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The San Giovanni Baptistery in Florence (Italy): characterisation of the serpentinite floor

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Abstract. The San Giovanni Baptistery in Florence (Italy) is an outstanding worldwide monument, representative of Romanesque architecture, dating back at least to the XII century. The whole edifice is externally revetted by white marble of different provenance and, subordinately, of serpentinite, commercially known as “green marble”. This latter is a rock formed from the transformation of ultramafic rocks during low-grade metamorphism or hydrothermal processes; it has been used for building and ornamental purposes since ancient times. In the San Giovanni Baptistery, in addition to the facade, the “green marble” was used on the floor, which consists of white and green tarsias forming an oriental motif. In this work, we studied, through a multi-analytical approach, the green tarsias to compositionally characterise the Baptistery’s floor. At the same time, serpentinite samples from different ancient Tuscany quarries were collected and studied to compare their characteristics with those of the “green marble” from Baptistery floor.

1. Introduction

Serpentinites are commercially referred to as “Green Marble”, but this name has no correspondence to their mineralogy, geochemistry and physical properties. Serpentinites are rocks forming, at low (100°C) to intermediate (700°C) temperature [1], in many different geologic settings, by the hydration of olivine-rich ultramafic rocks; they consist mostly of serpentine-group minerals (approximate formula $Mg_3Si_2O_5(OH)_4$) and subordinately by magnetite, brucite, talc, calcite and magnesite.

During the serpentinization process, the primary Mg-rich minerals (olivine, orthopyroxene, and clinopyroxene) are replaced by serpentine-group minerals. The typical combination of mineral products results in a fine-grained, dark green to black rock (commonly crossed by veins of variable composition), whose density is significantly lower than that of the primary peridotite [2]. The most common serpentine-group minerals are lizardite, chrysotile, and antigorite, characterised by different structures [3-5]. Lizardite, which displays a flat crystal structure, i.e. a triangular plate truncated at each corner [2], is the most common pseudomorph of olivine. Chrysotile, very poor in Al and Fe³⁺, is characterised by cylindrical fibre even several centimetres in length, which generally fills secondary microfractures crosscutting the serpentinite; it is the main constituent of commercial asbestos, a material showing good outstanding electric, thermal, and phonic insulation properties, but its fine dust is thought to be deleterious to human health [6]. Antigorite, with its interlocking texture, show difficult cleavage and enhanced hardness and seismic velocities compared to those of lizardite and chrysotile; it commonly occurs in partially recrystallised and metamorphosed serpentinite.

The serpentine minerals are stable under a wide range of temperature and pressure; in particular, lizardite and chrysotile are stable at low temperature (0-300°C) and pressure (<1GPa) conditions but, at high water/rock ratio, chrysotile becomes more stable than lizardite [7]. Antigorite is considered to be the high-temperature high-pressure stable phase of serpentine [1]. The serpentinization process produces variation and deformation of the original rock structure with the consequent weakness of its



mechanical properties. The resulting rock display relatively high porosity and absorption coefficient, and a high tendency to shear and failure. Also, the serpentinite can undergo a carbonation process through precipitation of carbonates in its shears and fractures or transformation of serpentine depending on the availability of magnesium and calcium in the precursor rock. The carbonation process will obviously influence the serpentinite behaviour.

Due to its compositional and physical-mechanical characteristics, serpentinite displays moderate weathering resistance which also depends on the environment conditions in which it is placed and whether it is carbonated or not. Despite its fragile behaviour, this rock has been worldwide used since ancient times for ornamental and building purposes. In this paper we studied the “green marble” used on the floor of San Giovanni Baptistery in Florence; we present the first compositional results of a wider study realised in collaboration with the Opera di Santa Maria del Fiore aimed to the complete characterisation of the materials prior than their use during restoration and replacement work.

2. The San Giovanni Baptistery and the “green marble”

The San Giovanni Baptistery is an outstanding worldwide monument, representing the oldest religious monument in Florence (Italy). Due to the lack of primary sources and specific dating issues, the Baptistery origins have been debated for a long time and are still controversial: different hypotheses, covering seven centuries, have succeeded. Among the hypotheses, it was believed built over the ruins of a Roman temple dedicated to Mars, dating back to the 4th-5th century A.D., or edified during the Longobard period [8]. The archaeological excavations effected in the period 1895-1915 seemed to strengthen the thesis of a medieval origin [9]. Recently, Bernabei et al. [10] studied the timber structure of the dome and obtained a radiocarbon dating of the chestnut from the 11th-12th centuries; also, they dated, through the dendrochronological analysis, a silver fir element to 1268. This date, possibly, represents a replacement coincident with the period, between 1270 and 1300, when a substantial part of the mosaics of the dome was positioned [10].



Fig. 1 - Detail of Baptistery floor, showing green (serpentinite) and white (marble) elements

The Baptistery, a representative of Romanesque architecture, has a typical octagonal plan layout, inscribed in a circle with a diameter of 36 m. Walls are doubled: an external wall of about 1.8 m width and an inner structure with columns at the ground level and squat pillars on the second and third Matroneo (Women’s Gallery) levels at 9 m and 15.6 m from the ground, respectively. An inner octagonal dome surmounts the Baptistery, covered on its outside by an octagonally shaped masonry. The whole edifice is externally revetted by white marble originating from Italy and Greece [11] and, subordinately, of serpentinite that, in addition to the facade, was used on the floor, which consists of white and green tarsias (Fig. 1) forming an oriental motif.

2.1. The Tuscany serpentinites

In Italy, serpentinite outcrops occur in the Alps, and in the Northern, Central and Southern Apennines. The Baptistery serpentinite has been historically referred to the Ophiolitic Complex (Northern Apennine), outcropping in Tuscany in different localities such as Florence, Impruneta, Prato, Pistoia,

Siena and Volterra. It originated, during the Jurassic period, through a serpentinization process of ultrabasic rocks in a seafloor environment [12]. The sequence of Tuscany Ophiolitic Complex mainly consists of two serpentinite masses separated by a gabbro lens. The ophiolitic sequence includes: a dark serpentinite, sometimes deeply altered, a granular metagabbro, and a bluish-green diabase, minor lenses and veinlets of ophicalcite, cherts, and ophiolite breccias.

From a variety of historical sources [13 and references therein] it results that the supply quarries of the Baptistery serpentinite, locally known with different name such as Verde di Prato, Nero di Prato [14], Marmo Nero [15, 16], Paragone [17,18], were those located in the area of Monte Ferrato (Prato) and Impruneta (Florence); in particular, the oldest quarries were on Piano di Gello, on the eastern slope of Monte Piccioli (Monte Ferrato area), which were already exploited since the eleventh century, and currently closed. Among the old descriptions of these rocks, the most complete is that of Targioni Tozzetti [19], who referred to the different lithologies as "gabbro". At those times, the Italian term *serpentino* and gabbro were considered synonymous. Von Buch [20], introduced the term gabbro in the scientific literature with his modern meaning in 1809, in a misinterpretation of the Tuscan use whereas the term ophiolite was used, for the first time, by Brongniart [21] in 1813, as Hellenism for the Italian term *serpentino* (*serpente* = snake), used in Tuscany for many centuries for a snake-skin-like ornamental stone [22]. The serpentinite rocks display a characteristic green colour, from light to almost black, with a bluish reflection at times; in some cases, whitish veins crosscut the rock. A variety of this rock, light green with a dense network of dark veins, is known by the local name of "Ranocchiaia" (frog rock) [17].

3. Sampling and Analytical Methods

During this work, serpentinite samples from the Baptistery floor and from some ancient quarries in the area of Monte Ferrato and a small outcrop at Impruneta were collected and analysed for their mineralogy and bulk major element composition. The mineralogical characterisation was obtained at the Dipartimento di Scienze della Terra and CNR-IGG (Firenze) by using polarising microscope, XRD and EPM; the bulk major and trace element composition was obtained by ICP at the Activation Laboratories, Ancaster (Canada).

The textures of the serpentinites were studied on thin sections (30 microns thickness) using a Zeiss Axio Scope.A1 polarising microscope, equipped with a camera (resolution 5 megapixel). XRD analysis was conducted using a PANalytical diffractometer with radiation $\text{CuK}\alpha 1$ ($\lambda=1.545 \text{ \AA}$) and graphite monochromator, operating at 40 kV, 20 mA, investigated range $2\theta=5-70^\circ$, software X'PertPRO and High Score for data acquisition and data interpretation of the mineralogical composition.

The mineral chemistry composition of major elements was performed by using a JEOL JXA-8600 microprobe equipped with four wavelength-dispersive spectrometers (WDS), under the following operating conditions: accelerating voltage at 15 kV, beam current at 10 mA and beam diameter at 3-5 μm . Counting time was 10s for Na, 15s for all other major elements and 40s for minor elements (such as Mn, Sr and Ba). Matrix effects were corrected by PAP algorithm, following the Pouchou and Pichoir method [23]. Analytical data on international reference standards measured during the analytical session show a good precision, with a variation coefficient lower than 3% on major elements, in accordance with the long-term accuracy and reproducibility of the lab as given in Vaggelli et al. [24].

For whole rock, major element analyses, samples were prepared in a batch system. Each batch contains a method reagent blank, certified reference material and 17% replicates. Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The molten melt was immediately poured into a solution of 5% nitric acid, containing an internal standard, and mixed continuously until completely dissolved (~30 minutes). The samples were run on a combination simultaneous/sequential Thermo Jarrell-Ash ENVIRO II ICP (inductively coupled plasma). Calibration was performed using seven prepared USGS and CANMET certified reference materials. One of the seven standards was used during the analysis for every group of ten samples. The detection limit is in the range 0.01 and 0.001 (%).

4. Results and Discussion

Serpentinite samples from the San Giovanni Baptistery and from serpentinite outcrops in the areas of Monte Ferrato and Impruneta display a general similar aspect; the collected Impruneta rock samples

show a darker green colour imputed to the uniform distribution of magnetite small crystals.

The studied rocks display an overall similar texture. The primary Mg-rich minerals, olivine, clinopyroxene and orthopyroxene, are completely replaced by serpentine (only chrysotile is recognisable in cross-fibre veins), fine-grained (20-80 μm) magnetite and spinel. Ghosts of pyroxenes, displaying a coarse particle size (2-4 mm), are easily distinguishable. The serpentine minerals are present as a lattice of cross-fibre veins (100-250 μm), that give rise to a mesh texture (serpentinisation of olivine) and as a bastitic texture (serpentinisation of pyroxenes), in variable percentages (Fig. 2 a). In the Impruneta rock sample, the mesh texture is subordinate to the bastites and shows a dominant fine lattice (50-100 μm). All the samples are affected by the presence of a variable abundance of late fractures (40-100 μm), filled with talc, which also occurs as small colourless grains scattered in the groundmass of serpentinite minerals. The studied rocks do not exhibit evidence of carbonisation processes.

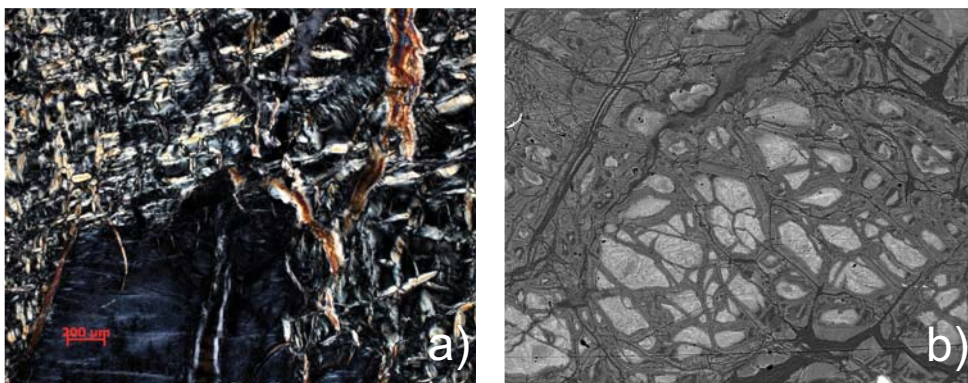


Fig. 2 - a) Polarised light micrograph showing mesh-textured and bastite from BPT1 sample; b) Back-scattered electron image (100 X) of BPT1 sample showing mesh texture

The diffractometric analyses permitted to distinguish two varieties of serpentine, not resolvable through the optical microscope. All the studied serpentinites show the same mineralogical composition, characterised by lizardite and chrysotile and subordinate presence of magnetite.

Based on the texture and mineralogy, the studied serpentinites can be ascribed to the pseudomorphic petrological type [5, 25]. These results are in agreement with the data obtained through electron microprobe analyses (in Table 1 are reported representative analyses of the serpentine-group minerals). The different analysed rock samples do not display significant compositional differences: in each sample two different serpentine-group minerals (Fig. 2b), whose composition corresponds to a different texture is present. According to previous studies [5, 26], serpentine pseudomorphs after olivine, orthopyroxene and clinopyroxene are indistinguishable as groups by their Fe, Mg, Mn and Ni contents.

Table 1 - Representative microprobe analyses of serpentine-group minerals from the studied rocks

Sample	SF1-1	SF1-3	SF1-6	SF1-9	SF1-10	SF3-1	SF3-2	SF3-3	SF3-5	SF3-7	SF3-8	SF3-9	SF3-11
<i>Texture</i>	<i>bastite</i>	<i>bastite</i>	<i>bastite</i>	<i>mesh</i>	<i>mesh</i>	<i>mesh</i>	<i>mesh</i>	<i>bastite</i>	<i>bastite</i>	<i>bastite</i>	<i>bastite</i>	<i>mesh</i>	<i>bastite</i>
SiO ₂	39.2	41.9	39.7	42.6	41.4	39.4	41.9	38.2	39.4	38.9	36.7	39.4	40.0
TiO ₂	0.004	0.040	0.040	-	0.069	0.015	0.012	0.094	0.017	0.075	-	0.128	-
Al ₂ O ₃	1.88	1.36	1.57	0.48	0.26	1.72	0.35	2.65	2.22	2.64	5.55	1.92	1.47
FeO	6.56	1.32	5.82	3.54	4.63	8.28	4.23	6.74	7.18	4.42	4.69	7.84	5.46
Cr ₂ O ₃	1.550	1.510	0.853	0.064	0.017	0.060	0.017	1.163	1.012	1.002	1.348	0.053	0.420
MnO	0.111	0.064	0.101	0.098	0.054	0.192	0.054	0.157	0.168	0.100	0.008	0.166	0.092
MgO	37.3	40.4	37.9	38.5	39.0	36.2	40.2	36.1	35.6	37.8	37.6	37.4	37.8
CaO	0.086	0.098	-	0.010	0.088	0.050	-	0.031	0.093	0.061	0.127	0.085	0.229
Na ₂ O	-	-	-	-	0.011	0.078	-	0.004	-	-	-	0.048	0.153
K ₂ O	0.019	-	-	-	0.003	0.040	-	-	0.013	0.006	0.014	0.009	-
Total	86.7	86.7	86.0	85.3	85.6	86.0	86.7	85.2	85.6	85.0	86.0	87.0	85.6
H ₂ O*	13.29	13.26	14.00	14.68	14.41	13.96	13.31	14.80	14.36	15.00	14.00	12.98	14.42
Impruneta						Baptistry							
Sample	SI1-1	SI1-3	SI1-5	SI1-6	SI1-9	SI1-11	BPT1-1	BPT1-4	BPT1-6	BPT1-10	BPT1-11	BPT1-12	BPT1-13
<i>Texture</i>	<i>bastite</i>	<i>bastite</i>	<i>bastite</i>	<i>bastite</i>	<i>bastite</i>	<i>bastite</i>	<i>bastite</i>	<i>bastite</i>	<i>bastite</i>	<i>mesh</i>	<i>mesh</i>	<i>bastite</i>	<i>bastite</i>
SiO ₂	42.7	37.7	36.5	38.3	39.4	38.7	40.4	37.8	39.8	41.3	41.0	37.7	39.5
TiO ₂	0.137	0.060	0.094	0.069	0.064	0.037	0.188	0.048	0.087	0.080	0.047	0.091	0.090
Al ₂ O ₃	1.47	4.07	3.40	3.27	4.71	4.87	1.47	5.30	2.76	1.19	4.05	4.95	1.92
FeO	5.43	5.78	7.66	6.68	6.43	5.60	6.97	2.71	5.41	8.06	2.59	4.18	7.01
Cr ₂ O ₃	0.964	0.890	0.942	0.695	0.850	1.064	0.694	1.539	0.877	0.014	0.130	1.253	0.968
MnO	0.100	0.072	0.112	0.144	0.138	0.078	0.172	0.028	0.137	0.146	0.066	0.086	0.202
MgO	33.3	35.0	35.7	34.2	35.6	34.5	35.9	38.6	35.6	34.5	36.8	36.8	35.7
CaO	0.319	0.095	0.065	0.071	0.008	0.009	0.064	0.000	0.166	0.048	0.068	0.150	0.056
Na ₂ O	0.159	0.062	-	0.083	0.080	0.185	0.062	0.196	0.019	-	-	0.070	0.010
K ₂ O	0.019	-	0.013	-	0.020	-	-	0.007	0.006	-	0.032	0.002	0.094
Total	84.6	83.8	84.6	83.5	87.4	85.1	85.9	86.2	84.9	85.4	84.7	85.3	85.6
H ₂ O*	15.37	16.20	15.44	16.49	12.63	14.90	14.08	13.75	15.15	14.60	15.26	14.75	14.44

*Estimated by difference

However, in the comparison of mesh-textured serpentine with bastites, significant differences, with respect to Cr, were observed; indeed, this element migrates very little during the serpentinisation process because of its low solubility in low temperature aqueous solutions [27]. Mesh-textured pseudomorphs, analysed in this study, contain only minor amounts of chromium (0.014-0.06 % Cr₂O₃). The Cr₂O₃ contents of px-bastites range from 0.40 to 1.5 %.

The chemical composition of the studied serpentinites from the three different provenances (Table 2) shows very small variability; the rocks have high MgO% (37.6–39.1) and SiO₂% (~38) contents with a considerable amount of iron (Fe₂O₃% = 7.6-8.3) as well as variable values of Al₂O₃% (0.8–1.7). The considerable amount of Fe₂O₃ may be attributed to the presence of magnetite and chromite minerals whereas the low CaO contents may be attributed to the absence of dolomite and calcite. All samples have high loss-on-ignition (LOI) values (13.5 to 15 wt.%) indicative of the extensive serpentinisation of the rocks.

Table 2 - Major element analyses (mean) of the studied serpentinites

Sample	Monte Ferrato	Impruneta	Baptistery
	SF1	SI1	BPT1
SiO ₂	37.7	37.8	37.8
TiO ₂	0.025	0.038	0.035
Al ₂ O ₃	0.85	1.70	1.60
Fe ₂ O ₃	8.30	7.80	7.60
MnO	0.071	0.099	0.117
MgO	39.1	37.6	38.6
CaO	0.02	0.10	0.03
Na ₂ O	< 0.01	0.01	0.02
K ₂ O	< 0.01	< 0.01	< 0.01
P ₂ O ₅	< 0.01	< 0.01	< 0.01
LOI	13.6	15.0	13.9
Total	99.7	100	99.7

5. Concluding remarks

The data obtained in this work revealed only small differences among the studied rock samples; these differences are not sufficient to assert with confidence that the serpentinite used in the Baptistery floor came from the Monte Ferrato or Impruneta quarries. Additional compositional analyses and physico-mechanical measurements are in progress on a wider number of rock samples. However, on the basis of: a) documents conserved at the Archivio dell'Opera di Santa Maria del Fiore; b) documents present in the Archivio di Stato di Firenze and Prato; c) old literature data [e.g.14-18, 27] we can assume that the greatest part of material supplies came from the Monte Ferrato quarries. This fact does not exclude that small quantities of material, possibly used only for decoration [27], were obtained from the Impruneta quarries.

From the preliminary obtained data, we conclude that the followed multi-analytical approach is a reliable one and permits to obtain details of textural and mineralogical characteristics of serpentinitic rocks; the availability of these data play a relevant role in any restoration and replacement work. In fact, according to several authors [e.g. 28] the main factor favouring the resistance of serpentinite to weathering seems to be the mineralogical composition of this type of rocks and, in particular, the nature of the serpentine-group minerals. Our research is, thus, focused on obtaining documentation of the details of the serpentine-mineral assemblage that characterises various commercially available serpentinites which allows the best possible choice of materials to be used for any architectural purpose.

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