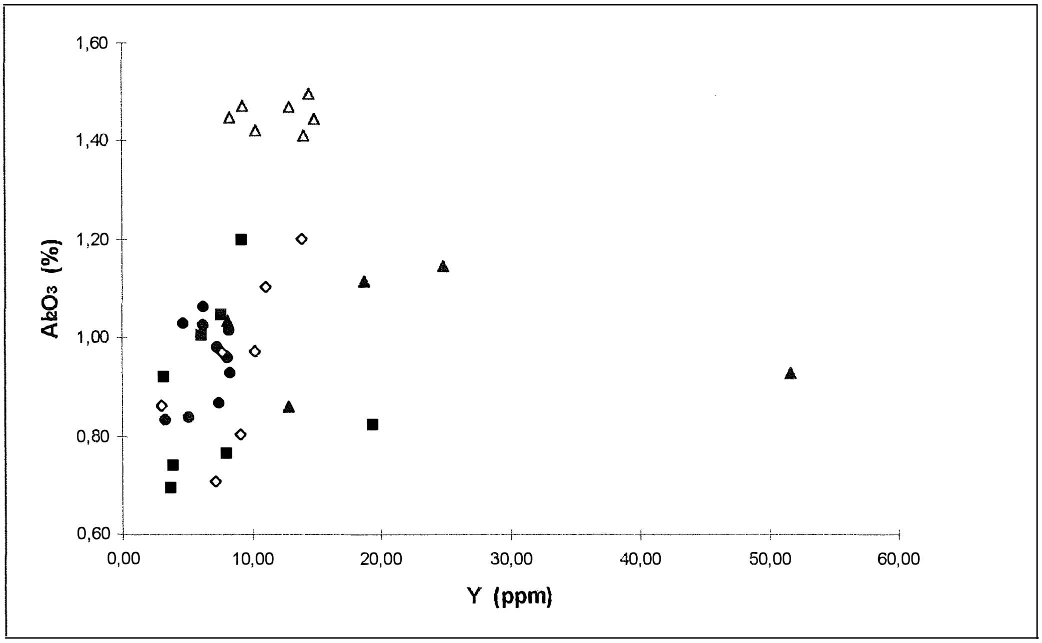

Fig. 13 – Plot of Y and Al_2O_3 contents in the «Cipollino Verde» from the Apuan Alps (only dolomite-free samples) and Southern Euboea. Contents are normalized to 5 wt% of IR (see text). (▲ = Arni, Δ = Isola Santa, ■ = eastern Euboea, ◇ = central Euboea, ● = western Euboea).

TABLE 3

Average major and trace element contents of «Cipollino verde» samples from the three districts (W = western, C = central and E = eastern) of Euboea (Masi et al., *1996 and 1999) and dolomite-free samples form Apuan Alps.*

	W E		**C E**		**E E**		**Ar ni**		**Isola Santa**	
	X	**±σ**	**X**	**±σ**	**X**	**±σ**	**X**	**±σ**	**X**	**±σ**
SiO_2	5.61	0.91	4.50	0.69	4.62	2.21	5.49	4.97	6.54	1.49
TiO_2	0.07	0.01	0.07	0.01	0.07	0.04	0.09	0.06	0.11	0.01
Al_2O_3	1.96	0.18	1.53	0.28	1.45	0.75	2.07	1.67	3.85	0.87
Fe_2O_3tot.	1.07	0.07	0.67	0.10	0.66	0.35	0.67	0.39	1.11	0.36
MnO	0.11	0.01	0.10	0.00	0.09	0.02	0.11	0.02	0.13	0.01
MgO	0.86	0.02	0.63	0.08	0.64	0.29	1.24	0.72	0.72	0.12
CaO	50.10	0.71	51.56	0.70	51.60	2.17	50.41	4.77	47.77	1.93
Na_2O	0.07	0.02	0.04	0.04	0.04	0.04	n.d.		0.11	0.04
K_2O	0.37	0.02	0.33	0.07	0.26	0.15	0.39	0.30	0.64	0.18
P_2O_5	0.04	0.01	0.03	0.00	0.03	0.00	0.10	0.08	0.04	0.00
LOI	39.80	0.84	40.42	0.59	40.55	1.73	39.53	3.40	38.97	1.09
Total	100.06	0.35	99.98	0.02	100.01	0.01	100.10	0.27	99.99	0.01
Rb	16.18	0.19	19.50	3.54	21.63	6.55	19.00	11.47	29.86	7.54
Sr	815.58	57.01	772.50	28.99	788.50	105.30	186.40	44.98	810.14	28.33
Ba	148.35	21.24	100.50	9.19	118.75	64.46	113.60	107.36	166.71	37.00
La	7.90	1.66	8.50	2.12	6.63	2.92	9.60	2.07	14.14	1.86
Ce	10.99	1.71	11.00	1.41	15.75	8.58	13.60	13.67	15.43	8.83
Y	13.58	1.42	13.00	4.24	9.50	3.82	32.00	6.96	30.86	3.89
Zr	8.00	1.73	22.00	0.00	22.63	10.45	16.40	13.81	38.00	4.04
Ni	38.85	3.16	20.00	4.24	21.25	11.97	30.60	23.78	25.14	2.54
Cr	46.67	25.57	25.50	4.95	21.88	26.47	14.60	8.76	22.29	6.97
V	20.11	5.43	22.00	4.24	15.63	8.70	11.60	10.64	28.00	6.71
IR	10.10	1.24	7.97	1.36	7.85	3.69	10.15	8.07	13.25	2.94

An effective distinction between the Apuan and Euboean samples can be obtained comparing Al_2O_3 and Y contents of the insoluble residues; in fig. 13, where Al_2O_3 and Y are normalized to 5 wt% of insoluble residue, the distinction between Euboean and Apuan samples is apparent.

CONCLUSIONS

In the Apuan Alps area, five lithotypes of «Cipollino Verde» marble have been petrographically characterized. Lithotypes I and II belong to the sector A (Arni area); lithotype I is phyllosilicates-poor, with heteroblastic crystalloblastic fabric and slightly isotropic texture, lithotype II shows more abundant phyllosilicates in large folded bands.

Other two lithotypes (III and IV) belong to the sector B (Isola Santa area); type III shows scarce phyllosilicates and homogeneous grain size, type IV presents abundant phyllosilicates and heterogeneous grain size.

In the sector C (Mt. Corchia) only one lithotype (type V), with saccharoid structure

TABLE 4

Carbon and oxygen isotopic composition of selected samples of «Cipollino Verde» form the Euboea (W = western, C = central, E = eastern). P = Pyrgari, US = Upper Styra, LS = Lower Styra, V = Vatesion, B = Brethela, K = Karystos.

		Samples	δ^{13}C (PDB)	δ^{18}O (PDB)
		P-I.1	2.58	-2.17
S		**P-I.5**	2.36	-3.48
		P-I.6	2.23	-3.25
		P-I.7	2.11	-3.73
		P-II.1b	2.03	-4.29
		P-II.4	1.80	-3.58
E		**P-II.5**	2.38	-2.96
		US-I.1	2.40	-3.01
		US-I.4	2.10	-3.11
	W	**US-II.2**	1.47	-3.25
		US-III.2	2.50	-2.72
C		**US-III.5**	2.00	-3.01
		LS-I.1	2.36	-2.62
		LS-I.4	1.64	-3.73
		LS-III.3	2.03	-2.57
		LS-IV.1	1.90	-4.46
T		**LS-V.1**	1.90	-4.85
		LS-V.2	2.00	-4.37
		$\bar{X}\pm\sigma$	2.10±0.30	-3.40±0.73
		V-I.4	1.60	-3.59
		V-II.2	1.80	-3.88
O		**V-III.5**	1.70	-3.78
	C	**B-I.3**	1.80	-3.98
		B-II.1a	1.80	-3.98
		B-III.5	2.00	-5.24
		B-IV.3	1.90	-4.46
R		$\bar{X}\pm\sigma$	1.80±0.13	-4.13±0.56
		K-I.3	1.40	-6.99
		K-I.4	1.70	-5.14
	E	**K-III.1a**	1.50	-5.24
		K-V.I	1.70	-6.21
S		**K-VI.4**	2.00	-4.85
		K-VII.2	1.60	-5.05
		$\bar{X}\pm\sigma$	1.65±0.21	-5.58±0.84

and large bands of slightly bended phyllosilicates, was found.

All the samples can be distinguished into two groups: dolomite-bearing and dolomite-free. The samples from the sector B are all dolomite-free.

The samples from the various sectors are, chemically, rather homogeneous; only P_2O_5 and Sr distinguish the samples from the sectors C and B. If samples from the sector A are considered as a whole, Ba and Y can be used as discriminant element.

The very narrow C isotope ratios range (2.16 to 2.80‰) is not useful to distinguish among the various samples. Also unuseful, for discriminating purpose, are the larger range of O and Sr isotope ratios (-1.6 to -4.23 ‰ and 0.70764 to 0.71002, respectively).

Petrographic, chemical and isotopic comparisons between Apuan and Euboean «Cipollino Verde» samples show large overlap; however, it is possible to distinguish between

TABLE 5

Strontium isotopic composition of selected samples of «Cipollino Verde» form the Euboea (W = western, C = central, E = eastern). US = Upper Styra, LS = Lower Styra, P = Pyrgari, B = Brethela, K = Karystos.

		Samples	^{87}Sr/^{86}Sr
		US-I.4	0.70792
S		**US-II.1**	0.70782
		US-III.1	0.70772
		US-III.3	0.70773
		LS-I.3	0.70795
	W	**LS-II,1**	0.70782
E		**LS-III.1**	0.70782
		LS-III.3	0.70755
		P-I.2	0.70774
		P-I.3	0.70783
		P-II.2	0.70788
C		**P-II.5**	0.70779
		$\bar{X}$	0.70780
		B1.1a	0.70768
	C	**B2.3bis**	0.70784
		B3.2	0.70782
T		**B4.3**	0.70771
		$\bar{X}$	0.70776
		K2.1	0.70766
	E	**K7.3**	0.70768
O		**K8.3**	0.70758
		K6.3	0.70781
R		$\bar{X}$	0.70768

the two groups on the basis of: 1) absence of dolomite in the Euboean samples and 2) Al_2O_3 *vs* Y diagrams normalized to 5 wt% of insoluble residue. A partial discriminant is represented by $\delta^{13}C$, that distinguish the Apuan samples only from those of eastern and central Euboea, and similarly by the $^{87}Sr/^{86}Sr$ ratio taking into account the values of Arni II samples.

As a whole, the data presented in this paper provide the archaeometrist with useful information for assigning the provenance to artifacts made of «Cipollino Verde» with respect to the two most important quarrying areas.

AKNOWLEDGEMENTS

This work has been partially carried out with the financial support of C.N.R. (National Committee of Science and Tecnology for Cultural Heritage; 15)

REFERENCES

BARBIERI M., MASI U., TUCCI P., VIZZINI G., BORGHI M. and AZZARO E. (1996) — *Geochemical and petrographic features of the Styra marble (Southern Euboea, Greece) and geodynamic implications.* In: Terranes of Serbia. Belgrade, 161-166.

CARMIGNANI L., DISPERATI L., FANTOZZI P.L., GIGLIA G. and MECCHERI M. (1993) — *Tettonica distensiva del Complesso Metamorfico Apuano.* Guida all'escursione. Pietrasanta 1-4 giugno, 1993, Università di Siena - Dip. di Scienze della Terra, 7-35.

CRAIG H. (1957) — *Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analyses of carbon dioxide.* Geochim. Cosmochim. Acta, **12**, 133-149.

LAZZARINI L., MASI U. and TUCCI P. (1995) — *Petrographic and geochemical features of the Carystian marble, «Cipollino Verde», from the ancient quarries of the Southern Euboea (Greece)* in: «The study of marble and other stones used in antiquity», Asmosia III, Athens: Transactions of the 3rd International Symposium of the Association for the study of Marble and Other Stones used in Antiquity, ed. by Y. Maniatis, N. Herz, Y. Basiakos, 161-169.

LAZZARINI L. (1998) — *Su un inedito cipollino verde Tenario,* In «Marmi Antichi II». Cave e tecnica di lavorazione, provenienze e distribuzione, P. Pensabene, «Studi Miscellanei», **31**, 207-212.

LUDWIG K.R. (1994) — *A computer program for control of a thermal ionization single collector mass spectrometer.* US Geol. Survey, Open File Report, 92-543.

MC CREA J.M. (1950) — *On the isotopic chemistry of carbonates and paleotemperature scale.* Jour. Chem. Phys., **18**, 849-857.

MASI U., TUCCI P., RUGGIERO G., TERRIACA R., KYRIAKOPOULOS K., MAGGANAS A., and BALTATZIS E. (1995) — *Geochimical and petrographic features of the mesozoic metamorphosed carbonatic sequence from the Mani Peninsula (Southern Peloponnesus, Greece).* XV Congress of the Carpatho-Balkan Geological Association, September 17-20, 1995, Athens, Greece.

MASI U., TUCCI P., PENSABENE P., VIZZINI G., and AZZARO E. (1997) — *Geochemical and petrographic characterization of archaeological remains of «Cipollino Verde» marble to serve for the provenance of materials (Rome, Italy)* in: IV Symposium on the conservation of Monuments in the Mediterranean Basin, Rhodes 6-11 May, 1997, A. Moropoulou, F. Zezza, E. Kollias, I. Papachristodoulou (eds), 313-322.

MASI U., TUCCI P., VIZZINI G., AZZARO E. and BARBIERI M. (1999) — *Further geodynamical evidence for the origin of the Styra marble (Southern Euboea, Greece).* Proceedings III International Congress of the Eastern Mediterranean Geology, Nicosia (in press).

TUCCI P. (1982) — *Le sequenze metamorfiche a precursori mesocenozoici del settore del Monte Corchia (Alpi Apuane). Una interessante anomalia chimica nelle sequenze carbonatiche.* Mineral., **51**, 95-135.

TURI B., MANFRA L. and FRUSCALZO A. (1976) — *Note sulla determinazione della composizione isotopica dell'ossigeno nei silicati e negli ossidi.* Mineral., **45**, 33-50.