



# Serpentinitic waste materials from the dimension stone industry: Characterization, possible reuses and critical issues

Alessandro Cavallo

Department of Earth and Environmental Sciences, University of Milan – Bicocca, Piazza della Scienza, 4, 20126 Milano, Italy



## ARTICLE INFO

### Keywords:

Quarry  
Dimension stones  
Serpentinites  
Waste recovery  
Secondary raw materials

## ABSTRACT

Serpentinites, ultramafic rocks with a peculiar chemical and mineralogical composition, can be used as dimension stones, but there are no significant re-uses of waste materials deriving from quarrying and processing. This paper presents the example from Valmalenco (central Alps, northern Italy), with a detailed mineralogical, chemical, physical and microstructural characterization of waste materials, ranging from shapeless blocks to residual sludge. The mineralogical composition is characterized by abundant antigorite and olivine, with minor chlorite, clinopyroxene and magnetite, and the chemical composition by high MgO grades. The preliminary results suggest interesting applications in the ceramic industry, especially in high-MgO ceramics and forsterite refractories materials, as well as alternative uses as filler for plastic and rubber materials, up to carbon dioxide sequestration. Special care must be taken to avoid chrysotile asbestos contamination.

## 1. Introduction

Italy is one of the leader countries in the production and import of ornamental stones, with an annual internal production of about 9 Mt of raw material (referred to the time interval 2011–2013; Ceruti, 2013). The extraction and processing of marbles, rocks and granites produces a significant amount of waste materials, in the form of shapeless and defective blocks, splints, chips and sludge (approximately 50 wt% of the processed raw material; Dino et al., 2013). One of the most critical residual products is represented by sludge deriving from processing activities (EWC code 01 04 13; Environmental Protection Agency, 2002). Current regulations and a greater concern to the environment promote the reuse of these wastes (Almeida et al., 2007; Careddu et al., 2013; Careddu and Dino, 2016; Luodes et al., 2012): quartz-feldspathic materials are successfully re-used for ceramics, crushed porphyry as track ballast, whereas carbonatic wastes for lime, cement and fillers. The best solution for the recycling is the use of the waste in the industrial production, substituting higher cost quarry materials. However, a prerequisite for this use is the possibility to regularly “feed” the industrial production with the required amount of waste materials with controlled and constant chemical-mineralogical and physical compositions. Different proposals for the use of dimension stone quarry wastes have been investigated in different Italian areas of production of ornamental stones. Summing-up, two main ways of re-use can be found:

1) use of wastes for their “physical” characteristics as grain-size (e.g.

sludge), apparent specific gravity, permeability and so on (Almeida et al., 2007; Careddu and Dino, 2016; Dino et al., 2014; Lee et al., 2008).

2) use of wastes for their “mineralogical-chemical” characteristics, as starting components for industrial productions or as raw material for processes of industrial minerals production (Diaz and Torrecillas, 2007; Marras and Careddu, 2017; Montero et al., 2009).

As far as the first group of uses is concerned, some applications were already tested, as the use as low-permeability diaphragm, in the production of high-strength concrete, as a filler for the production of “agglomerated stones” and concrete tiles and for quarry rehabilitation, mixed with compost in different proportions. The results appeared satisfactory for most uses, but economically convenient only in peculiar cases, often replacing low-cost quarry materials. Generally, before their use, waste must be treated (e.g. drying, grain size selection, magnetic separation of iron scrap abrasives).

### 1.1 Serpentinites, dimension stones and waste products

There are currently no significant reuses for minor stones, for example serpentinitic materials [ultramafic rocks composed mainly of serpentine  $Mg_6(OH)_8Si_4O_{10}$  and minor olivine  $(Mg, Fe)_2SiO_4$ ]; chemistry and mineralogy of these peculiar rocks can be inferred from the specific literature (Bodinier and Godard, 2003; O’Hanley, 1996; Wicks and O’Hanley, 1988 and references therein). A striking example is

E-mail address: [alessandro.cavallo@unimib.it](mailto:alessandro.cavallo@unimib.it).

<https://doi.org/10.1016/j.resourpol.2018.08.003>

Received 28 January 2018; Received in revised form 17 May 2018; Accepted 6 August 2018

Available online 17 August 2018

0301-4207/ © 2018 Elsevier Ltd. All rights reserved.

### Nomenclature

SS	schistose serpentinite
MS	massive serpentinite
NOA	naturally occurring asbestos
LOD	limit of detection

represented by the Valmalenco area (central Alps, northern Italy), a relatively small productive district, in which quarrying and processing activities are mainly concentrated in the Chiesa in Valmalenco and Lanzada territories. The global production of the Valmalenco area cannot be compared in amount to the production of the main Italian productive centers, but the need of a heedful care in the treatment of the waste material is enhanced by morphological condition (high mountain areas) and by the touristic vocation of the territory. In this area, 22 different enterprises operate in the quarrying and/or processing of serpentinites with various textures, schistose [SS] to massive [MS], and color shades; the commercial products are used all over the world and are known with many commercial names (e.g. “Serpentinoscisto Valmalenco”, “Verde Giada”, “Verde Vittoria”, “Verde Mare”). The serpentinites derive from the Malenco unit, a huge ultramafic body exposed over an area of 130 km<sup>2</sup>, at the Penninic to Austroalpine boundary zone, interpreted as a sub-continental mantle fragment (Münterer et al., 2000). The most important environmental concern in this area is represented by naturally occurring asbestos [NOA], in the form of sporadic chrysotile veins and lodes (mining occurred between the end of the XIX century and 1975). However, detailed studies revealed that the airborne asbestos concentrations in quarries and processing plants are below the occupational exposure limit, and no problems with the finished serpentinite products (Cattaneo et al., 2012; Cavallo and Rimoldi, 2013). On the other hand, these studies highlighted the importance of geological surveys to avoid the interception of asbestos veins, as well as the importance of block squaring-off directly in the quarry, removing all visible chrysotile for subsequent disposal. The extraction of serpentinites occurs in open cast hill-side quarries (Fig. 1) and is based on a combined use of explosives (detonating cord) and diamond wire cutting; in many cases, the block squaring-off occurs directly in the quarry (Fig. 2). The [SS] varieties are mainly cut by diamond disk in smaller blocks (1.5 × 1 × 1 m) and then splitted in thin slabs, by hammer and chisel, whereas the [MS] varieties are processed in many ways after being sawn by multi-blade gang-saw, generally with diamond cutting tools, rarely with steel-shoot gang-saw (Cavallo, 2005). The total amount extracted in the quarries is estimated around 195,000 t/yr. (66,500 t/yr. [MS] and 128,500 t/yr. [SS]) and the resulting commercial blocks and products can be estimated around the 40–50 wt% of the extracted material (Fig. 3). The processing wastes can

vary significantly according to the finished product: 35 wt% of waste can be estimated in the case of splitted slab production [SS], whereas 50 wt% can be estimated in the case of gang-saw cutting of [MS] blocks.

The total estimate of the processing rock waste in the Valmalenco area is about 43,600 t/yr.; together with the quarry waste, the total amount of waste produced in the area is more than 128,000 t/yr. The sludge (approximately 20,800 t/yr.) mainly derived from the cutting (by diamond disk and multi-blade gang-saw) and polishing of [MS] is filter-pressed before disposal.

## 2. Materials and methods

A total of 68 rock debris (irregular blocks and slabs, splints and chips), and 45 sludge samples, collected between 2012 and 2017, were characterized for mineralogical composition by X-ray powder diffraction (XRPD), bulk chemistry [inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS)], particle size, morphology, crystal chemistry and asbestos content [scanning electron microscopy and energy-dispersive spectroscopy (SEM-EDS)]. The sludge was also investigated for grain size distribution [ASTM D421-85(2007); D422-63(2007)], Atterberg limits (ASTM D4943; D4318), and water content (ASTM D2216-90).

### 2.1. Mineralogical and chemical composition

XRPD analysis was performed using a Bragg–Brentano  $\theta$ – $\theta$  PANalytical X'Pert PRO PW3040/60 x-ray powder diffractometer, with Ni-filtered Cu K $\alpha$  radiation at 40 kV and 40 mA,  $\frac{1}{2}^\circ$  divergence and receiving slits, and step scan of  $0.02^\circ 2\theta$ , in the  $3$ – $80^\circ 2\theta$  range. The limit of detection [LOD] of XRPD depends on the crystallinity of the mineral phase, and for serpentine minerals it is approximately 0.5% wt. The qualitative phase analysis was performed using the PANalytical HighScore Plus software version 2.2c; quantitative phase analysis was carried out running the FULLPAT software (Chipera and Bish, 2002). To verify the accuracy of the quantitative analysis, the FULLPAT procedure was carried out on pure phases mixtures (antigorite, olivine, chlorite, diopside and magnetite) in known ratios. Bulk geochemistry was assessed for major elements (ICP-AES, whole rock fusion with meta-borate), trace elements (ICP-MS), C and S (LECO<sup>®</sup>) at the Chemistry Labs, Vancouver (Canada).

### 2.2. Microstructures, mineral chemistry and asbestos concentration

The SEM (Vega TS Tescan 5163 XM) was used in combination with an EDS analyzer (EDAX Genesis 400) with 200 pA and 20 kV as standard conditions, for the determination of crystal chemistry and



Fig. 1. Open-cast hillside serpentinite quarries with huge debris fans.



Fig. 2. Serpentinite processing activities, diamond wire squaring off of blocks (on the left) and diamond disk cutting (on the right).

morphology. The quantitative determination of asbestos by SEM-EDS was achieved following the analytical procedures indicated by the Italian law (Italian Ministry of Health, 1994), improved following the indications for the NOA context (Cattaneo et al., 2012; Cavallo and Rimoldi, 2013; Gualtieri et al., 2014). The [LOD] of the SEM-EDS analyses is about 100 ppm; data below the [LOD] were considered as [LOD]/2 and included in the analysis.

### 3. Results and discussion

#### 3.1. Mineralogical composition

All the performed quantitative XRPD analyses always evidenced an excellent fit and little errors in phase quantification (< 5 wt%), even phases characterized by structural disorder (antigorite and chlorite); results are listed in Table 1. The antigorite content is quite variable (57–89 wt%), as well as olivine (3–31 wt%) and chlorite (1.5–17 wt%). The clinopyroxene (diopside) content is generally low (mean 2–7 wt%), likewise magnetite (1–6 wt%). Differences in mineralogical composition, variable from quarry to quarry, depend on the protolith and on the degree of metamorphic recrystallization: the SS varieties generally have a higher olivine (up to 31 wt%) and chlorite content (up to 17 wt%), reflecting a more lherzolitic protolith. The mineralogical composition of the residual sludge is comparable with the processed serpentinites; small amounts (up to 2.5 wt%) of quartz, feldspars, mica (muscovite) and carbonates (calcite) were detected, linked to occasional processing of granitic and carbonatic rocks.

#### 3.2. Chemical composition

The chemical data (Table 2) evidence a moderate variability, due to the mineralogical heterogeneity and the variable serpentinization degree. The LOI (loss on ignition) is quite variable, it ranges from 5.4 wt% to 10.4 wt%, due to the degree of serpentinization and metamorphic recrystallization. The Cr and Ni contents are high ( $2300 < Cr < 4100$  ppm and  $1280 < Ni < 2360$ ); Sc (8–14 ppm), Co (87–123 ppm) and V (29–70 ppm) are homogeneous among all samples, and typical for ultramafic rocks. The chemical composition of residual sludge, deriving from almost exclusive processing of serpentinites, evidences some differences especially in  $Al_2O_3$ ,  $K_2O$ ,  $Na_2O$  and to a lesser extent  $SiO_2$  content. Some differences can be observed also in trace elements: the sludge has higher contents in Cu, Sn, Ba and W, if compared with the rock materials (Table 2). These chemical features can suggest a limited mixing of serpentinite with sludge derived from sporadic processing of granitic and carbonatic blocks, and to a minimal extent to the cutting and polishing tools.

#### 3.3. Microstructures, mineral chemistry and asbestos concentrations

There are important differences between [SS] and [MS], especially in grain size and microstructure (Fig. 4): the [SS] is characterized by marked mylonitic foliation and interlocking equigranular texture, whereas the [MS] varieties have a coarser grain size, a wider spaced foliation and interpenetrating texture. The main rock-forming minerals are antigorite, olivine and clinopyroxene (diopside), with minor amounts of Cr-rich chlorite, magnetite and brucite. Accessory minerals are chromite, Ti-clinohumite, Fe–Ni alloys and Cu–Fe–Ni sulfides. The antigorite amount is variable, ranging from completely serpentinized



Fig. 3. Quarry production, quarry and processing waste for [SS] and [MS] in t/yr.

**Table 1**

Mineralogical composition (wt%) of debris rock samples ([SS] and [MS] varieties) and residual processing sludge, determined by quantitative XRPD (Chiperá and Bish, 2002).

	Antigorite mean (range)	Olivine mean (range)	Clinopyroxene mean (range)	Chlorite mean (range)	Magnetite mean (range)	Brucite mean (range)
SS schistose serpentinite debris	63.5 (59.4–73.7)	19.6 (9.6–31.1)	6.1 (3.0–8.9)	6.6 (1.5–17.4)	3.6 (0.5–6.8)	0.5 (< 0.5–1.5)
MS massive serpentinite debris	75.5 (71.4–89.3)	14.3 (3.0–28.4)	3.6 (0.5–9.8)	3.3 (1.8–12.2)	2.6 (1.1–5.7)	0.7 (0.5–2.0)
residual processing sludge	69.1 (57.1–79.5)	18.5 (7.2–31.4)	5.3 (1.1–6.1)	3.5 (1.5–11.7)	3.1 (1.2–6.0)	0.5 (< 0.5–1.1)

**Table 2**

Chemical composition of debris rock samples ([SS] and [MS] varieties) and residual processing sludge, determined by ICP-AES, ICP-MS and LECO<sup>®</sup>.

	[SS] debris mean (range)	[MS] debris mean (range)	Residual processing sludge mean (range)
wt%			
SiO <sub>2</sub>	40.75 (39.18 – 41.93)	39.33 (38.73 – 40.67)	42.21 (38.12 – 45.41)
TiO <sub>2</sub>	0.02 (0.02 – 0.06)	0.03 (0.01 – 0.11)	0.11 (0.01 – 0.18)
Al <sub>2</sub> O <sub>3</sub>	2.23 (0.78 – 2.54)	1.74 (1.36 – 2.65)	2.48 (0.95 – 5.54)
Fe <sub>2</sub> O <sub>3</sub>	8.11 (7.15 – 8.95)	8.35 (7.72 – 9.57)	7.75 (7.54 – 7.93)
MnO	0.10 (0.09 – 0.13)	0.09 (0.09 – 0.12)	0.11 (0.11 – 0.15)
MgO	39.42 (37.46 – 43.84)	40.31 (35.07 – 42.78)	36.24 (29.83 – 41.22)
CaO	1.88 (0.81 – 2.89)	1.42 (0.12 – 3.16)	1.71 (0.67 – 3.62)
Na <sub>2</sub> O	0.01 (< 0.01 – 0.04)	0.01 (< 0.01 – 0.03)	0.38 (0.02 – 0.98)
K <sub>2</sub> O	0.02 (< 0.02 – 0.03)	0.03 (< 0.02 – 0.05)	0.26 (< 0.02 – 0.67)
P <sub>2</sub> O <sub>5</sub>	0.05 (< 0.01 – 0.08)	0.04 (< 0.01 – 0.07)	0.05 (0.02 – 0.08)
Cr <sub>2</sub> O <sub>3</sub>	0.31 (0.23 – 0.39)	0.33 (0.28 – 0.41)	0.29 (0.25 – 0.37)
C	0.01 (0.01 – 0.04)	0.01 (0.01 – 0.04)	0.19 (0.09 – 0.43)
S	0.01 (< 0.01 – 0.05)	0.01 (0.01 – 0.05)	0.02 (0.01 – 0.04)
LOI	7.1 (5.4 – 10.4)	8.3 (6.3 – 9.9)	8.2 (6.7 – 9.2)
ppm			
Sc	(9–14)	(9 – 13)	(8 – 10)
V	(33 – 66)	(44 – 70)	(30 – 47)
Co	(97 – 124)	(87 – 118)	(88 – 134)
Ni	(1317 – 1965)	(1279 – 2357)	(1621 – 2118)
Cu	(1.9 – 24.5)	(5.3 – 17.1)	(32 – 72)
Zn	(19 – 41)	(21 – 36)	(32 – 45)
Ga	(1.1 – 2.8)	(1.1 – 2.9)	(1.3 – 6.2)
Rb	(< 0.5 – 1)	(< 0.5 – 0.8)	(< 0.5 – 21.1)
Sr	(0.7 – 12.5)	(< 0.5 – 3.8)	(1.4 – 101.2)
Y	(0.3 – 2.3)	(0.1 – 3.5)	(0.4 – 4.8)
Zr	(< 0.5 – 2.6)	(< 0.5 – 3.1)	(0.5 – 4.8)
Nb	< 0.5	< 0.5	(< 0.5 – 3.2)
Mo	(< 0.1 – 0.1)	(< 0.1 – 0.1)	(0.1 – 4.5)
Sn	< 1	< 1	(3 – 7)
Sb	(< 0.1 – 0.1)	(< 0.1 – 0.1)	(< 0.1 – 0.3)
Cs	(< 0.1 – 1)	(< 0.1 – 0.5)	(< 0.1 – 0.5)
Ba	(< 0.5 – 3)	(< 0.5 – 2)	(1 – 154)
Hf	< 0.5	< 0.5	(< 0.5 – 1.8)
Ta	< 0.1	< 0.1	(< 0.1 – 0.3)
W	(< 0.1 – 0.2)	(< 0.1 – 1.6)	(1 – 3.4)
Pb	(< 0.1–0.4)	(< 0.1–0.2)	(0.1 – 0.7)
As	(< 0.5 – 1.3)	(< 0.5 – 1.1)	(< 0.5 – 1.3)

rocks to serpentinites with considerable amounts of mosaic aggregates of metamorphic olivine and diopside.

Crystal chemistry analyses (EDS) evidenced two different antigorite types: the first occurs as fine-grained lamellae with appreciable amounts of Cr<sub>2</sub>O<sub>3</sub> (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 types were observed: the first exhibits cataclastic or porphyroclastic texture, and the composition varies from Fo<sub>91</sub> to Fo<sub>94</sub>; the second generation occurs with equigranular crystalloblastic texture, and more

fayalitic compositions (Fo<sub>85</sub>–Fo<sub>88</sub>). Two types of clinopyroxene can be distinguished: the first corresponds to diagenetic relict grains (1–6 mm), with variable amounts of Na<sub>2</sub>O (0.1–0.6 wt%), Al<sub>2</sub>O<sub>3</sub> (0.05–2.4 wt%) and Cr<sub>2</sub>O<sub>3</sub> (0.06–0.5 wt%).

Grain size measurements of residual sludge are almost constant (d<sub>50</sub> = 7.9 μm) and more than 95% has grain size < 50 μm. The water content was tested to range from 11.5 to 19.4 wt%. The bulk density of the filter-pressed sludge is about 1.74 kg/dm<sup>3</sup>; no plasticity was found after Atterberg test. The morphology of residual sludge particles is characterized by sharp lamellar antigorite particles (Fig. 5), with high aspect ratio and specific surface.

SEM-EDS investigations evidenced little amounts of chrysotile asbestos fiber (Table 3), in form of fiber bundles and isolated fibrils (Fig. 6): concentrations were mostly well below the 1000 ppm threshold, with higher concentrations in wastes deriving from [MS] varieties; amphibole asbestos was never detected. These relatively small asbestos concentrations derive from cracks, fissures and veins of the waste blocks: chrysotile occurs in discrete veins, along the most important discontinuities of the rock mass, and for this reason it can be found on the external surface of waste blocks (Cavallo and Rimoldi, 2013).

#### 3.4. Serpentinic waste materials possible reuses

The peculiar chemical and mineralogical composition of serpentinites and serpentinized peridotites can be exploited for many applications. There are very few published studies on the reuse of serpentinitic wastes, but a quite large number of references can be found, regarding the use of more or less deeply serpentinized ultramafic rocks as a starting material for ceramic productions. The simplest reuse could be in the production of crushed serpentinite for artificial tiles and stones, exploiting the deep-green color and the excellent mechanical properties (Cavallo, 2005; Lee et al., 2008). The lamellar crystalline habit, the high specific surface and the moderate hardness of antigorite could make it a valid substitute or a supplement to talcum in plastic materials and rubber (Radosta and Trivedi, 1987). From the chemical and mineralogical composition, the most promising target in the ceramic industry is represented by forsterite and/or high-MgO ceramics and forsterite refractories (with periclase addition, e.g. Othman and Khalil, 2005), but also by cordierite ceramics (adding kaolin) and high-hardness vitroceramics (Vergilov et al., 1979). Porcelain stoneware with good technical and chromatic properties was obtained from serpentinite muds (Diaz and Torrecillas, 2007), but the starting material was almost peridotitic. The potential capability of waste serpentine from chromite mines as a raw material to be used in high temperature refractory and ceramic products was tested, revealing high refractoriness and high sintering temperature, applicable in refractories for iron and steel industry (Nemat et al., 2016). Serpentinic rocks, with periclase addition, are currently used as starting material to produce forsterite refractories (e.g. Antonov et al., 1994) but much larger is a number of industrial and laboratory experiences in which high-MgO materials are added to kaolin in order to obtain good quality cordierite ceramics (Ribeiro and Lucas, 1992; Grosjean, 1993; Ibrahim et al., 1995; Kabayashi et al., 2000; Othman and Khalil, 2005). The main issue for

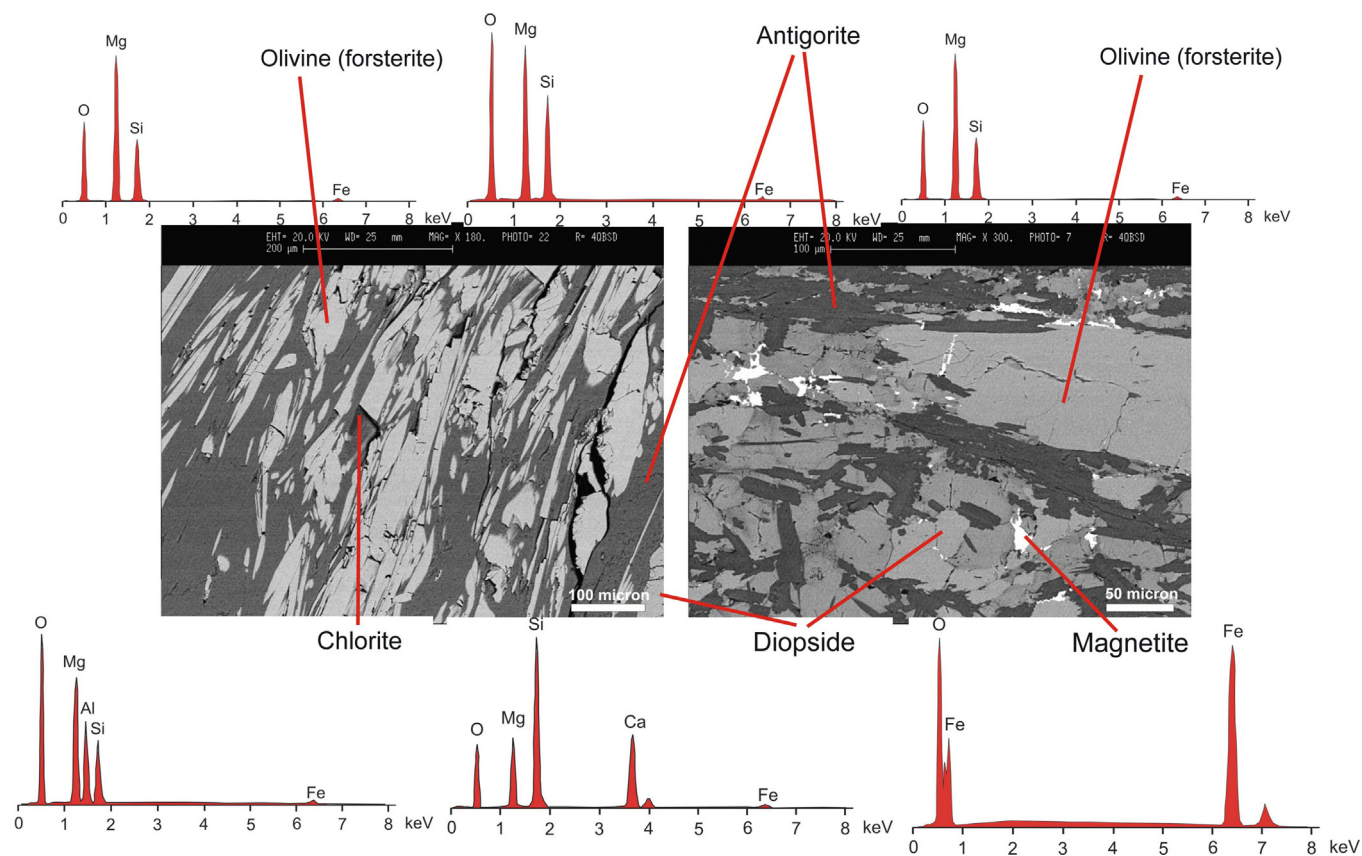


Fig. 4. SEM back-scattered electrons micrographs of the main serpentinite varieties, [SS] on the left and [MS] on the right). Dark grey areas are antigorite blades, whereas light grey grains are mainly olivine and clinopyroxene (diopside).

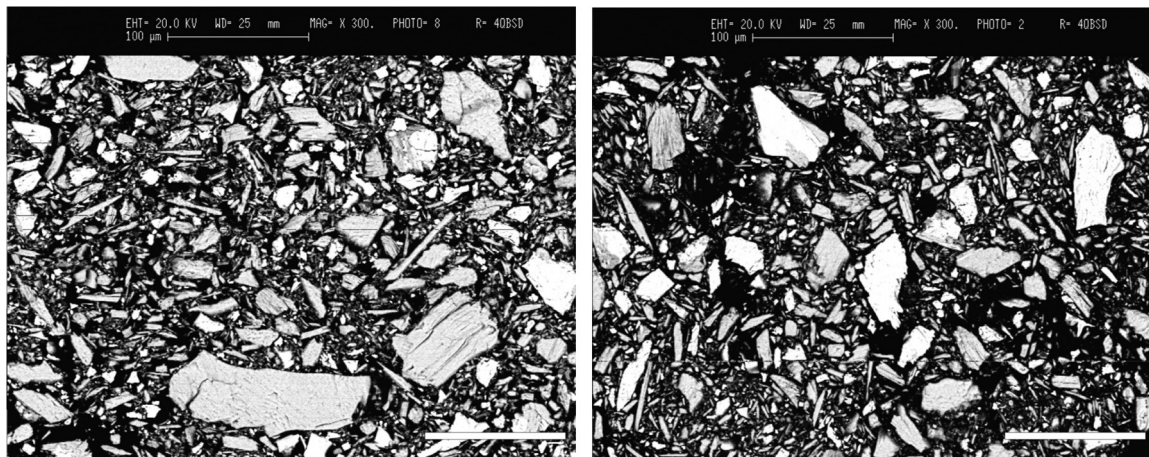


Fig. 5. SEM back-scattered electrons micrographs of residual sludge deriving from serpentinite processing; scale bar is 100 μm.

Table 3

Chrysotile asbestos concentrations (mean values and range + 1σ, experimental error related to counting statistics) of debris rock samples ([SS] and [MS] varieties) and residual processing sludge.

	Chrysotile mean	Chrysotile range + 1σ
[SS] debris	< 100	< 100–350
[MS] debris	390	< 100–1600
residual processing sludge	250	< 100–670

the reuse in the ceramic industry is represented by the relatively high FeO<sub>tot</sub> content, which could however be easily reduced with magnetic separation of magnetite and possible iron scrap from gang-saw-shoot. Another problem is represented by the presence of chrysotile asbestos fibers: maximum effort must be made to avoid the contamination of processing plants, by squaring-off the blocks directly in the quarry. Anyway, the temperatures reached during the production of ceramic materials are high enough (≥ 1000 °C) to ensure a complete re-crystallization of any possible asbestos fiber (Gualtieri et al., 2008). Extensive laboratory tests to validate the use of serpentinitic materials in the ceramic industry are needed, including: tests of magnetic separation of magnetite crystals and/or iron abrasives, firing test up to

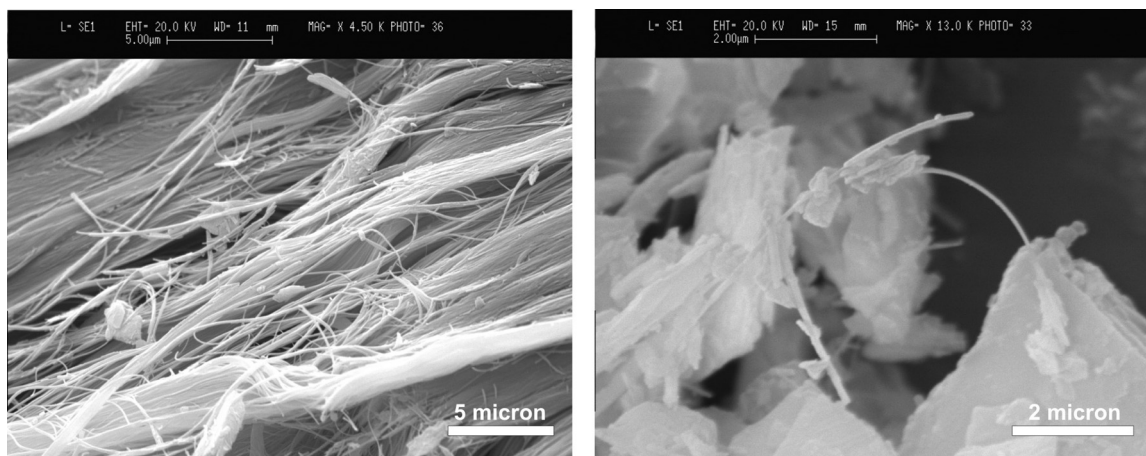


Fig. 6. SEM secondary electrons micrographs of chrysotile asbestos aggregates on rock surface (on the left) and isolated fibrils in residual sludge (on the right).

1400 °C with materials of different composition, starting from pure serpentinitic waste and progressively adding high- $\text{Al}_2\text{O}_3$  or high- $\text{MgO}$  components. The resulting ceramics will be investigated for both mineralogical phases and textures obtained; preparation and processing of samples reproducing or approaching the conditions of the industrial production. The technical characteristics of the ceramic products will be tested for their possible end uses (dielectric characteristics, refractoriness) and possible problems, if any, related to the industrial processing. Nevertheless, the economic significance of the obtained results must be estimated in depth, if a practical utilization is expected. For these reasons, also some alternative uses of the serpentinitic waste should be evaluated, for example, as a reactive fixing carbon dioxide ( $\text{CO}_2$ ) released during the use of fossil fuels (Kelemen et al., 2011; Lackner et al., 1995). Serpentinites offer a highly reactive feedstock for carbonation reactions and the capacity to sequester  $\text{CO}_2$  on a global scale, using high-temperature carbonation reactors, by carbonating alkaline mine wastes, or by subsurface reaction through  $\text{CO}_2$  injection into serpentinite-hosted aquifers and serpentinitized peridotites (Balucan and Dlugogorski, 2013; Power et al., 2013). Industrial mineral carbonation processes are commonly represented by the reaction of olivine or serpentine with  $\text{CO}_2$  to form carbonates (magnesite) + quartz  $\pm$   $\text{H}_2\text{O}$ . The rate of  $\text{CO}_2$  fixation is related to dissolution kinetics, which favor the reaction of brucite or olivine over serpentine. However, many factors contribute to dissolution rates, including the high reactive surface areas of serpentine-group minerals (Brantley, 2003), often enhanced by comminution during mineral processing. The [SS] varieties are the most promising materials for this target, for their relatively high olivine content (up to 31% wt) and their extremely fine grain size.

#### 4. Conclusions

The mineralogical and chemical characterization of the serpentinitic waste products of the dimension stone industry in Valmalenco allowed to quantify the compositional range of these materials, especially the variability in mineralogy (relative contents of serpentine and olivine). The particle size and the aspect ratio of antigorite lamellae in residual sludge offer an interesting starting point for applications as filler for plastics and rubber. Considering the preliminary data, the main goal could be the investigation of the use of serpentinitic waste as a possible starting material to produce forsterite and/or cordierite ceramics. The evaluation of the real possibility of an industrial use of these materials will require a large amount of experimental work because no relevant previous experiences are available. Special care must be taken to avoid asbestos contamination.

#### Funding

This work was supported by the University of Milan-Bicocca (fondi FAR 2013–2016), by the Italian Worker's Compensation Authority INAIL (INAIL-Contarp and INAIL-Direzione Generale Roma), and by private companies of the dimension stone sector (Consorzio Estrattori Pietre Valtellina).

#### References

- Almeida, N., Branco, F., Santos, J.R., 2007. Recycling of stone slurry in industrial activities: application to concrete mixture. *Build. Environ.* 42, 810–819.
- Antonov, G.I., Yakobchuk, L.M., Prokudin, V.Y., Galuska, N.V., 1994. Serpentine rocks from the Sokolovskoe deposit. *Refractories* 35, 376–380.
- Balucan, R.D., Dlugogorski, B.Z., 2013. Thermal activation of antigorite for mineralization of  $\text{CO}_2$ . *Environ. Sci. Technol.* 47, 182–190.
- Bodinier, J.L., Godard, M., 2003. Orogenic, ophiolitic, and abyssal peridotites. *Treatise Geochem.* 2, 103–170.
- Brantley, S.L., 2003. Reaction kinetics of primary rock-forming minerals under ambient conditions. *Treatise Geochem.* 5, 73–117.
- Careddu, N., Dino, G.A., 2016. Reuse of residual sludge from stone processing: differences and similarities between sludge coming from carbonate and silicate stones—Italian experiences. *Environ. Earth Sci.* 75, 1075.
- Careddu, N., Siotto, G., Siotto, R., Tilocca, G., 2013. From landfill to water, land and life: the creation of the Centre for stone materials aimed at secondary processing. *Resour. Policy* 38, 258–265.
- Cattaneo, A., Somigliana, A., Gemmi, M., Bernabeo, F., Savoca, D., Cavallo, D.M., Bertazzi, P.A., 2012. Airborne concentrations of chrysotile asbestos in serpentine quarries and stone processing facilities in Valmalenco, Italy. *Ann. Occup. Hyg.* 56, 1–13.
- Cavallo, A., 2005. Il Serpentino della Val Malenco: caratteristiche giacimentologiche, petrografiche, tecniche e problematiche ambientali (Ph.D. Thesis). Università degli Studi di Milano.
- Cavallo, A., Rimoldi, B., 2013. Chrysotile asbestos in serpentinite quarries: a case study in Valmalenco, Central Alps, Northern Italy. *Environ. Sci. Process. Impacts* 15/7, 1341–1350.
- Ceruti, F., 2013. Il settore estrattivo in Italia. Analisi e valutazione delle strategie competitive per lo sviluppo sostenibile (Ph.D. Thesis). Università degli Studi di Milano-Bicocca.
- Chipera, S.J., Bish, D.L., 2002. FULLPAT: a full-pattern quantitative analysis program for X-ray powder diffraction using measured and calculated patterns. *J. Appl. Cryst.* 35 (6), 744–749.
- Diaz, L.A., Torrecillas, R., 2007. Porcelain stoneware obtained from the residual muds of serpentinite raw materials. *J. Eur. Ceram. Soc.* 27, 2341–2345.
- Dino, G.A., Clemente, P., Lasagna, M., De Luca, D.A., 2013. Residual sludge from dimension stones: characterisation for their exploitation in civil and environmental applications. *Energy Proced.* 40, 507–514.
- Dino, G.A., Passarella, I., Ajmone Marsan, F., 2014. Quarry rehabilitation employing treated residual sludge from dimension stone working plant. *Environ. Earth Sci.* 73 (11), 7157–7164.
- Environmental Protection Agency, 2002. European Waste Catalogue and Hazardous Waste List Valid from 1 January 2002. EPA, Dublin, Ireland.
- Grosjean, P., 1993. Cordierite Ceramics 42. *Interceram*, pp. 11–15.
- Gualtieri, A.F., Lassinantti Gualtieri, M., Tonelli, M., 2008. In situ ESEM study of the thermal decomposition of chrysotile asbestos in view of safe recycling of the transformation product. *J. Hazard. Mater.* 156, 260–266.
- Gualtieri, A.F., Pollastri, S., Bursi Gandolfi, N., Ronchetti, F., Albonico, C., Cavallo, A., Zanetti, G., Marini, P., Sala, O., 2014. Determination of the concentration of asbestos

- minerals in highly contaminated mine tailings: an example from abandoned mine waste of Crêtaz and Èmarese (Valle d'Aosta, Italy). *Am. Miner.* 99/7, 1233–1247.
- Ibrahim, D.M., Naga, S.M., Abdel Kader, Z., Abdel Salam, E., 1995. Cordierite-mullite refractories. *Ceram. Int.* 21, 265–269.
- Italian Ministry of Health, 1994. Normative e metodologie tecniche di applicazione della legge 27 marzo 1992. 257 Istituto Poligrafico e Zecca dello Stato, Roma, Italy.
- Kabayashi, Y., Katsushiro, S., Kato, E., 2000. Preparation of dense cordierite ceramics from magnesium compounds and kaolinite without additives. *Ceram. Int.* 26, 739–743.
- Kelemen, P.B., Matter, J., Streit, E.E., Rudge, J.F., Curry, W.B., Blusztajn, J., 2011. Rates and mechanisms of mineral carbonation in peridotite: natural processes and recipes for enhanced, in situ CO<sub>2</sub> capture and storage. *Annu. Rev. Earth Planet. Sci.* 39, 545–576.
- Lackner, K.S., Wendt, C.H., Butt, D.P., Joyce Jr, E.L., Sharp, D.H., 1995. Carbon dioxide disposal in carbonate minerals. *Energy* 20, 1153–1170.
- Lee, M., Ko, C., Chang, F., Lo, S., Lin, J., Shan, M., Lee, J., 2008. Artificial stone slab production using waste glass, stone fragments and vacuum vibratory compaction. *Cem. Concr. Compos.* 30, 583–587.
- Luodes, H., Kauppila, P.M., Luodes, N., Aatos, S., Kallioinen, J., Luukkanen, S., Aalto, J., 2012. Characteristics and the environmental acceptability of the natural stone quarrying waste rocks. *Bull. Eng. Geol. Environ.* 71, 257–261.
- Marras, G., Careddu, N., 2018. Sustainable reuse of marble sludge in tyre mixtures. *Resour. Policy*. <https://doi.org/10.1016/j.resourpol.2017.11.009>. (in press – corrected proof, available online 28 November 2017).
- Montero, M.A., Jordan, M.M., Hernandez-Crespo, M.S., Sanfeliu, T., 2009. The use of sewage sludge and marble residues in the manufacture of ceramic tile bodies. *Appl. Clay Sci.* 46, 404–408.
- Münterer, O., Hermann, J., Trommsdorff, V., 2000. Cooling history and exhumation of lower-crustal granulite and upper mantle (Malenco, eastern Central Alps). *J. Petrol.* 41, 175–200.
- Nemat, S., Ramezani, A., Emami, S.M., 2016. Possible use of waste serpentine from Abdasht chromite mines into the refractory and ceramic industries. *Ceram. Int.* 42, 18479–18483.
- O'Hanley, D.S., 1996. *Serpentinites: Records of Tectonic and Petrological History*. Oxford University Press, New York, pp. 277.
- Othman, A.G.M., Khalil, N.M., 2005. Sintering of magnesia refractories through the formation of periclase–forsterite–spinel phases. *Ceram. Int.* 31, 1117–1121.
- Power, I.M., Wilson, S.A., Dipple, G.M., 2013. Serpentinite carbonation for CO<sub>2</sub> sequestration. *Elements* 9, 115–121.
- Radosta, J.A., Trivedi, N.C., 1987. Talc. In: Katz, H.S., Mileski, J.V. (Eds.), *Handbook of Fillers for Plastic*. Van Nostrand Reinhold, New York, pp. 216–231.
- Ribeiro, M.P.J., Lucas, D.B., 1992. Cordierite bodies obtained from clay, bauxite and serpentine; *Ceramics* 4:13, 92-97.
- Vergilov, V., Fekeldhiev, G., Radkova, A., 1979. Possibility of synthesizing high-hardness vitrocrySTALLINE materials based on serpentinite 20. *Stroitelni Materiali i Silikatna Promishlenost*, pp. 25–27.
- Wicks, F.J., O'Hanley, D.S., 1988. Serpentine minerals: structures and petrology, in S.W. Bailey (Eds.), *Hydrous phyllosilicates (exclusive of micas)*, *Min. Soc. Am. Rev. Min.* 19, 91–167.