



10.5281/zenodo.160952

VERIFYING THE RELIABILITY OF HISTORICAL SOURCES THROUGH A MINERALOGICAL AND PETROGRAPHIC APPROACH: THE CASE OF THE “BLACK-GREEN STONE” FROM THE MESSINA CATHEDRAL (SICILY, ITALY)

G. Sabatino^{1*}, M. Di Bella¹, S. Quartieri¹, A. Giuliano², F. Italiano³,
G. Marciandò¹, A. Tripodo¹, D. Romano¹

¹*Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, University of Messina, Viale G. d'Alcontres 31, 98166 S. Agata, Messina*

²*Museo Regionale di Messina, Viale della Libertà 465, 98121 Messina*

³*Istituto Nazionale di Geofisica e Vulcanologia, Sez. Palermo, Via Ugo La Malfa, 153, 90146 Palermo, Italy*

Received: 05/07/2016

Accepted: 12/10/2016

Corresponding author: Giuseppe Sabatino (gsabatino@unime.it)

ABSTRACT

The aim of this work is obtaining information on the provenance of some very peculiar green (or black-green) stones used both as façade and floor decorations in the Messina Cathedral. Historical sources and available literature data suggest that these materials could belong to the amphibolite of the Peloritani Mountains. In order to verify the true provenance, some stone samples were studied through various analytical methods (SEM-EDS, XRPD, XRF). The investigated specimens resulted to be metabasites showing pseudomorph and vein textures, with relicts of olivine replaced by serpentine - forming a mesh textures - and orthopyroxene mostly altered to bastite. Pseudomorph minerals are serpentine (lizardite and chrysotile), magnetite, amphibole (tremolite-actinolite series) and chlorite (talc-chlorite). These results demonstrate that the analysed green stones cannot belong to the amphibolite outcrop of the Peloritani Mountains. Otherwise, they show mineralogical and petrographic features very similar to those of “verde Calabria”, a rock typology largely exposed in the Northern Calabria area - belonging to the ophiolitic series - and widely used in the last century as building material.

KEYWORDS: Messina Cathedral, green decorative stones, amphibolites, petrography, Calabrian ophiolitic series

1. INTRODUCTION

During the past centuries, several historic buildings of the Messina town - as well as of some villages in the province - were widely decorated using a typical black-green stone. Important examples are visible in the façade decorations of the Messina Cathedral (Figures 1a and b). After 1908 Messina earthquake, remains of collapsed historical buildings (Fig. 1c) were saved and transferred in a vast area next to

a silk factory, right out the city centre (named Filanda Mellinhof). In the same area, the City Regional Museum was then built after some decades. From these remains - coming from different known locations and provided by the Museum authority - some stone samples used for floor and façade decorations (XIIIth - XIVth century) were selected for this study, in order to define their origin provenance.

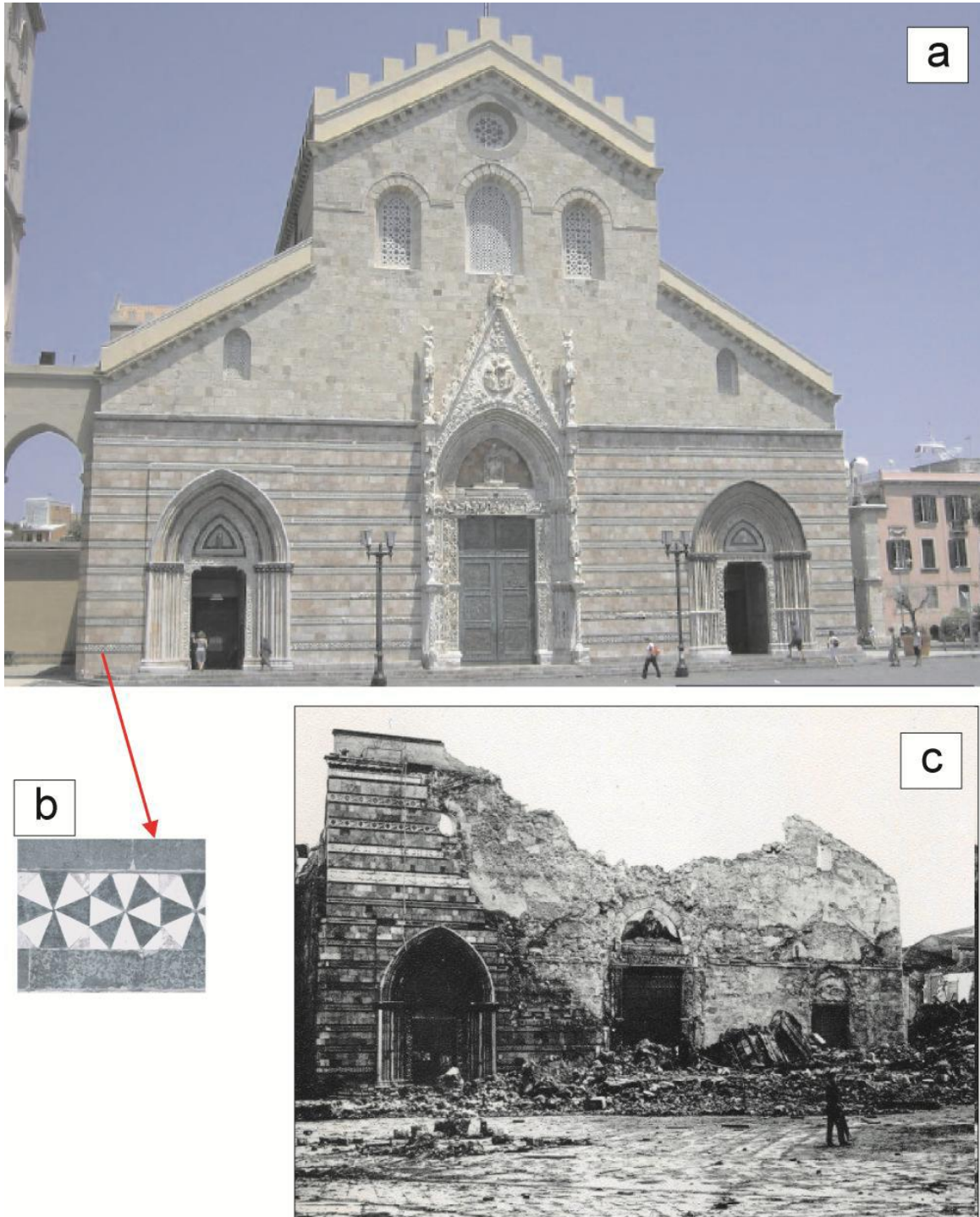


Figure 1. a) Messina Cathedral today; b) Particular of the decorative rows; c) Image of Messina Cathedral after the 1909 earthquake

The Historical Notary Archives of Messina and Palermo retain several documents reporting legal transactions and purchasing of decorative stones. Some examples are reported in the following.

- 1- Legal transaction 1494-1500. "... in lu quali autarectu sia unu pavimentu a scaccheri di petri russi et nigri di Zaffaria..." and then "... lu quali pavimentu divi esseri laboratu di petri russi di Tauromena, di nigri di Zaffaria et marmuri ..." Order for a chess-like floor and a small altar made with reddish stone from Taormina and black stones from Zafferia.
- 2- Legal transactions 1540-1550. "Messina 30-11-1546, pagati 27 Tari ... a mastro Salvo di Rugeri, alias Gallo di Zaffaria. Sonno per portari petri nigri di Zaffaria, iuxta lu ordini et misura, chi li havi dato mastro Dominico Vanello, capo mastro scarpellino per la fruntera di nostri matri ecclesia ...". This transaction reports the date of the order - given to the artisans Salvo di Rugeri and Gallo from the Larderia and Zafferia Villages - for providing "black stones" for the building of the main Church façade.
- 3- "Messina 22-12-1550" ... unza 1.12, pagati per comandamento di lo ditto mastro di opera Angilo di Rugeri, alias Gallo di Zaffaria. Etso per prezo di novanta pezi di petra nigra a gr. 9 per uno, stimati per mastro Bastiano Fiorentino et mastro Leonardo Carrara, mastri Scarpellini, approbato per lo m.co Jo. Angelo Montursulo, capomastro scultori di la ecclesia: quali petri hanno servir per lo pavimento, che si fa in la nostra matri ecclesia ... pagati per lo banco di Ansaluni unza 1.12 ..." In this transaction, dated a couple of years after the first quoted one, a reference is made to stone workers - who followed the florentine architect Montorsoli (known to work in the Church in that period) - using the mentioned stones for the floor decorations of the Main Church.

These documents indicate, as material provenance, the quarries located in the nearby of the Larderia Village (Peloritani Mt., about 8 km South of Messina) and in the close Zafferia Village, where metamorphic amphibolitic rocks belonging to the Aspromonte Unit outcrop.

Moreover, in two previous studies performed by Stagno and Zipelli (1985) and Principato and Triscari (1999), the black-green stone used in many façade and floor decorations was classified as an "amphibolite" from the Peloritani Mountains.

To verify the reliability of the historical sources and to provide more precise information on this

decorative material, we carried out an archaeometrical characterization of four stone fragments through a multidisciplinary approach, involving petrographic, mineralogical and chemical analysis.

1.1 HISTORY OF THE MESSINA CATHEDRAL AND FINDINGS IN SAID PROVINCE OF THE INVESTIGATED STONES

The most impressive historical evidence here discussed is the Messina Cathedral (XIIIth - XIVth century). The foundation of this church is probably dated to the Norman Roger II. The official consecration took place on September 22th, 1197 in the presence of Emperor Henry VI. From ongoing research, it seems that at the time of the consecration, the Cathedral was not completed, either in the structural and decorative parts.

Many interventions were made - since the middle of the '500 - by the Florentine architect Giovanangelo Montorsoli (pupil of Michelangelo), who, according to some documents, worked on the main façade and to some of the floor decorations. The façade (Fig. 1a) - originally decorated in the XIV cent. and completed in the XVII cent. - presents now about 20 rows of a geometric inlay decoration performed with black-green stones embedded in a Carrara white marble support (Fig. 2 a-e), alternating with reddish Mesozoic limestones coming from a quarry near Taormina (50 Km to the South) (Bottari 1929).

A wonderful geometric mosaic originally covered the entire Cathedral floor, but it was destroyed during the 1908 earthquake (Triscari 2010). After this event, a new floor was built. The present one (Fig. 2c-d-e-f) was made in 1945-47, after the heavy damages following the anglo-american bombing of the town occurred on June 1943. For the same reason, the original twenty façade marble inlay decoration rows were reduced to only nine (Fig. 1a and b) and subsequently reconstructed with the original marble fragments. The original recovered portions - both of the floor and of the front wall decoration - are still preserved in the Regional Museum of Messina and attributed to this church on the basis of recent artistic/historical studies (Giuliano 2012). Messina Museum also preserves some fragments of the wall and floor decoration - apparently coming from the Cathedral - with fantastic animal figures, probably dated XIIIth or beginning of XIVth century (Giuliano 2015; Fig. 2e).

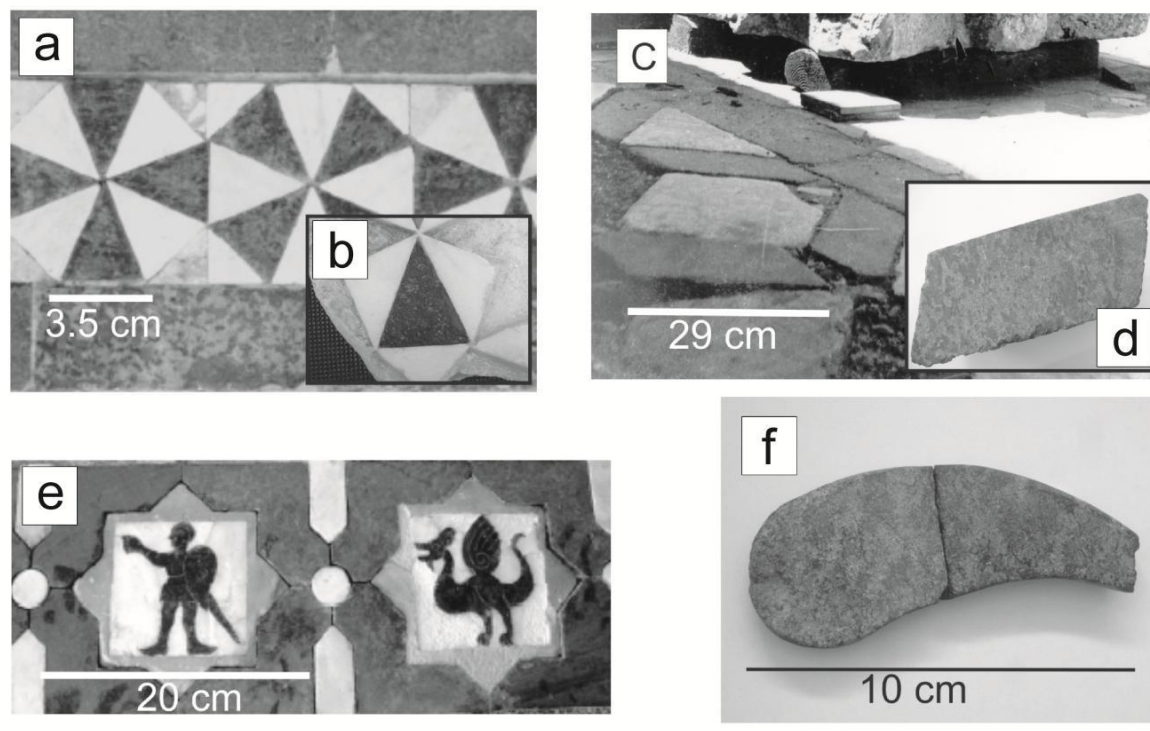


Figure 2. a) Geometric inlay decoration in black-green stones embedded in a Carrara white marble from the façade and b) particular; c-d) portion of a decorative band from the original floor; e); fragments of wall/floor decoration with fantastic animal figures; f) ornament from the façade

In the Messina Museum collections and deposits, fragment specimens coming from other unknown sites are preserved, together with an impressively large jar (about 60 cm high) entirely excavated in a single block of this supposed “amphibolite” and probably originally exhibited in the Cathedral.

The peculiar black-green stone was also largely used for the floor decoration of the S. Francesco all’Immacolata Church, built in 1254. Also this floor was destroyed during 1908 earthquake, but the preservation of the original materials allowed its partial reconstruction. Nowadays, the church floor is formed by at least the 30% of the original decorations.

No further uses of this black-green stone are known in the Messina area or in the surrounding, except for part of a geometric floor decoration of the main Church of Casalvecchio Siculo (about 30 km South of Messina), dated before the XVIIth century (Di Bella *et al.* 2010).

As clearly evident from this introduction, the only information on the provenance of this black-green stone derives from historical documents of financial transactions (payments for the provided materials and for the performed works) and by the archaeological research conducted by the Regional Museum of Messina. However, no specific archaeometric data are available. This work aims at filling this gap by

providing mineralogical and petrographic evidence, essential for ascertaining the true provenance area of this building material.

2. SAMPLES AND ANALYTICAL METHODS

The decoration specimens from the Messina Cathedral (Fig. 2) were provided by the Regional Museum of Messina. Specifically:

- sample MC1: from the Cathedral façade decorations (Fig. 2a, b)
- sample MC2: from the Cathedral façade decorations (Fig. 2e)
- sample MC3: tile from the floor (Fig. 2c-d)
- sample MC4: decorative frieze (Fig. 2f).

To minimize the damage, a small piece of each sample was extracted from the rear surface of the fragments. From each fragment, the corresponding thin section was made to perform petrographic and Scanning Electron Microscopy-EDS (SEM-EDS) investigations. Small portions of the three samples (MC2, MC3, MC4) were powdered to perform X-ray Powder Diffraction (XRPD) analyses, whereas the triangular decorative tile MC1 was not powdered and directly analyzed, due to its small size. Bulk composition was determined for all the samples measuring major and some trace elements concentration by X-ray Fluorescence (XRF) analysis. Analytical investigations were performed using the instruments of the CERISI Geochemical Laboratory, the Earth

Sciences Laboratory and the Diffractometric Laboratory of the University of Messina.

Specifically:

- a) Petrographic analyses were performed by polarizing optical microscopy, to define texture and preliminary mineral composition;
- b) Micro-textural and compositional analyses were made by an ESEM-FEI Inspect-S electron microscope coupled with an Oxford INCA PentaFETx3 EDX spectrometer, a Si(Li) detector equipped by a ATW2 ultra-thin window with a resolution of 137 eV at 5.9 keV (Mn K α 1). The spectral data were acquired in ESEM (Environmental Scanning Electron Microscope) conditions at a working distance of 10 mm, with an accelerating voltage of 20 kV, counting time of 60 s, count rate of approximately 3000 cps with dead time below 30%. The results were processed by INCA Energy software. This software uses the XPP matrix correction scheme developed by Pouchou and Pichoir (1984, 1985).
- c) X-ray powder diffraction analyses were carried out using a BRUKER D8 ADVANCE diffractometer, with Cu K α radiation, on a Bragg-Brentano theta-theta goniometer equipped with a SiLi solid-state detector Sol-X. Acquisition conditions are 40 KV and 40 mA. Scans were performed typically from 2 to 80 degrees 2 θ , with step size of 0.02 degrees 2 θ , with a counting time of 1 second. Observed peak positions were matched against the ICDD-JCPDS database. The data analysis was performed using EVA software. The raw diffraction scans were stripped of K α 2 component, the background was corrected and the digital data were smoothed with a Fourier digital filter. The observed peak positions (Fig. 4) were matched against the ICDD JCPDS database.
- d) Chemical analyses were performed by wavelength dispersion XRF spectrometry (WDXRF), measuring major, minor and trace elements with a Bruker model S8 Tiger setup

(Bruker 2015a, b). The excitation source was a Rh tube at 4 kW. The power and the current intensity were changed according to the analyzed element and their amounts, in order to avoid detector saturation. The concentrations of major and minor elements were calculated through the software package GEO-QUANT M, an accurate method for measuring 11 elements using more than 20 certified materials as standards in the calibration process (Bruker 2015a, b). The software GEO-QUANT T was used for the calculation of the trace elements (Bruker 2015a, b).

3. RESULTS

3.1 Messina Cathedral stones

From the macroscopic point of view, the studied rock samples are dark-green to greyish-green in colour, and are characterized by the peculiar presence of swarthy patches and a schistose structure. Petrographic investigations reveal different degrees of pseudomorphic serpentinization. Colourless to pale-green serpentine replaces olivine, forming polygonal mesh texture arranged as an irregular network among olivine relics, and filling cracks within olivine porphyroclasts. The samples show mainly pseudomorphic to relict-granular texture, with minor portions characterized by nematoblastic structure (Fig. 3 a-b-e-f). The main parageneses include serpentine, relicts of olivine and pyroxene, with variable amount of amphibole, chlorite, talc and opaque minerals.

The mineralogical analysis of the four samples provided evidence for the presence of clinocllore, tremolite, clinochrysotile, lizardite, forsterite, and talc (Fig. 4). The amounts of these phases in the studied samples - determined by Rietveld method and expressed in weight % - range as following: clinocllore (60.5 - 31.1 %), tremolite (12 - 31 %), clinochrysotile (11 - 32 %), lizardite (6 - 17 %), forsterite (0 - 5 %) and talc (0.9 - 1.8 %).

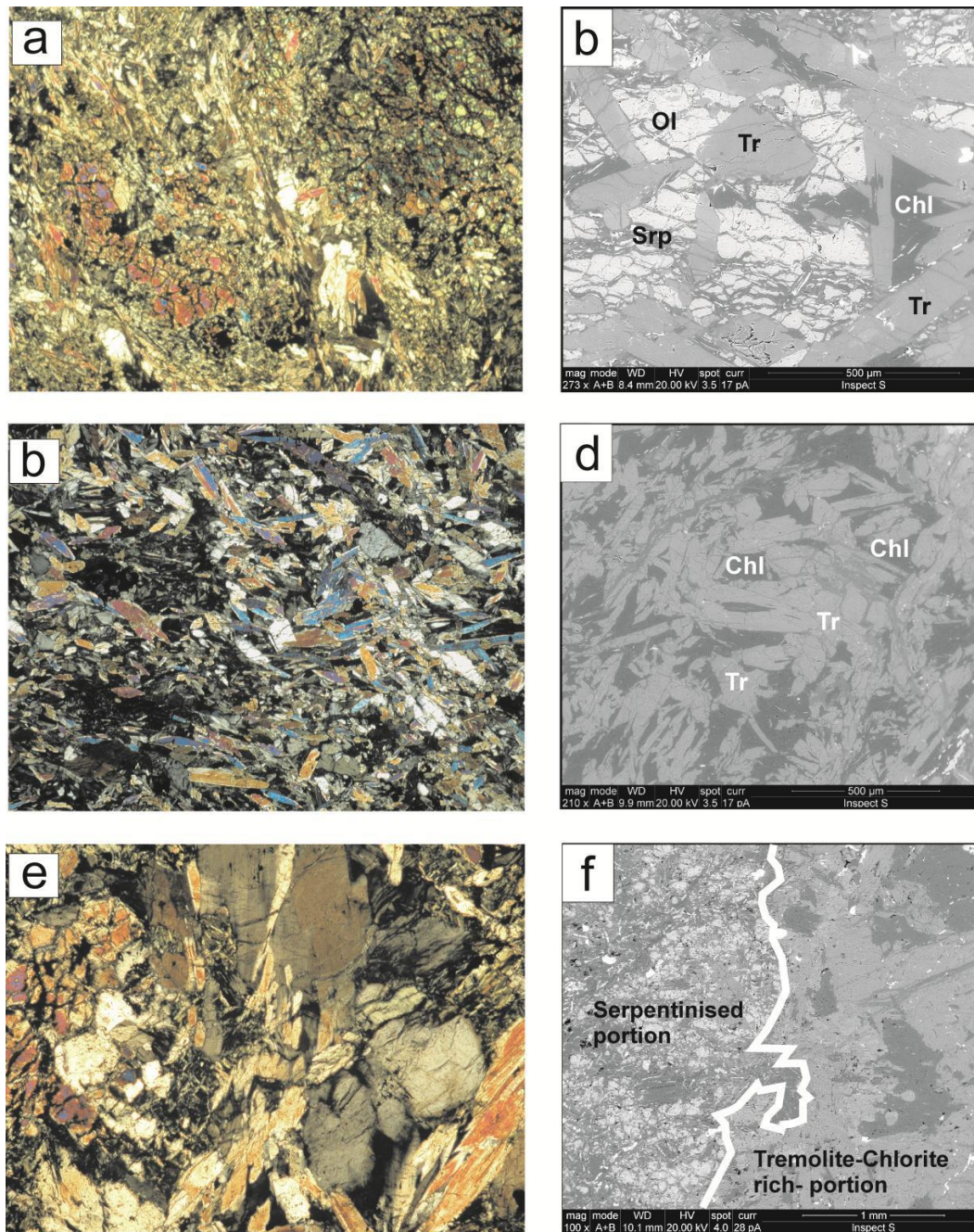


Figure 3. Crossed polar light photomicrographs of the representative structures of the studied stone samples (a-c-e) and SEM-EDS images of some selected area (b-d-f). In details: (a, b) serpentinized micro-domains displaying pseudomorphic to relict-granular texture; (c, d) tremolite- and chlorite-bearing micro-domain; (e, f) contact between the two different types of micro-domains.

The characteristic dark speckles visible on the hand specimens represent the serpentine-rich areas characterized by mesh texture juxtaposed to nematoblastic amphibole- and chlorite-rich portions. In particular, hetero-granular *olivine* is in colourless dismembered relict crystals. SEM-EDS analyses (Tab. 1) show forsterite-rich compositions (~ 80% Fo). The grains are pseudomorphically replaced by mesh-work isotropic serpentine (Fig. 3a-b). The replacement starts along the crystal boundaries and proceeds inwards. *Serpentine* group minerals occur as

the polymorphs lizardite and chrysotile, as evidenced by XRPD analysis (Fig. 4). Minor amounts of *orthopyroxene* grains appear deeply replaced by "basaltite". *Amphibole* is in randomly oriented stubby-prismatic to long-prismatic colourless nematoblastic crystals (Fig. 3c-d), that - based on the optical features, the chemical composition (Table 1) and the XRPD data (Fig. 4) - can be classified as tremolite. Its composition is better defined using the relative amphibole classification diagram (Meeker et al., 2006) reported in Fig. 5a. *Chlorite* forms small-sized colour-

less and irregular flakes (Fig. 3c-d), having anomalous brown interference colours, usually arranged in close spatial association with the serpentine minerals. It is Mg-rich (Mg# = 0.94) and compositionally defined as clinocllore. On the relative classification diagram (Hey 1954; Fig. 5b) its composition falls in the talc-chlorite field. Magnetite is the most common opaque mineral phase and is produced as a consequence of olivine serpentinization. It forms small ir-

regular grains frequently scattered in the rock, mainly among serpentine and chlorite minerals. Chemical data indicate a chromium enrichment (Table 1). Among the opaque minerals, also abundant Ni-rich sulphides grains were found (Table 1). Calcite veins occur rarely.

Overall, the chemical, mineralogical and petrographic data suggest that the studied stones may be classified as serpentinized ultramafic rocks.

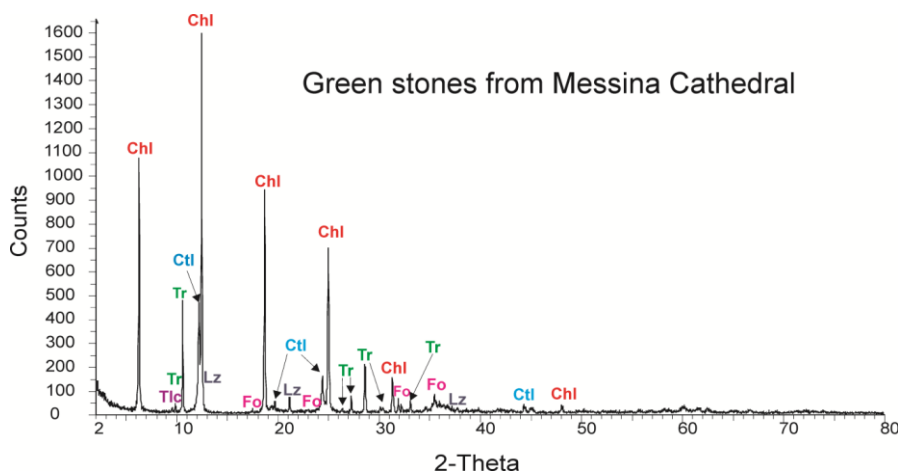


Figure 4. X-ray powder diffraction pattern representative of the analyzed green stones.

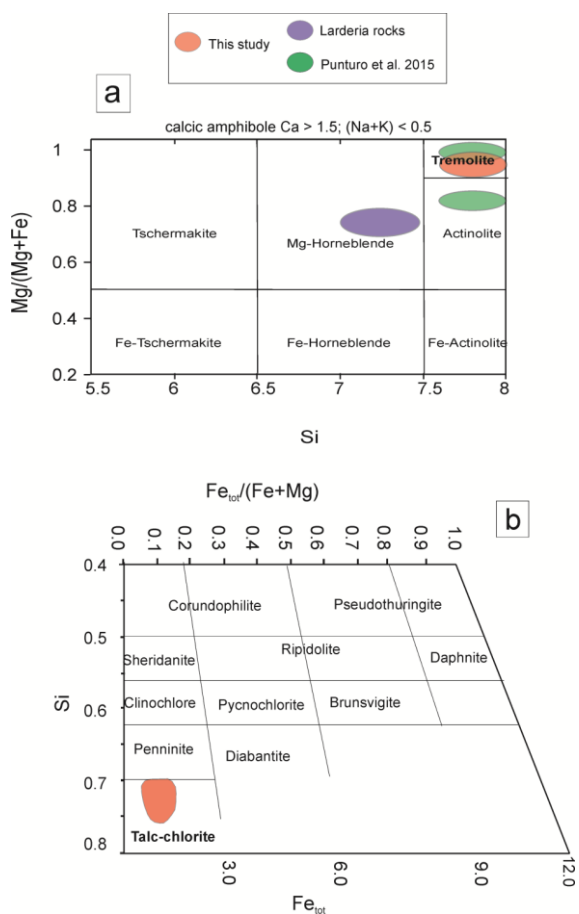


Figure 5. Classification of analyzed amphibole after Leake et al. (1997) (a) and chlorite according to Hey (1954) (b) - For comparison, the areas of the amphibole from Larderia amphibolites and from the Calabrian serpentinites (Punturo et al., 2015) are also drawn.

Table 1 - Chemical data (SEM-EDS) of amphibole, chlorite and olivine present in the studied green-stone specimens.

	AMPHIBOLE					CHLORITE					OLIVINE						
SiO₂	59.72	58	60.4	58.1	58.4	SiO₂	44.16	42.73	42.12	45.15	41.97	SiO₂	43.2	42.3	42.8	43.1	42.3
TiO₂	0.88	1.61	0.63	0	0.44	Al₂O₃	12.83	13.35	14.87	9.23	14.58	FeO	15.8	17.4	16.9	18.6	19.2
Al₂O₃	3.75	4.75	3.6	1.87	1.14	Cr₂O₃	0	0.57	0	0.47	0.6	Al₂O₃	0.93	0.72	0.55	0.97	0.87
FeO	24.23	25.7	23.9	4.09	4.61	FeO	6.75	6.87	7.04	8.11	6.62	MgO	39.7	39.3	39.2	37.3	37.6
MgO	11.43	9.98	11.5	25.7	25.3	MgO	34.22	35.31	34.57	36.25	35.58	CaO	0.44	0.36	0.59	0	0
CaO	0	0	0	9.77	10.2	CaO	2.03	1.17	1.4	0.79	0.65	Total	100	100	100	100	100
Total	100	100	100	100	100	Total	100	100	100	100	100						
												Si	1.13	1.1	1.11	1.12	1.1
Si	7.963	7.77	8.04	7.78	7.81	Si	7.28	7.064	6.96	7.487	6.92	Al	0.03	0.02	0.02	0.41	0.42
Al^{IV}	0.037	0.23	0.04	0.22	0.18	Al	2.493	2.601	2.896	1.804	2.835	Fe²⁺	0.34	0.38	0.37	1.45	1.46
Tot.	8	8	8	8	7.99	Cr	0	0.075	0	0.062	0.078	Mg	1.54	1.52	1.52	0.03	0.02
						Fe²⁺	0.931	0.95	0.973	1.125	0.913	Ca	0.01	0.01	0.02	0	0
Al^{VI}	0.101	0.02	0.14	0.08	0	Mg	8.41	8.702	8.516	8.962	8.752	Tot.	3.05	3.04	3.04	3.01	3.01
Ti	0	0	0	0	0.04	Ca	0.359	0.207	0.248	0.14	0.115						
Mg	4.816	4.98	4.73	4.92	4.96	Tot.	19.474	19.598	19.592	19.58	19.618	End Members					
Fe	0.083	0	0.13	0	0	Group	chlorite	chlorite	chlorite	chlorite	chlorite	Fo	81.8	80.1	80.5	78.1	77.8
Tot.	5	5	5	5	5	Name	Clino-chl	Clino-chl	Clino-chl	Clino-chl	Clino-chl	Fa	18.2	19.9	19.5	21.9	22.3
Mg	0	0.14	0	0.21	0.08												
Fe	0.335	0.53	0.27	0.46	0.52	Ni-rich SULPHIDES					Cr-rich MAGNETITE						
Ca	1.633	1.43	1.64	1.4	1.46	MgO	9.39	9.27	21.71			MgO	17.35	19.23	9.25		
Tot.	1.968	2.11	1.91	2.07	2.06	Al₂O₃	0	1.24	14.45			Al₂O₃	1.83	0	0		
Mg#	0.91	0.94	0.92	0.96	0.92	SiO₂	14.51	13.77	2.17			SiO₂	19.45	20.07	8.67		
Group	Calcic	Calcic	Calcic	Calcic	Calcic	SO₃	40.59	36.91	24.31			CaO	1.04	0	0.5		
Subgroup	Tr-Ac	Tr-Ac	Tr-Ac	Tr-Ac	Tr-Ac	CaO	1.93	1.36	2.54			TiO₂	1.65	0	2.23		
Name	Tr	Tr	Tr	Tr	Tr	FeO	16.23	22.78	31.46			V₂O₅	0.87	0	0.93		
						NiO	17.36	14.69	3.38			Cr₂O₃	10.49	4.47	5.52		
						Total	100	100	100			FeO	47.32	56.23	72.9		
												Total	100	100	100		

3.2 ASPROMONTE-PELORITANI UNIT AND THE AMPHIBOLITES FROM LARDERIA

The Peloritani Mts. constitute the Sicilian portion of the Calabria-Peloritani Arc, a tectono-metamorphic edifice characterized by a complex folded geological structure, where several metamorphic units are recognized (Bonardi et al. 1976; Messina et al. 1995, 1997). The locality of Larderia, indicated in the historical sources as the provenance quarry area of the green building stones, belongs mainly to the Aspromonte Unit. This Unit consists of amphibolite-facies metamorphic rocks, mainly represented by paragneiss, migmatitic paragneiss and augen gneiss, with minor marble and amphibolite, diffusively intruded by late Variscan granitoid plutons. In the

same area, sporadic outcrops of the Mela Unit are also exposed, consisting of a poli-metamorphic basement represented mainly by paragneiss and mica-schist, with subordinate meta-mafic rocks and silicates marble. It must be underlined that no outcrops of serpentinitic tremolite-bearing rocks occur in the Peloritani Metamorphic Units, because the origin of these rocks is linked to a different/peculiar evolution process.

Some mafic rocks from Larderia and Zafferia localities, belonging to the Aspromonte metamorphic Unit (Peloritani Mts.), were collected for this study and analysed through SEM-EDS and XRPD (Fig. 6).

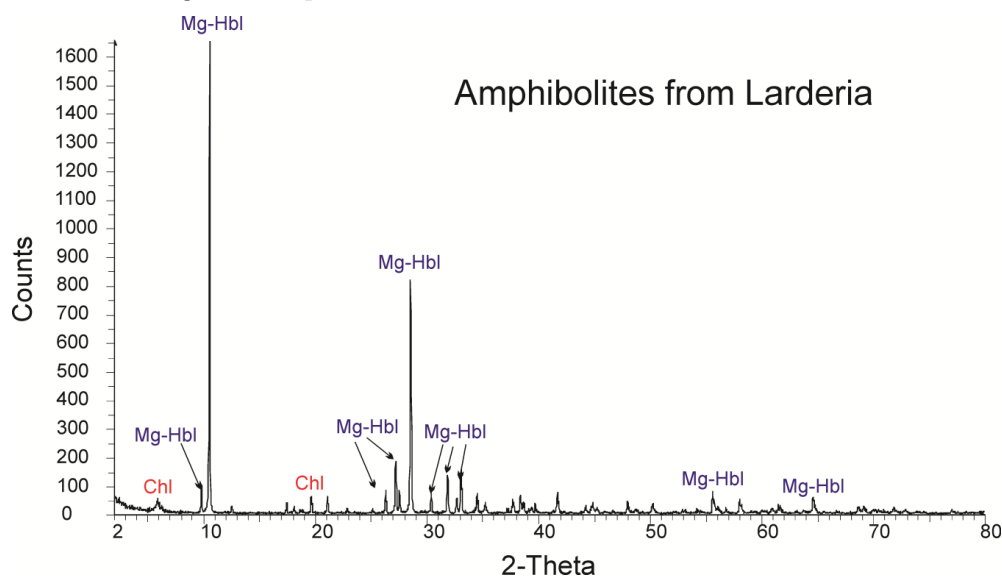


Figure 6. X-ray powder diffraction pattern of amphibolite sample from Larderia

The samples show dark green colour, foliated structure and fine to medium grain-size. They result to be amphibolite or metahornblendite, composed by prevalent granoblastic to nematoblastic green Mg-hornblende (95%), minor chlorite, rare plagioclase, and titanite (3%), magnetite and zircon as accessory minerals. These mineralogical and petrographic features are not compatible with those of the studied ornamental stones.

4. DISCUSSION

All the previously reported information about the metamorphic rocks from the Larderia area - and in general from the Aspromonte Unit and Peloritani Mts. metamorphic units - points towards different compositional and structural features with respect to those of the green stones here studied.

Differently, we suggest that our samples could derive from the Calabrian ophiolite sequences of the Calabrian Peloritani Arc (Fig. 7). Indeed, similar

rocks - commercially known as "pietra verde" ("green stone") or "Verde Calabria" - are very abundant in the Sila Piccola and Catena Costiera, and have been extensively used in the past as building and decorative materials. The terms "green stone" or "black-green stone" include two lithotypes: serpentinite and metabasite associated in ophiolitic sequences, both having been quarried and used as construction material (Rodolico 1946). The quarrying district "Verde Calabria", with its main sites in the territory of the villages of Conflenti, Martirano, Decollatura and Gimigliano (South-Eastern Sila Piccola; Punturo et al. 2004, 2015), and in the Mt. Reventino area (South-Western Sila Piccola), constituted an important economic reality linked to the extraction and processing of green stone since prehistoric times (Punturo et al. 2004, 2015; Zakrzewska et al. 2008). The most famous "green stone" masons worked in Delianuova (Calabria) until a few decades ago.

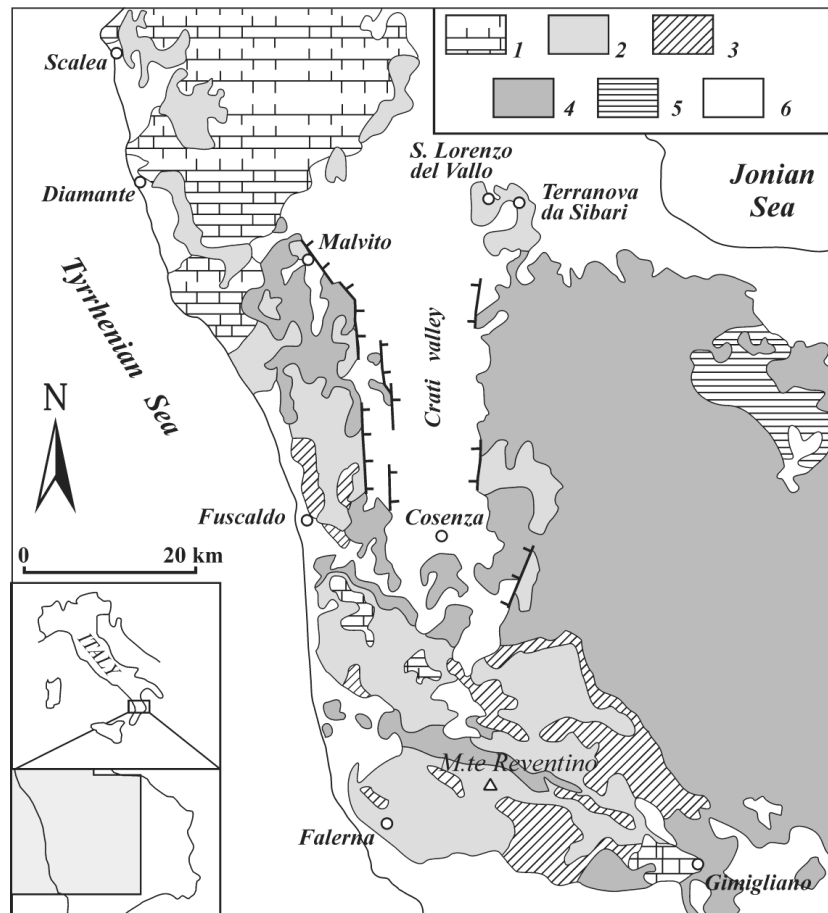


Figure 7. Geological sketch map of the northern sector of the Calabrian-Peloritani Arc (after Punturo *et al.* 2004). 1) Apennine Units Complex; 2) Ophiolite Units; Continental Crust Units; 3) Castagna Unit; 4) Calabride Units; 5) sedimentary cover of the Calabride Units; 6) Liguride Complex of the Calabrian-Lucanian boundary; 7) Miocene-Oligocene sedimentary sequences

These green stones show remnants of the original protogranular texture, which has been inherited from their harzburgitic-lherzolitic protoliths. The mineral assemblage of serpentinite from Mt. Reventino Area - where the quarries are located - is mainly made of serpentine group minerals \pm magnetite \pm tremolite-actinolite \pm chlorite \pm Cr-spinel. The serpentine group minerals and small magnetite grains completely replace former olivine and orthopyroxene crystals and appear as pseudomorphic aggregates with typical net-like and mesh-textures. Different dilatation vein systems filled by serpentine group minerals crosscut the rock. Orthopyroxene grains appear deeply replaced by "bastite", whereas clinopyroxene is present as millimetric grains or inclusions within rarely preserved holly-leaf shaped Cr-spinel of peridotitic origin, that, in most cases, are almost completely retrogressed to magnetite and chlorite (Punturo *et al.* 2004, 2015). These features of the ultramafic serpentinitic rocks from the Calabrian ophiolitic sequence are therefore in agreement with those of the ornamental stones here studied. Fur-

thermore, based on the literature data of Punturo *et al.* (2004, 2015), we can better define the compatibility of our samples with the rocks of the ophiolitic sequence, particularly in terms of mineral chemistry of the amphibole tremolite (Fig. 5a) and of the trace element signature. For this purpose we considered high field strength elements (HFSE; Table 2), which are rather immobile during weathering, hydrothermalism and metamorphism (Wood *et al.* 1979; Bienvenu *et al.* 1990). In particular, the plots Ti vs V and Nb/Y vs Ti/Y of Fig. 8 report the fields of the Calabrian-Lucanian metabasites (Spadea 1979), the M. Reventino-Gimigliano Unit serpentinites (Spadea 1979) and the samples studied by Punturo *et al.* (2004). On these plots we also reported the XRF data (Table 2) of the studied green stones (red stars). As one can see, the samples from the Messina Cathedral are chemically comparable to the "Pietra Verde" coming from the historical quarries of S. Mango D'Aquino and Mt. Reventino (Calabria, Italy) studied by Punturo *et al.* (2004).

Table 2 - X-ray fluorescence data for major (%) and trace elements (ppm) in the studied green stones.

Samples	MC1	*se	MC2	*se	MC3	*se	MC4	*se
Oxides %								
SiO ₂	40.95	0,26	40.94	0,28	42.87	0,28	41.16	0,28
TiO ₂	1.34	1,26	1.77	1,23	1.59	1,84	1.48	1,12
Al ₂ O ₃	4.61	0,92	3.56	0,92	3.4	1,02	3.87	1,02
Fe ₂ O ₃	10.99	0,13	6.79	0,15	7.14	0,14	7.99	0,15
MnO	0.19	1,47	0.17	1,6	0.15	1,65	0.17	1,71
MgO	28.14	0,25	36.1	0,21	36.18	0,21	33.69	0,21
CaO	5.27	0,46	0.69	1,56	0.36	1,91	2.1	1,84
Na ₂ O	0.48	9	0.57	9,67	0.42	9,5	0.67	8,7
P ₂ O ₅	0.01	0,9	0.01	0,9	0.01	0,9	0.01	0,9
L.O.I.	8.99		9.96		7.67		9.4	
Total	100.97		100.56		99.79		100.54	
Trace elements (ppm)								
Y	9	3,04	10	3,55	12	3,41	9	5,67
Nb	7	4,74	7	7,68	8	7,14	6	8,89
La	19	8,1	16	8,4	18	8,4	17	8,4
Ce	40	15,8	21	16,7	30	16,4	18	16,3
Cr	3068	0,23	3373	0,17	3559	0,21	2633	0,22
Ni	1226	0,25	1228	0,2	1342	0,2	1565	0,2
Rb	4	7,17	3	7,16	3	9,42	4	7,12
Ba	15	4,8	12	17,2	16	25,2	14	22,2
Pb	14	0,97	10	5,87	9	7,06	12	6,31
Th	10	10,3	6	16,6	6	17,6	7	16,8
Sc	22	4,48	24	3,12	24	3,73	23	3,66
V	188	0,72	190	0,73	205	0,9	198	0,95
Co	117	0,34	81	0,42	97	0,4	94	0,41
Sr	9	6,58	5	4,71	7	6,82	8	6,33
Zr	40	0,83	24	0,53	20	0,6	38	0,74
Zn	77	1,18	35	1,64	38	1,79	45	1,9

*se = standard error evaluated with the Poisson's Law ($\sigma_N = \sqrt{N}$), it includes error of concentration, preparation and calibration.

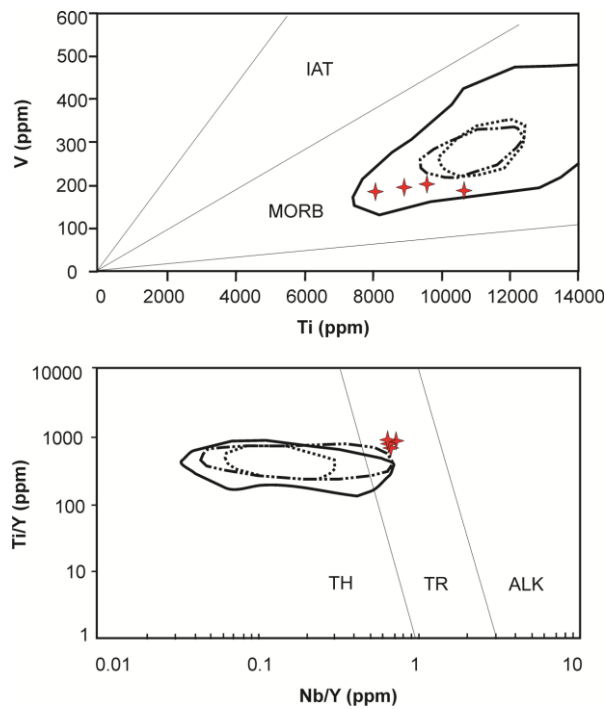


Figure 8. Ti vs V and Nb/Y vs Ti/Y plots after Punturo et al. (2004). On the diagram the following fields are represented: Calabrian-Lucan metabasites (continuous line) (Spadea, 1979); M. Reventino-Gimigliano Unit serpentinites (dashed line) (Spadea, 1979); samples studied by Punturo et al. (2004) (dotted line). The red star represents the XRF composition of the green-stone samples analysed in the present work.

5. CONCLUSIONS

The investigated specimens of the “green stones” used for decorating the façade and the floor of the Messina Cathedral resulted to be metabasites showing pseudomorphic and vein textures, with relicts of olivine replaced by serpentine - forming a mesh textures - and orthopyroxene mostly replaced by basite. The pseudomorphic minerals are serpentine (lizardite and chrysotile), magnetite, amphibole (tremolite-actinolite series) and chlorite (talchlorite).

The results of this chemical, mineralogical and petrographic study bring into question the reliability of some historical documents that - concerning the

provenance of this decorative and building material - indicate the region of the medium-high amphibolite facies metamorphic rocks present nearby the Sicilian Zafferia and Larderia villages. The presence of a historical decorative handicraft and of a quarrying activity in the nearby of these villages is not questioned. However, our data suggest that the most reliable provenance region is the famous Calabrian “Green Stone district” where, since prehistoric times, serpentinites and metabasites associated in an ophiolitic sequence have been quarried and used as construction material.

ACKNOWLEDGEMENTS

The authors are grateful to the various Directors of the Messina Regional Museum for providing the samples, allowing the entrance in the Museum repositories and for the useful collaboration and discussion. Thanks are also due to Prof. Maurizio Triscari (University of Messina, now retired) and Prof. Rosolino Cirrincione (Catania University) for the useful suggestions. This research exploited the analytical facilities of the Laboratory of Geochemistry of “CERISI” (Progetto Centro di Eccellenza Ricerca e Innovazione Strutture e Infrastrutture di grandi dimensioni - Cod. PONA3_00422, European Regional Development Fund) in Messina.

REFERENCES

- Bienvenu, P., Bougault, H., Joron, J.L., Treuil, M. and Dmitrieff, L. (1990) MORB alteration: Rare earth elements/ non rare earth hygromagmaphile element fractionation, *Chemical Geology*, Vol. 82, pp. 1-14.
- Bonardi, G., Giunta, G., Liguori, V., Perrone, V., Russo, M. and Zappetta, A. (1976) Schema geologico dei Monti Peloritani, *Boll. Soc. Geol. It.*, Vol. 95, pp. 49-74.
- Bottari, S. (1929) Il duomo di Messina, Messina-Bruker (2015a) Product overview: advanced analytical solutions.
- Bruker (2015b) XRF lab report - S8 TIGER plus GEO-QUANT M.
- Di Bella, M., Giuliano, A., Sabatino, G. and Triscari, M. (2010) Peculiar medieval floor decorations and artefacts from the town of Messina. In proceedings of A.I.Ar. Meeting, Pavia, February, Italy, pp 15-18.
- Giuliano, A. (2012) Una significativa novità sulle origini del Duomo di Messina in “*Archivio Storico Messinese*” n. 93, Messina 2012.
- Giuliano, A. (2015) Il ritrovamento dell’antica soglia del Duomo di Messina ed altro ancora. In: “IV Corso di aggiornamento per insegnanti e guide turistiche” Museo Regionale di Messina, 11 febbraio 2015.
- Hey, M.H. (1954) A new review of the chlorites. *Min. Mag.*, Vol. 30, pp. 1-277.
- Leake, B.E. et al. (1997) Nomenclature of amphiboles: report of the subcommittee on amphiboles of the international mineralogical association, commission on new minerals and mineral names, *The Canadian Mineralogist*, Vol. 35, pp. 219-246.
- Compagnoni, R., Giacobbe, A. and Russo, S. (1995) Pre-Alpine poly-metamorphism in a new thrust sheet of the Calabrian-Peloritan Arc: Mela Unit. In: Proceedings of SIMP, Meeting, Venezia, September, Italy 1995; Vol. 14, pp. 225-226.
- Messina, A., Giacobbe, A., Perrone, V. and De Francesco, A.M. (1997) The Mela Unit: a new medium-grade metamorphic unit in the Peloritani Mts. (Calabrian-Peloritan Arc, Italy), *Boll. Soc. Geol. It.*, Vol. 115, pp. 1-16.
- Principato, A. and Triscari, M. (1999) Tappeti marmorei pavimentali in provincia di Messina. In: Proceedings of F.I.S.T., Meeting, Bellaria, Italy, Vol. 22, pp. 314-316.
- Pouchou, J.L., Pichoir, L. (1986) Les éléments très légers en microanalyse X - Possibilités des modèles récents de quantification, *J. Microsc. Spectrosc. Electron.*, Vol. 11, pp. 229-250.

- Pouchou, J.L. and Pichoir, L. (1984) Possibilités d'analyse en profondeur à la microsonde électronique, *J. Microsc Spectrosc Electron*, Vol. 9, pp. 99-100.
- Punturo, R., Fiannacca, P., Lo Giudice, A., Pezzino, A., Cirrincione, R., Liberi, F. and Piluso, E. (2004) Le cave storiche della "Pietra Verde" di Gimigliano e Monte Reventino (Calabria): studio petrografico e geochimico, *Boll. Acc. Gioenia Sc. Nat.*, Vol. 37, pp. 35-57.
- Punturo, R., Bloise, A., Critelli, Catalano, Fazio and Apollaro (2015) Environmental Implications Related to Natural Asbestos Occurrences in the Ophiolites of the Gimigliano-Mount Reventino Unit (Calabria, Southern Italy), *Int. J. Environ. Res.*, Vol. 9, pp. 405-418.
- Rodolico, F. (1946) *Le pietre delle città di Italia*. Ed. Le Monnier. Italy, Firenze.
- Spadea, P. (1979) Contributo alla conoscenza dei meta basalti ofiolitici della Calabria settentrionale e centrale e dell'Appennino Lucano, *Rendiconti della Società Italiana di Mineralogia Petrologia*, Vol. 35, pp. 251-76.
- Stagno, F. and Zipelli, C. (1985) Risorse naturali del territorio messinese utilizzate in passato. Le "pietre nere" (petri nigri) delle fasce nel prospetto del Duomo di Messina. In *Atti Acc. Peloritana Pericolanti*, pp. 63-23.
- Triscari, M. (2010) Georisorse del costruito a Messina: una storia di 25 secoli e l'abdicazione ai calcestruzzi armati. In: *Accademia Nazionale delle Scienze, "La ricerca scientifica dopo il terremoto siculo-calabrese del 1908" Scritti e documenti*, XLIII, pp.164-191, Tip. Della Pace Roma. Italy.
- Zakrzewska, A.M., Capone, P.P., Iannò, A., Tarzia, V., Campopiano, A., Villella, E., Giardino, R. (2008) Calabrian ophiolites: dispersion of airborne asbestos fibers during mining and milling operations, *Periodico di Mineralogia*, Vol. 77, pp. 27-34.
- Wood, D.A., Joron, J.L, and Treuil, M. (1979) A re-appraisal of the use of trace element to classify and discriminate between magma series erupted in different tectonic settings, *Earth and Planetary Sciences Letters*, Vol. 45, pp. 326-336.