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"*Serpentino della Valmalenco*" (Central Alps, Northern Italy): A green dimension stone with outstanding properties

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ABSTRACT

the "*Serpentino della Valmalenco*", a group of serpentinite varieties, was quarried and used as a dimension and building stone since the XI century, especially in thin slabs for roof covering. The extractive activity initially took place in underground, moving to open pit quarries in the 20th century. It is currently a widely used and appreciated material on the international market, commercialized in several commercial varieties and processed in many ways. The schistose varieties are characterized by a marked mylonitic foliation, which confers excellent attitude to splitting, whereas the "massive" ones are suitable for paving and cladding. The rocks are made up of abundant antigorite, with minor olivine, clinopyroxene, chlorite and magnetite. The excellent values in compressive and flexural strength, as well as the extremely low porosity, are documented by ultra-centenarian roofs and high-stress applications. The significant historical heritage, represented by underground quarries, historic buildings, and trade routes, deserves to be enhanced with the development of geotouristic routes. At the same time, the peculiar chemical, mineralogical and microstructural characteristics of the material open the horizons to new applications.

1. Introduction

"*Serpentino della Valmalenco*" is the commercial term referred to the varieties of serpentinite extracted in Valmalenco (Sondrio, Central Alps, Northern Italy): it is a dimension and building stone extracted at least since the XI century, historically used in slabs for roofing, currently marketed worldwide in many varieties, and appreciated for its technical qualities and colour shades. Serpentinites are ultramafic metamorphic rocks, deriving from the hydration of peridotites (peridotite + H_2O + O_2 → serpentinite, mainly as ocean-floor metamorphism), composed mainly of serpentine polymorphs (the most important are antigorite, lizardite, and chrysotile), occurring in ophiolitic and sub-continental mantle complexes (O'Hanley, 1996; Bodinier and Godard, 2003).

In the field of dimension stones, the "*Serpentino della Valmalenco*" historically belongs to the "slate" sector (Càrdenes et al., 2014; Cárdenes et al., 2019), having always been worked into slabs by manual splitting. However, the numerous applications of "massive" varieties since the early 20th century (floorings and cladding) have also placed it in the "marble" sector, i.e., polishable rocks of moderate hardness (Cassar et al., 2014; Cooper, 2018; Hannibal et al., 2020).

As mentioned above, there are two main commercial varieties (Consorzio Artigiani Cavatori della Valmalenco, 2002; Cavallo, 2005): schistose or "slaty" ("*Serpentinoscisto*", quarried in the Sasso Corvi, Agnisci, Alpe Fora and Sellette extractive areas) and "massive" serpentinite ("*Serpentino Massiccio*", marketed under several trade names, e.g. "*Verde Mare*", "*Verde Vittoria*", "*Verde Giada*", "*Verde Torre*"), exploited in the Torre S. Maria, Castellaccio, Le Prese, Valbrutta and Dossi di Franscia areas (Fig. 1). It is a relatively small extractive district, centred mainly in the municipalities of Chiesa in Valmalenco, Lanzada and Torre S. Maria; 22 enterprises in the valley perform quarrying and processing of the serpentinite, with more than 180 workers involved. Apart from two companies who have set at an industrial level, the remaining operate in the handicraft, and are grouped in the "*Consorzio Artigiani Cavatori Valmalenco*", an association that promotes and finances various enterprises aimed at improving and developing stone products. The overall production of this area is rather limited, compared to the most important Italian quarrying areas, but here the need for proper management of the stone industry is deeply felt, because of the complex environmental conditions (high mountain areas with touristic vocation).

The purpose of this article is to highlight the origins of the success of this material for almost 1000 years, which are rooted in the peculiar mineralogical and microstructural properties and give it great potential both in modern applications and in terms of history and cultural heritage. In a modern and circular economy perspective, a deep knowledge

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of the chemistry, mineralogy, and petrography is essential, to explain technical properties, predict material durability, and propose innovative applications.

1.1. Historical background and applications

The first historical information about the extraction and processing of the “*Serpentino della Valmalenco*” date back to the XI century: just above the village of Chiesa in Valmalenco, where there is a natural ridge (1140 m AMSL), the serpentinite is particularly schistose. It didn’t cost much to the local craftsmen, already experts in the excavation of the local iron mines, to "test" those rocky banks that easily split into slabs to pave the huts, or even better, to cover the roofs. The serpentinite slabs were of considerable surface area, and at the same time flat, thin and light, easily transportable, and weatherproof. The experience acquired in the extraction of iron ore, using elementary tools such as mallets, hammers, wedges, and levers, as well as the effect of fire in inducing the fracturing of the rock, facilitated the birth and evolution of serpentine extraction techniques. The more schistose rock banks (called "*banche buone*" or “*preda malenca*”), several meters thick, were interspersed with more massive benches: the local quarries, called "*giovelli*", were then distinguished by local names. The quarry workers, called "*giovellai*", started with the excavation following the best benches, i.e., the most fissile ones, using the fire (produced with dry wood), similarly to the ancient iron mines. The first quarries were therefore underground, and as they progressed deeper, some of the waste material was used to stabilize the underground voids. The blocks, extracted by force of blows with mallets and wedges, were often of considerable size, and were later reduced in smaller pieces called "*lot*", that is, in such a size that they could be transported outside on the back of a man or dragged along the steep and uncomfortable gully. The interior of the quarry was obviously dark and was lit by resinous wood chips that held a flame and could be moved easily.

The extraction of stone slabs, initially based on the use of fire, rapidly developed by the end of the XVII century, when gunpowder (explosive) was introduced. Near the entrance of the tunnel a modest roof ("*la teciàda*") was built, which served as a forecourt and workshop for the splitting of the blocks into slabs. The shed, in addition to the space reserved for work, included two other spaces: one was used as a rustic kitchen, the other served as a deposit of the few tools and wood for the fire of the quarry. Towards the end of the nineteenth century, fire and oil for interior lighting also gave way to more modern and user-friendly tools such as first oil lights and acetylene lamps afterwards. All the quarrymen were federated into a confraternity (with social and religious purposes) and were also dedicated to agriculture and sheep farming, two other essential activities of their economy. The serpentine slabs, called "*piode*", were divided among the partners at the end of the day, stacked and transported by packhorse along the valley road: towards the south those destined for the rest of Italy, towards the north those for the buyers in the Graubünden canton (Switzerland).

Serpentine slabs were abundantly used in Sondrio in the 14th century, then reached other towns in Valtellina, while some documents attest to their transportation in the Graubünden canton in the 16th century, also reaching Chur and its surroundings. Following the construction of the Valmalenco road up to the village of Chiesa in Valmalenco in the 19th century, a new handicraft category arose in the village, that of the carters: soon they were traders of slabs ("*piode*"), and in the first decades of the 20th century, following the arrival of motorized vehicles, they became truck drivers. In the 20th century, there was a gradual shift to open-pit quarrying, increasing production considerably; the demand for slabs, after the lull of the Second World War, had an exceptional increase, with a wide use in residential buildings. The

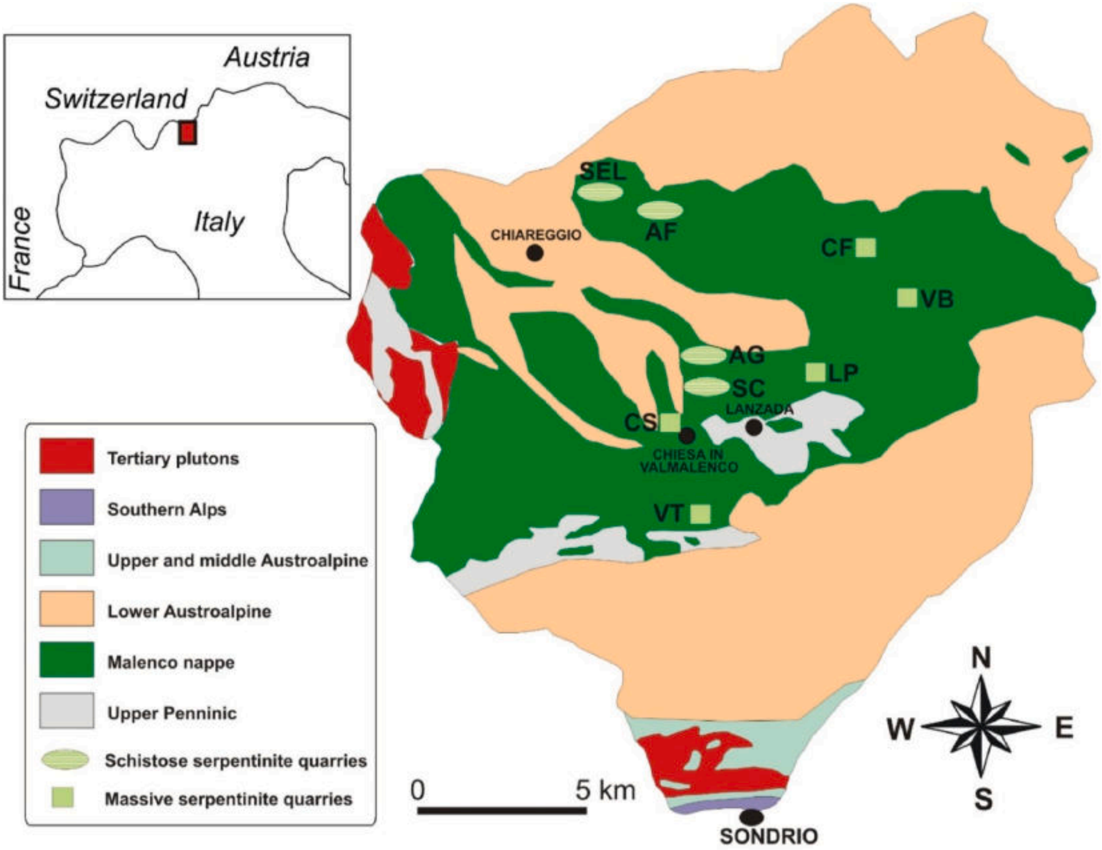

Fig. 1. Simplified geological sketch-map of the Valmalenco area (geological domains from Trommsdorff et al., 2005). The main quarry areas are highlighted: Torre S. Maria (VT), Chiesa Valmalenco (CS), Lanzada (LP), Sasso Corvi (SC), Agnisci (AG), Valbrutta (VB), Campo Franscia (CF), Alpe Fora (AF) and Sellette (SEL).

modernization of extraction and processing techniques, implemented in recent decades, enabled the development of a local, national, and international market for these products.

The typical "*piode*" roof (Fig. 2) is characterized by larger slabs in the eaves and, going up towards the ridge, by smaller and smaller slabs. The current thickness is around 1 cm, while the shape that is preferred is the rectangular one (less the square one). There are also other minor products, such as "*spaccatello*" (slabs for exterior cladding, measuring 15 × 31 cm up to 30 × 30 cm), "*spacco*" (irregular fragments between 2 and 3 cm thick), typically used for *opus incertum* cladding or masonry, and small boulders (usually cubes), used for paving roads and sidewalks. A niche use is represented by large slabs of irregular shape ("*ciatun*") for cooking foods.

Currently, the "*Serpentino della Valmalenco*" is appreciated and marketed worldwide, and as examples of prestige applications (Fig. 2) we can include: the Bundeskanzleramt (Berlin, Germany), Platz von Neuen Tor (Berlin, Germany), Harmony Office Center (Warsaw, Poland), Erste Bank (Budapest, Hungary), Garak Tower (Seoul, South Korea), Basel-Mulhouse-Freiburg airport (Basel, Switzerland), Messe Neubau (Zurich, Switzerland), Bormio Terme (Bormio, Italy), Orly Airport (Paris, France), Cheung Kong Centre (Hong Kong), Moscow Bank (Moscow, Russia), Fendi Beijing Mitsukoshi (Beijing, China).

1.2. Geological framework

The geological setting of the Valmalenco area (Fig. 1) is characterized by the following tectonic units, from bottom to top (Trommsdorff et al., 2005): upper Penninic (Suretta, Monte Forno and Malenco nappes) and lower Austroalpine (Margna, Sella, Bernina, Campo and Grosina-Tonale nappes). The Malenco nappe and the basement of the Margna nappe represent the pre-Alpine lithosphere of the Adria plate; both units are cut by the Permian Fedoz Gabbro, intruded at the limit between the lithospheric mantle and the lower continental crust (Trommsdorff et al., 1993; Müntener and Hermann, 1996). The tectonic contact between the Malenco and Margna nappes is characterized by mylonites and breccias referable to both units (Breccia d'Ur). In the

Fig. 2. Examples of applications of the "*Serpentino della Valmalenco*": (a–b) typical rural houses (Caspoggio and San Giuseppe villages, Valmalenco); (c–d) slabs for roof covering (Valtellina, northern Italy); (e) Bundeskanzleramt (Berlin, Germany); (f) external cladding (Switzerland); (g) bathroom top and washbasins; (h) pellet stoves.

western Valmalenco area the nappe pile is crosscut by the Oligocene Bergell and Triangia intrusives (Trommsdorff et al., 2005). The Malenco nappe (lower crust-mantle complex) is exposed over an area of 130 km^2 at the Penninic to Austroalpine boundary zone, interposed between the Margna and Suretta nappes, and has been integrated in the Alpine nappe pile during the Late Cretaceous (Münterer and Hermann, 1996). The Malenco nappe was initially interpreted as a Mesozoic ophiolitic suture, but field data demonstrate that the Malenco ultramafics formed the lithospheric subcontinental mantle below the Margna basement during pre-Alpine, post-Variscan times (Münterer et al., 2000). Most of the Malenco ultramafics consists of schistose antigorite-olivine-diopside-chlorite-magnetite bearing rocks, showing various degrees of deformation, serpentinization and recrystallization: the spectrum ranges from massive, layered lherzolites to schistose, completely serpentinized rocks. In some areas, however, primary structures like the original mantle textures (tectonites and mylonites) and relic mineralogies are still preserved (especially banded clinopyroxenites and websterites). Regional metamorphism in serpentinites is defined by mineralogical associations that define a prograde sequence from the upper stability limit of chrysotile to the lower stability limit of olivine (Münterer and Hermann, 1996).

1.3. Quarrying and processing

The traditional extraction of the “*Serpentinoscisto*” (schistose serpentinite) occurred mainly in small underground quarries at the historical “*Giovello*” site, close to the Chiesa Valmalenco village: this area is characterized by numerous underground tunnels, with many evidences of the ancient quarrying activity, such as cableways with counterweight for the transport downstream of the stone slabs. There is a project aimed at the geotouristic and ethnographic enhancement of the site, with the securing of some tunnels, the arrangement of historical quarrying equipment, guided tours, and a museum. A milestone for the development of quarrying was undoubtedly the introduction of explosives, which involved the manual drilling of blasting holes and the use of black powder. In the early 30’s, with the introduction of helicoidal wire cutting, the serpentinite began to be extracted to produce blocks. Since the 80s, with the introduction of diamond wire, quarrying gradually reached current levels. At present time there are 19 active quarries: the production of the single quarries is highly variable, from few hundreds up to 10,000 m^3/yr, and the total volume extracted is assessed around 89,000 m^3/yr. The resulting commercial blocks and products can be estimated around the 40–50% of the extracted raw material (Cavallo, 2018).

The serpentinites are extracted in relatively small open-cast mountain quarries (Fig. 3), opened on the slopes or sometimes on the peaks; climatic restrictions (ice, snow, elevation between 870 m and 2020 m AMSL) are at times important and may involve long periods of inactivity. Generally, the quarries are worked from the top downwards, by means of horizontal beds and large banks, creating one or more terraces, involving the following operational phases: primary cut, tip-over, block cutting and squaring off. The extraction technologies are based on a combined use of diamond wire cutters (plastic coated wire) and drilling with explosives (“dynamic splitting” using detonating cord). For a short period also the chain saw has been tested, however, the relative hardness of the rock has not allowed good results. In the schistose serpentinite quarries, the primary cut is made by dynamic splitting, exploiting two important discontinuity surfaces of the rock mass; rarely the lateral separation surface must be created, and in this case diamond wire cutter is used. Due to the different characteristics of the rock mass, the massive serpentinites are quarried almost exclusively with the diamond wire cutter. Once the separation of the bank from the rock mass has been completed, it must be tipped over on the quarry floor (with hydraulic cushions or using a bucket excavator) and squared off (to form commercial blocks) using diamond wire shaping machines, block cutters or manual rock-splitting devices. The commercial blocks are then transported to the processing facilities. In all quarries, the rock mass has excellent geotechnical properties, with a considerable regularity in the spacing and linear persistence of fractures. The total production, in terms of rock removed from the deposits, is assessed around 46,000 m^3/yr and 43,000 m^3/yr for schistose and massive serpentinite respectively.

The schistose serpentinite, because of its very fine grain-size and marked foliation, is mainly split by hand into thin slabs (5–10 mm thickness, Fig. 3c) for various commercial applications, especially for

Fig. 3. a) Sasso Corvi schistose serpentinite quarry; b) Valbrutta “massive” serpentinite quarry; c) traditional manual splitting by hammer and chisel in thin slabs; d) Diamond disc cutting of a “massive” serpentinite block.

roof covering. Currently, the schistose serpentinite blocks that arrive at the laboratory undergo two distinct processes: first mechanical and then manual. The mechanical action, obtained with diamond disk cutting machines, is used to make cuts of the desired length orthogonal to the schistosity. The second operation, manual, is aimed at obtaining the finished product: exploiting the peculiar fissility of the rock along the schistosity planes, using hammers and chisels it is possible to obtain perfect slabs of various thicknesses. Generally, the length of the "*piode*" varies from 60 and more cm for the larger ones, scaling 5 cm until you get the smaller ones of about 35 cm.

The "massive" serpentinites have a coarser grain-size and a less evident foliation, and are extracted in squared blocks, that are cut by steel shot multi-blade gangsaw or diamond disc (Fig. 3d), and then processed in many ways: honed, polished, sandblasted, bush hammered, flamed, antiqued, and worked with computerized numerical control machines (CNC). Over time, the market has evolved considerably, and the material is also used to make complex components (e.g., high-end pellet stove inserts with bas-reliefs and intricate designs, Fig. 2g and h).

1.4. Environmental concerns and quarry waste management

The most important environmental concern in this quarrying area is represented by naturally occurring asbestos (NOA), in the form of sporadic chrysotile veins, that occur within the rock mass along fractures and cracks. Detailed field and laboratory studies, as well as extensive airborne particulate sampling, highlighted airborne asbestos concentrations below the occupational exposure limit (OEL), and no issues with the finished serpentinite products (Cavallo and Rimoldi, 2013; Cavallo, 2018). At the base of a good result, remains the importance of detailed preliminary geological and petrographic studies, to avoid the interception of asbestos veins and fractured rock masses.

The second challenge is represented by quarrying and processing waste: approximately 45–50% of the gross volume of the extracted rock is lost in the quarry in the form of shapeless blocks, whereas the processing waste (ranging from rock debris to sawing sludge) is about 43,600 t/yr (Cavallo, 2018). At present time, there are no significant reuses of serpentinitic waste products, but the peculiar mineralogical and chemical composition suggests interesting applications in the ceramic and refractories sector (high MgO ceramics and forsterite refractories, Dìaz and Torrecillas, 2007; Cavallo, 2018), artificial rocks, filler for plastic and rubber, up to CO_2 sequestration by antigorite and olivine carbonation (Balucan and Dlugogorski, 2013; Power et al., 2013).

2. Materials and methods

A total of 120 commercial stone samples (45 schistose and 75 massive serpentinites), collected between 2012 and 2020, were characterized by polarized light microscopy (PLM) on thin sections, X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS). From 120 samples investigated by thin-section textural analysis, 47 were selected for microprobe work: rock-forming minerals were analysed with an electron probe microanalysis (EPMA) in wavelength-dispersion mode (WDS). Whole-rock geochemistry was determined for major elements by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS)]. The technical characterization of commercial samples was based on the following tests: compressive strength, flexural strength, abrasion resistance, and mercury-intrusion porosimetry (MIP).

2.1. Mineralogy, petrography and mineral chemistry

The PLM analyses (Leica DME 13595 microscope), both in transmitted and reflected light mode, were performed on polished thin sections, following the criteria summarized by Wicks & O'Hanley (1988) and O'Hanley (1996). The XRPD analyses were performed using a PANalytical X'Pert PRO PW3040/60 X-ray diffractometer with Ni-filtered Cu Kα radiation at 40 kV and 40 mA, ½° divergence and receiving slits, and step scan of 0.02 °2θ, in the 3–80 °2θ range; the limit of detection of XRPD for serpentine minerals it is approximately 0.5 % wt. The qualitative phase analysis was performed using the PANalytical HighScore Plus software version 2.2c using the ICSD PDF2-2008 database; quantitative phase analysis was carried out running the FULLPAT software (Chipera and Bish, 2002). The quantitative phase analysis was calibrated and verified on pure phases mixtures (antigorite, olivine, chlorite, diopside and magnetite) in known ratios. Mineralogy and microstructures were assessed also by SEM (Vega TS Tescan 5163 XM) in combination with an EDS analyzer (EDAX Genesis 400), with 200 pA and 20 kV as standard conditions, on carbon coated samples. Quantitative mineral chemistry on rock forming minerals was performed using a Jeol JXA-8200 EPMA-WDS; the system was operated with an accelerating voltage of 15 kV, a beam current of 15 nA and a counting time of 60 s on peak and 30 s on backgrounds, using a series of minerals as standards (kaersutite for Al, K, Na and Ti; fayalite for Mg; niccolite for Ni; omphacite for Si and Ca; spessartine for Fe and Mn). The results were processed for matrix effects using a conventional $\Phi(\rho Z)$ routine in the Jeol softwares.

2.2. Whole-rock geochemistry and technical properties

Whole-rock geochemistry was assessed for major elements (ICP-AES, whole rock fusion with meta-borate), trace and rare earth (RE) elements (ICP-MS), C and S (LECO®) at the Chemistry Labs, Vancouver (Canada). The technical characterization was performed at the certified laboratory Studio Sperimentale Stradale (Fizzonasco, Italy): compressive strength (UNI 9724/3, 1990), flexural strength (UNI 9724/5, 1990), abrasion resistance (Amsler, R.D. n. 2234, 1940); compressive strength was determined both orthogonally and parallel to the foliation; tensile strength orthogonally to the foliation. Total porosity and pore size distribution was assessed by MIP with a Thermofinnigan Pascal 240 Hg-porosimeter, with pressure ranging from 0 to 200 MPa.

3. Results and discussion

3.1. Mineralogy and petrography

The petrographic investigations on thin sections by PLM and SEM-EDS evidenced significant differences in fabric and mineralogy: except for a few samples with pseudomorphic textures, most of them exhibit interpenetrating and interlocking non-pseudomorphic textures, with various degrees of deformation and serpentinization (Fig. 4). The mineralogical composition of the serpentinites is characterized by various generations of antigorite, olivine, clinopyroxene (diopside), chlorite, magnetite and little amounts of chromite, Fe–Ni alloys, Fe–Ni sulphides and Ti-clinohumite; no relics of orthopyroxene were found. The antigorite amount is variable, and the spectrum ranges from completely serpentinized rocks to serpentinites with considerable amounts of olivine and diopside (up to 40–45% modal).

The most important rock-forming mineral is antigorite, occurring in two main generations (Fig. 4e): the first consists of thin sub-idioblastic lamellae aligned along the main foliation, the second of larger, almost perpendicularly oriented idioblastic laths. Olivine occurs in two generations: the first consists of larger xenoblastic crystals (500–600 μm), frequently fractured and with inclusions of opaque minerals; the second generation consists of small (50–100 μm), clear idioblastic crystals, with granoblastic mosaic texture. The first olivine generation is quite rare in the schistose varieties. There are two main diopside generations: the first is represented by relatively large crystals (even more than 3 mm, Fig. 4d) with abundant inclusions of opaque minerals (mainly magnetite), whereas the second by small crystals (with characteristic "mosaic" texture) or by epitaxial growth along the margins of the first-generation

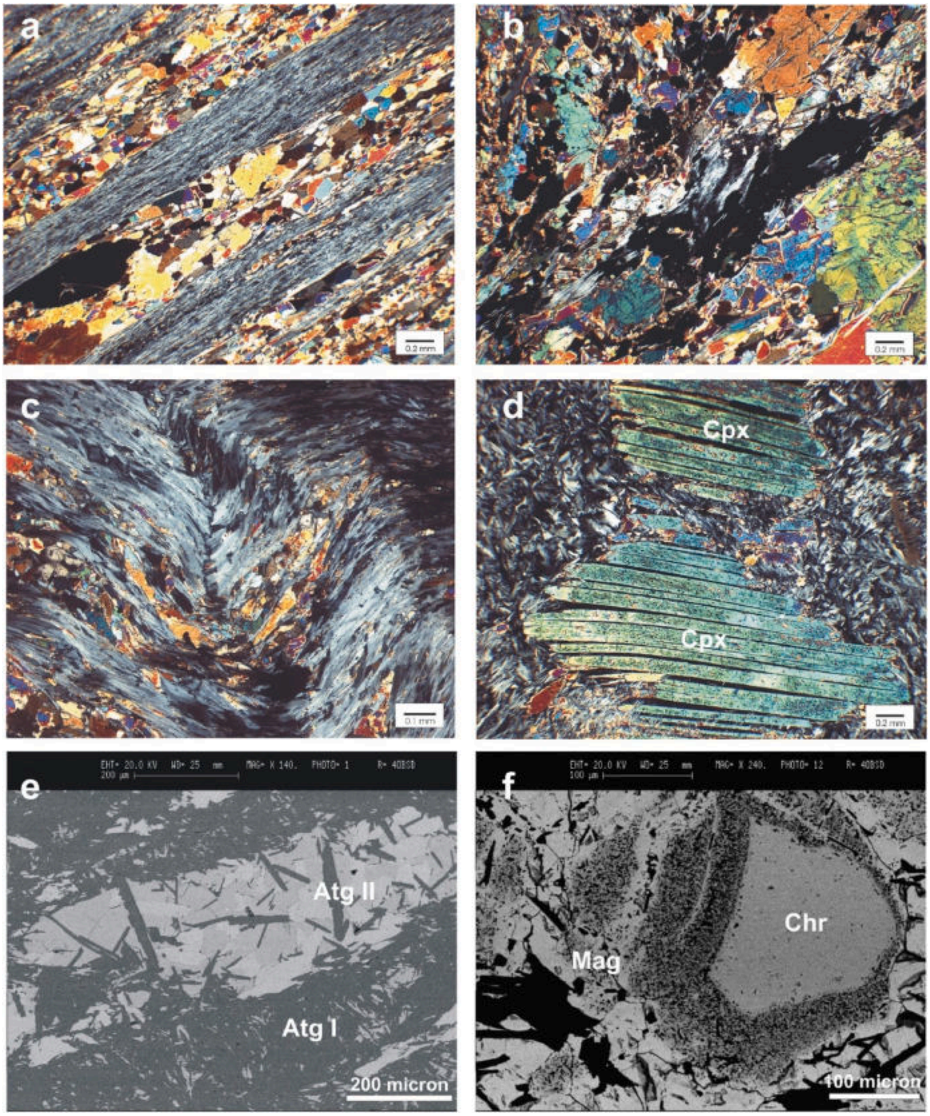

Fig. 4. a - d) PLM micrographs, crossed polars: schistose serpentinite ("*Serpentinoscisto*") with alternating domains of antigorite and mosaic olivine-diopside (a); "massive" serpentinite – Verde Vittoria (b); folded serpentinite - Verde Mare (c); diopside (Cpx) relics in "massive" serpentinite – Verde Torre. e – f) SEM backscattered electrons micrographs: two antigorite (Atg I and II) generations, differing in crystal size and orientation (e); magnetite (Mag) with Cr-rich core (Chr) (f).

crystals. Chlorite is always present in varying proportions, arranged in flakes parallel to the main foliation or, more commonly, in aggregates around magnetite crystals. Brucite is quite rare, in small fibrous aggregates intergrown with antigorite.

The schistose varieties frequently display mylonitic microstructures (sometimes folded, Fig. 4c) with marked foliation (Fig. 4a), and antigorite forms an interlocking equigranular texture composed of grains 20–350 μm in diameter, whereas olivine and diopside form mosaic textures (100–350 μm in diameter). The "massive" serpentinite (Fig. 4b) has a coarser grain size (antigorite up to 700 μm and olivine/diopside up to 2–3 mm), a less evident foliation, interpenetrating textures and quite rare bastites (mostly clinopyroxene, Fig. 4d). Magnetite is by far the most abundant opaque mineral, in small xenoblastic crystals or aggregates, frequently zoned, with Cr rich cores (Fig. 4f).

Bulk mineralogy was assessed by XRPD (Table 1): the performed quantitative analyses evidenced an excellent fit and little errors in phase quantification (<5% wt.), even phases characterized by structural disorder (Fig. 5). The antigorite content is extremely variable (58–85 wt%), as well as olivine (4–30% wt.) and chlorite (2–15% wt.). The clinopyroxene (diopside) content is generally low (2–9% wt.), likewise magnetite (1–6% wt.) and brucite (0.5–1.5% wt.). Generally, the "massive" varieties are characterized by higher contents in antigorite, whereas

Table 1
Mineralogical composition (mean and range) of schistose and "massive" serpentinite varieties (a total of 120 samples), determined by quantitative XRPD (Chipera and Bish, 2002). Abbreviations: Atg, antigorite; Chl, chlorite; Ol, olivine; Cpx, clinopyroxene; Mag, magnetite; Brc, brucite.

	Atg wt.% mean (range)	Ol wt.% mean (range)	Cpx wt.% mean (range)	Chl wt.% mean (range)	Mag wt.% mean (range)	Brc wt.% mean (range)
Schistose serpentinite	**64.1** (58.9–74.3)	**20.1** (10.3–30.4)	**5.9** (3.3–8.6)	**6.4** (1.8–15.5)	**3.8** (0.9–6.5)	**0.4** (<0.5–1.0)
Massive serpentinite	**74.7** (68.6–85.3)	**14.5** (4.1–27.7)	**3.9** (1.2–9.5)	**4.0** (2.4–10.7)	**3.0** (1.4–5.8)	**0.6** (0.5–1.7)

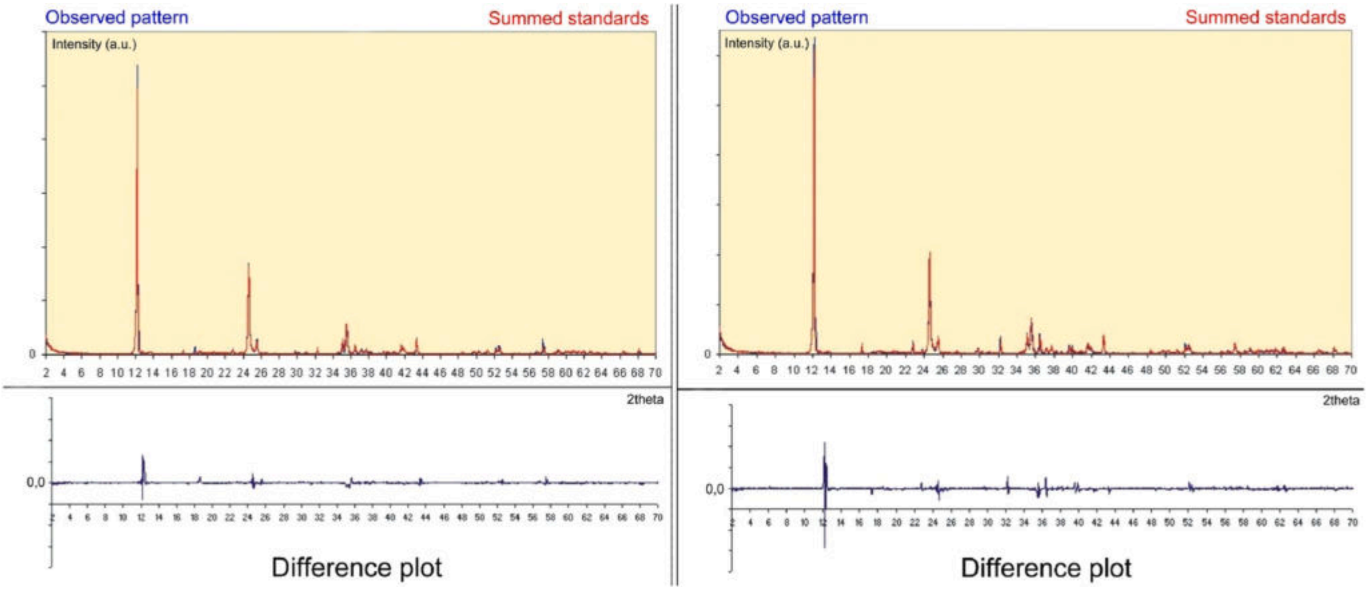

Fig. 5. Representative XRPD patterns and difference plots of schistose (on the left) and "massive" serpentinites (on the right), performed using the FULLPAT software (Chipera and Bish, 2002).

schistose varieties by higher amounts in olivine and clinopyroxene.

3.2. *Mineral chemistry*

The EPMA-WDS analyses (Table 2) evidenced chemical differences of the two different antigorite generations: the first occurs as fine-grained lamellae with appreciable amounts of Cr_2O_3 (0.3–0.7% wt.) and NiO (0.2–0.3% wt.), whereas the second is represented by coarser idioblastic blades with higher amounts of FeO (6–6.5% wt.). Two texturally and chemically distinct olivine generations were observed: the first exhibits cataclastic or porphyroclastic textures, and the composition varies from Fo_{91} to Fo_{94}; the second generation occurs with equigranular and crystalloblastic texture and composition from Fo_{85} to Fo_{88}. In a fair number of cases, MnO contents are higher than NiO, a feature that seems typical of metamorphic olivine ultramafic source; low content of other elements (TiO_2, Al_2O_3, Cr_2O_3 and CaO typically <0.1% wt.). Two generations of clinopyroxene (diopside) can be distinguished: the first corresponds to diallage relict grains (1–6 mm diameter), rich in exsolution lamellae, with variable amounts of Na_2O (0.1–0.6 wt %), Al_2O_3 (0.05–2.4 wt%) and Cr_2O_3 (0.06–0.5 wt%). The second generation of clinopyroxene, typically with 0.03–0.3 mm diameters and crystalloblastic texture, is close to the end-member diopside composition $CaMgSi_2O_6$. Chlorite (clinochlore) is characterized by high MgO (33.3 < MgO <34.8% wt.), Al_2O_3 (11–13% wt.) and Cr_2O_3 contents (1–3% wt.). Magnetite occurs as very fine-grained aggregates, elongated parallel to the main foliation, and as large, isolated grains with a size of 0.3–2 mm; most magnetite in the rocks show detectable amounts of Cr_2O_3 (0–12.5% wt.), with frequent relics of primary Cr-spinel (Fig. 4f). Ti-clinohumite [$M_8Si_4O_{16}Ti_x$ (OH) $_{2\text{-}2x}O_{2x}$ M = Mg, Fe^{2+}, Mn, Ni, $0 < x < 0.5$) is a typical accessory mineral, occurring in nodules and sometimes associated with apatite. Other common accessory minerals are represented by ilmenite $FeTiO_3$, sulphides [pyrrhotine $Fe_{1\text{-}x}S$, pentlandite $(Fe, Ni)_9S_8$, heazlewoodite Ni_3S_2] and alloys (awaruite Ni_3Fe, native Cu).

Table 2
Representative mineral chemistry of antigorite (Atg), olivine (Ol) and clinopyroxene (Cpx, diopside) generations (I and II generation, core), determined by EPMA-WDS (on 47 polished thin sections). For clinopyroxene the FeO/Fe^2O^3 ratio has been determined by stoichiometry (Droop method).

wt.%	Atg (I)	Atg (II)	Ol (I)	Ol (II)	Cpx (I)	Cpx (II)
SiO_2	41.02	40.38	41.37	39.86	53.29	55.15
TiO_2	0.04	0.01	0.13	0.02	0.38	–
Al_2O_3	2.65	2.93	0.09	0.07	1.65	0.06
Cr_2O_3	0.48	0.27	0.01	0.05	0.64	0.01
Fe_2O_3	–	–	–	–	1.69	0.50
FeO tot	3.43	6.54	6.22	14.02	0.52	0.79
MnO	0.12	0.03	0.32	0.48	0.13	0.08
NiO	0.36	0.08	0.26	0.21	–	–
MgO	39.27	35.37	51.59	44.99	18.46	17.48
CaO	0.01	0.17	0.01	0.04	23.16	25.98
Na_2O	–	–	0.01	–	0.18	0.06
K_2O	0.01	–	–	–	0.02	–
Total	87.39	85.78	100.01	99.74	100.12	100.11
	Ions on the basis of 28 O		Ions on the basis of 4 O		Ions on the basis of 6 O	
Si	7.707	7.814	0.999	1.001	1.929	1.994
Ti	0.006	0.000	0.002	0.000	0.010	0.000
Al	0.587	0.668	0.003	0.002	0.070	0.003
Cr	0.071	0.041	0.000	0.001	0.018	0.000
Fe^{3+}	–	–	–	–	0.046	0.014
Fe^{2+}	0.539	1.058	0.126	0.294	0.016	0.024
Mn	0.019	0.005	0.006	0.010	0.004	0.002
Ni	0.053	0.012	0.004	0.003	–	–
Mg	10.999	10.203	1.857	1.684	0.996	0.953
Ca	0.002	0.035	0.000	0.001	0.898	1.006
Na	0.000	0.000	0.000	0.000	0.013	0.004
K	0.002	0.000	0.000	0.000	0.001	0.000

3.3. *Whole-rock geochemistry*

The results (Table 3) evidence a moderate variability in the geochemical composition, linked to different protoliths (lherzolites and/or harzburgites) and variable serpentinization degree. The SiO_2 contents show a relatively small range between 38.68% wt. and 42.22% wt. TiO_2 is usually lower than 0.10% wt., and the samples containing Ti-clinohumite do not contain more TiO_2 in the bulk rock than samples without. Al_2O_3 and Fe_2O_{3tot} range from 0.82 to 2.77% wt. and from 7.21 to 9.84% wt., respectively. MgO is moderately variable, between 35.22% wt. and 44.05% wt. The CaO content is highly variable, it ranges from 0.22% wt. to 3.27% wt., and mostly depends on the protolith (lherzolites have higher CaO contents). Na_2O and K_2O are very low (<0.05% wt.) for all samples, whereas LOI (loss on ignition) is extremely variable, ranging from 5.6% wt. to 10.5 wt%, due to the degree of serpentinization and metamorphic recrystallization. The Cr and Ni contents

Table 3

Whole-rock geochemistry (mean and range) of schistose and “massive” serpentinite varieties (a total of 120 samples), determined by ICP-OES, ICP-MS and LECO®.

	Schistose serpentinite mean (range)	Massive serpentinite mean (range)
Wt. %		
SiO_2	**40.83** (39.21–42.22)	**39.21** (38.68–40.87)
TiO_2	**0.02** (0.02–0.07)	**0.03** (0.01–0.12)
Al_2O_3	**2.27** (0.82–2.62)	**1.68** (1.34–2.77)
Fe_2O_3	**8.06** (7.21–9.08)	**8.42** (7.62–9.84)
MnO	**0.09** (0.08–0.14)	**0.08** (0.07–0.12)
MgO	**39.34** (37.38–44.05)	**40.37** (35.22–42.65)
CaO	**1.92** (0.83–3.02)	**1.38** (0.22–3.27)
Na_2O	**0.02** (<0.01–0.05)	**0.01** (<0.01–0.04)
K_2O	**0.02** (<0.02–0.04)	**0.03** (<0.02–0.06)
P_2O_5	**0.04** (<0.01–0.08)	**0.04** (<0.01–0.08)
Cr_2O_3	**0.33** (0.24–0.38)	**0.34** (0.27–0.48)
C	**0.01** (0.01–0.04)	**0.01** (0.01–0.05)
S	**0.01** (<0.01–0.04)	**0.01** (0.01–0.05)
LOI	**7.2** (5.6–10.5)	**8.1** (6.2–10.1)
ppm		
Sc	(8–15)	(9–18)
V	(34–72)	(45–76)
Co	(101–132)	(91–127)
Ni	(1298–2018)	(1266–2385)
Cu	(1.7–28.4)	(5.0–20.1)
Zn	(19–44)	(20–39)
Ga	(1.0–2.7)	(1.2–3.2)
Rb	(<0.5–1.2)	(<0.5–0.9)
Sr	(0.8–13.3)	(<0.5–5.4)
Y	(0.2–2.5)	(0.1–3.9)
Zr	(<0.5–2.9)	(<0.5–3.3)
Nb	<0.5	<0.5
Mo	(<0.1–0.2)	(<0.1–0.3)
Sn	<1	<1
Sb	(<0.1–0.1)	(<0.1–0.2)
Cs	(<0.1–0.8)	(<0.1–0.6)
Ba	(<0.5–2.7)	(<0.5–2.3)
Hf	<0.5	<0.5
Ta	<0.1	<0.1
W	(<0.1–0.6)	(<0.1–1.8)
Pb	(<0.1–0.3)	(<0.1–0.2)
As	(<0.5–1.2)	(<0.5–1.0)

are typically high, and the chondrite-normalized REE patterns (Anders and Grevesse, 1989) suggest homogeneous chondritic trends, sometimes with slight LREE (light-REE) enrichments and flat HREE (heavy-REE) patterns (Fig. 6).

3.4. Technical properties

The technical tests (Table 4) evidenced excellent properties: the compressive strength is anisotropic among the varieties, as a function of the load applied parallel (≈120–140 MPa) or perpendicular (≈150–200 MPa) to the foliation of the rock; the best values belong to the “massive” serpentinite varieties (up to 219.4 MPa). The flexural strength is influenced by the grain size and the planar anisotropy and shows excellent values between 25.4 MPa (“massive” Verde Mare) and 83.9 MPa (schistose varieties). All the schistose serpentinites display high and homogeneous flexural strength (≈70–80 MPa), and as a matter of fact they are successfully used for roof slabs, cladding and in conditions of high mechanical stress. The Amsler wear tests evidenced a marked anisotropy in sliding friction resistance, as a function of the test carried out parallel (5.93–10.31 mm) or perpendicular to foliation (1.57–3.65 mm): relatively easy to “flake off” along the foliation, tough along the hard way (perpendicular to foliation). The results of the investigations based on MIP show that the different varieties have very similar features: the porosity values are extremely low (0.02–0.18% vol.). The meso-pore size distributions of the samples are scattered and give diameters ranging from 0.03 to 8.2 μm (Fig. 7). These extraordinary low porosity values are the consequence of the mineralogy, the mylonitic fabric and the interpenetrating textures, especially for the schistose serpentinites, in which the antigorite laths build up a close and tight lamellar crystal “network”. The results of the performed physical and mechanical tests are generally much better or at least comparable with those of other dimension stones with similar commercial use (Càrdenes et al., 2014; Dino and Cavallo, 2015; Cavallo et al., 2019; Cárdenes et al., 2019). The performed tests evidence that workability and mechanical properties of the serpentinites are strongly influenced by microstructural and mineralogical features.

4. Conclusions

In the frame of heritage stone designation, there are some basic criteria as: historical use for at least 100 years, wide-ranging geographical application, utilization in important public projects, being a cultural icon, quarrying and availability today (Cassar et al., 2014; Cooper, 2014, 2018; Marker, 2014; Hannibal et al., 2020). Historical evidence dating back to the eleventh century, peculiar processes of extraction, processing, as well as historical and present applications, make the "*Serpentino della Valmalenco*" a material that fully deserves the designation of heritage stone.

The commercial varieties of the "*Serpentino della Valmalenco*" represent a stone with technical characteristics of durability that have no

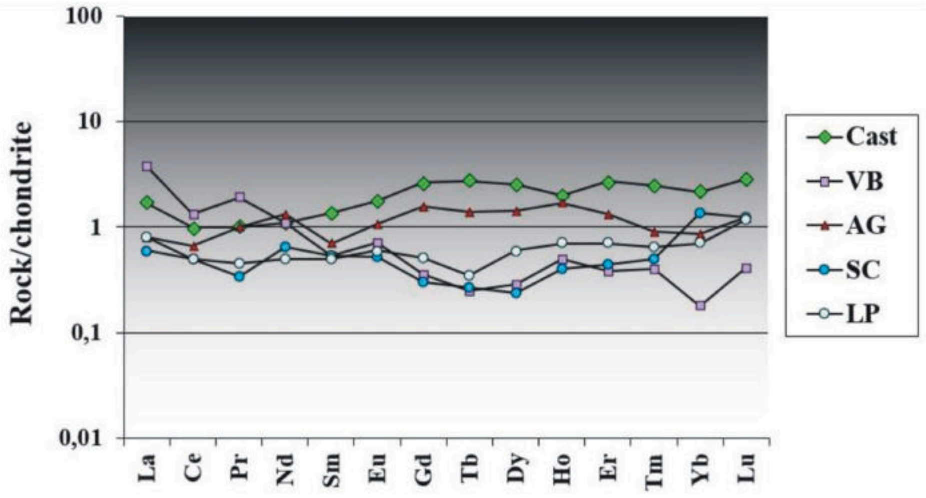

Fig. 6. Representative chondrite-normalized REE patterns (Anders and Grevesse, 1989) of schistose (SC, AG) and “massive” serpentinites (CAST, VB, LP).

Table 4
Technical properties of schistose and “massive” serpentinite varieties (a total of 120 samples); *load at right angle to foliation; $^{\#}$load parallel to foliation; $^{+}$wear parallel to foliation.

	Compressive strength* (MPa) mean (range)	Compressive strength$^{\#}$ (MPa) mean (range)	Flexural strength* (MPa) mean (range)	Abrasion resistance^{+} (mm) mean (range)	Porosity (MIP) (%) mean (range)
Schistose serpentinite	**164.3** (147.8–181.9)	**140.8** (128.9–144.5)	**73.7** (71.9–83.9)	**5.9** (2.4–7.5)	**0.05** (<0.02–0.12)
Massive serpentinite	**172.1** (139.1–219.4)	**135.3** (98.9–170.5)	**42.6** (25.4–43.5)	**7.3** (2.4–10.7)	**0.08** (0.03–0.15)

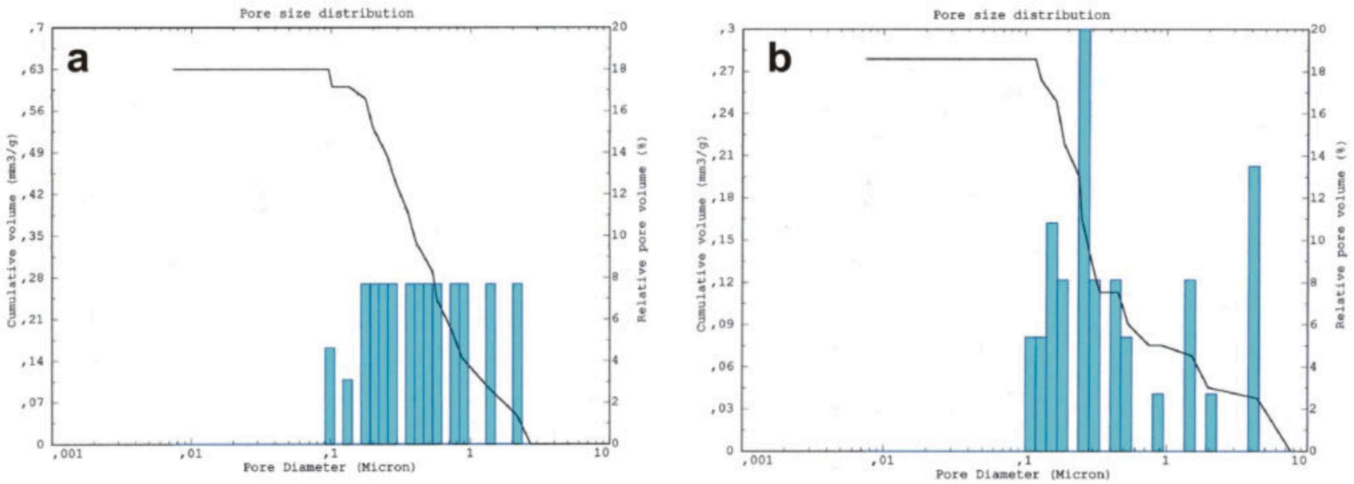

Fig. 7. Pore size distribution (MIP, pore diameter vs. cumulative Hg volume) of schistose (on the left) and “massive” serpentinite (on the right).

equal in the panorama of "green marbles" and slates, for paving, shelving, cladding in areas with significant wear and mechanical stress. Especially the schistose variety, which has been used for hundreds of years to cover roofs, in thin and very resistant slabs, is of great importance in historical buildings, but also in the present ones, respecting the local historical building characteristics of the alpine valleys. The "massive" varieties are widely established, also and above all on the international scene, as evidenced by numerous high-profile applications. The peculiarities linked to the past extraction and trading, for example in the historical “Giovello” site close to the Chiesa Valmalenco village, deserve to be enhanced, with a view to geotouristic routes. The project foresees the restoration of the paths, the placement of informative signs and the restoration of a laboratory and a quarry to be used as a museum, creating a path that allows the visitor to immerse himself in the roots of an activity that has deeply marked the social and economic life of Valmalenco. This action is integrated with an equal initiative carried out with the Swiss Museum Plattas da Fex Sils Maria (Engadine, Switzerland).

This research evidences also the great benefit of a combined mineralogical, petrographical, geochemical, and geotechnical approach in the characterization of dimension stones, most of all for the relations among mineralogy, microstructures and technical properties (i.e. durability).

In a vision of circular economy, it would be desirable to develop projects aimed at the reuse of quarrying and processing waste: the particular chemical and mineralogical composition provides interesting ideas, both in the "traditional" (e.g. ceramics and refractories), and in the futuristic sectors (CO_2 fixation by antigorite carbonation). As far as environmental issues are concerned, preliminary geological and petrographic investigations, as well as a rational exploitation of quarries, are certainly able to minimize the impact.

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Author statement

Alessandro Cavallo: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Roles/Writing - original draft, Writing - review & editing.

Data availability

Data will be made available on request.

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