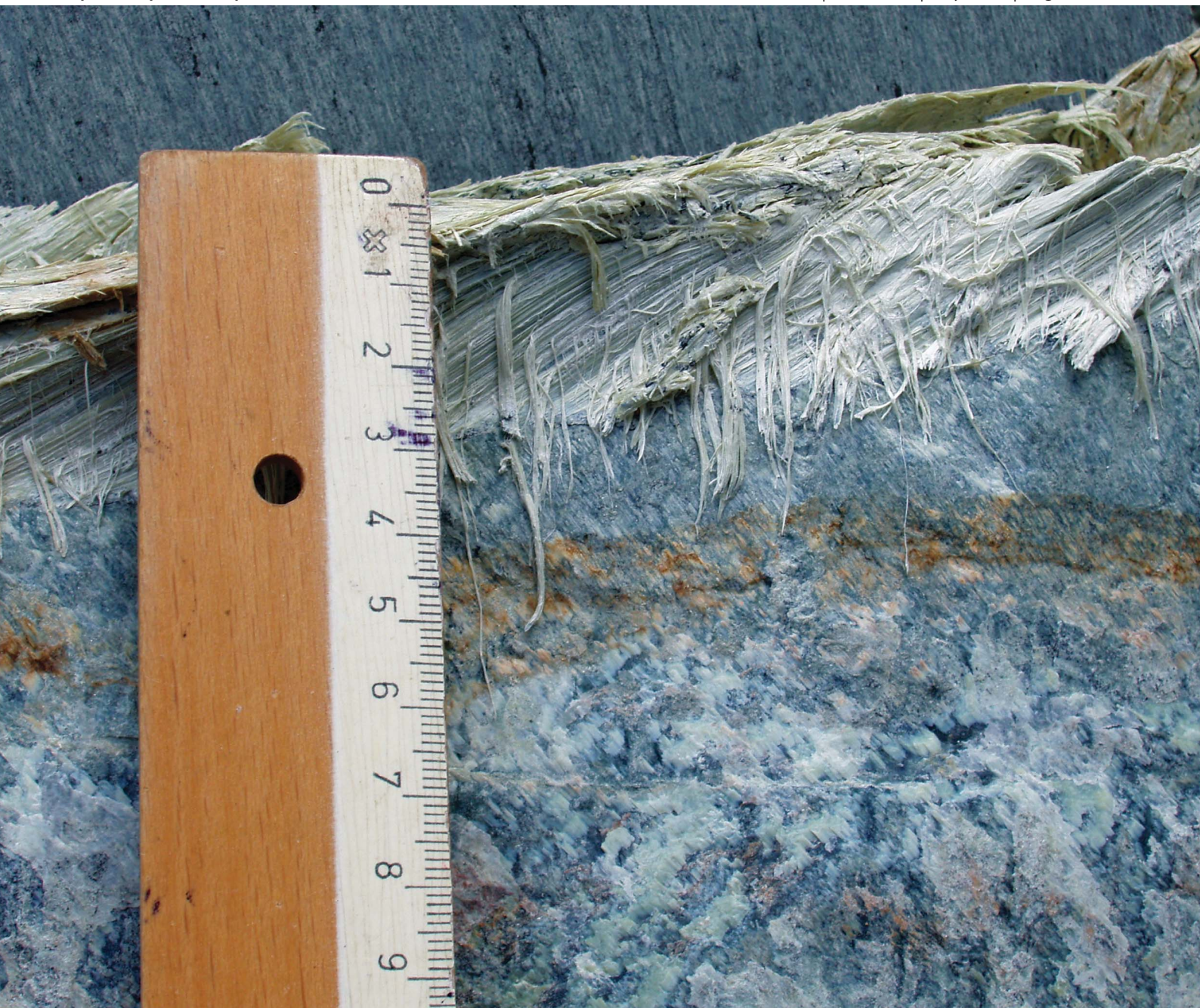


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Chrysotile asbestos in serpentinite quarries: a case study in Valmalenco, Central Alps, Northern Italy

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The Valmalenco serpentinite (Central Alps, Northern Italy) is marketed worldwide as dimension and decorative stone. However, the same area was once subject to chrysotile asbestos mining, from the XIX century until 1975. Asbestos is a well-known carcinogen, and there is the possibility of releasing fibres during quarrying, subsequently exposing workers. From 2004 to 2011, extensive sampling and monitoring of quarry fronts, asbestos veins, commercial stones and airborne asbestos was carried out. Massive rock and vein samples were analyzed by a combined use of optical microscopy, X-ray powder diffraction (XRPD) and quantitative electron microscopy (SEM). Asbestos is concentrated almost exclusively in discrete horizons, that coincide with the main discontinuities of the rock mass. Commercial stones without fractures and veins are practically asbestos free, whereas there is a slight contamination (sometimes exceeding the 1000 ppm threshold) close to hydrothermal selvages. Quarry floors were always quite contaminated by chrysotile "beards" detached from the surface of the blocks. The airborne asbestos concentrations (PCM and SEM) were distributed over a wide range, mostly below the occupational exposure limit of 0.1 f ml⁻¹. Concentrations at the quarry property border or at the closest villages were always below the environmental exposure limit of 0.002 f ml⁻¹. The extreme thinness of chrysotile fibrils produced during quarrying activities, and the abundance of pseudo-fibrous antigorite cleavage fragments proved the SEM-EDS analytical procedure to be the most suitable. It is of crucial importance to avoid the interception of veins during quarrying and to remove all visible asbestos from the extracted blocks, before any further processing.

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Environmental impact

The quantification of naturally occurring asbestos, both in bulk rocks and airborne, is a complex analytical issue, due to the presence of non-asbestiform polymorphs. The scientific literature concerning the presence of asbestos in quarries of ornamental stones is rather poor, or focussed exclusively on certain specific topics. This paper presents the results of an 8 years long experience in serpentinite quarries, covering all critical aspects: rock mass, commercial stones, mineralized veins, extraction technologies and airborne asbestos. In cooperation with the Italian Workers' Compensation Authority, all tasks were considered, and critical phases were identified, providing guidelines for a correct approach in occupational risk management, and an effective policy for proper use of asbestos-containing rocks.

1 Introduction

Serpentinites are metamorphic rocks produced by hydration of peridotitic rocks during ocean-floor metamorphism, and represent a significant and worldwide component of ophiolitic and exhumed subcontinental mantle complexes. They principally consist of the trioctahedral serpentine-group layer silicate minerals Mg₃Si₂O₅(OH)₄: antigorite, lizardite and chrysotile, together with polygonal and polyhedral serpentine,¹⁻³ with accessory magnetite, brucite, Mg and Ca–Al silicates (mainly

olivine, pyroxenes, chlorite, amphiboles, talc). Chrysotile is the least abundant of the three main serpentine minerals, but it represents more than the 90% of the world asbestos.

Asbestos is a commercial term that indicates an entire family of minerals with fibrous-asbestiform habit (easily separated into long, thin, flexible, strong fibres): chrysotile (serpentine asbestos), actinolite, amosite, anthophyllite, crocidolite and tremolite (amphibole asbestos). More information on the classification of asbestos can be found in specialized monographs.⁴⁻⁶

Sometimes serpentinites host chrysotile asbestos deposits (grade >3 wt%), or, more frequently, non-mineable veins and fillings. The last case is also known as "naturally occurring asbestos" (NOA), a general all encompassing name given to asbestos minerals found in-place in their natural state, in such low quantities that mining and commercial exploitation are not feasible.

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It has been scientifically proven that the inhalation of asbestos fibres can cause severe illnesses, like mesothelioma and lung cancer.^{7–9} It has been suggested that airborne asbestos may be released from NOA deposits, especially within the past decade, when concerns in asbestos exposure have spread from the occupational setting to the natural environment.^{10–14} Without appropriate knowledge and engineering controls, NOA deposits may pose a potential health hazard if these rocks are crushed or exposed to natural erosion or to human activities creating dust (drilling, blasting, milling).

Generally, outcrops of serpentinitic rocks are highly fractured and tectonized, and the material can only be used as crushed stone or ballast. However, in rare cases, like in Valmalenco (Central Alps, Northern Italy, Fig. 1), fractures are regular and well spaced, and the rock mass has good geotechnical quality, ideal conditions for the extraction of dimension stone blocks. The Valmalenco serpentinite is marketed worldwide as dimension and decorative stone, with remarkable mechanical properties and pleasing colours and textures.¹⁵ However, the same area was once subject to chrysotile asbestos mining, and some serpentinite quarries at times “cross” tunnels of the old asbestos mines. The chrysotile veins (some cm thick) are concentrated along the main fractures, that at present time “guide” the serpentinite extraction.

The concentration of airborne asbestos close to outcrops of serpentinite, or during the extraction and processing of these rocks (as ballast) was evaluated in the U.S.,¹⁶ Japan¹⁷ and

Italy,^{18–20} and the conclusions are that the highest concentrations are found nearby the quarries and roads paved with asbestos-containing serpentinites, whereas concentrations just outside of these contexts are negligible.

In Italy the extraction, importation, exportation, trading and production of asbestos (or asbestos containing materials) were definitely banned with law 257/1992.²¹ The guidelines for detection and quantification of asbestos in artificial and natural materials are described in the Italian laws D.M. 06.09.94 (ref. 22) and D.M. 14.05.96 (ref. 23) and in their respective updates in the D.L.152/2006 (ref. 24): the contamination threshold is fixed at 1000 ppm. In 1987, the World Health Organization (WHO) fixed a limit value of 0.001 fibres per ml ($f\ ml^{-1}$) for air quality protection.²⁵ The Italian law D.M. 06.09.94 (ref. 22) states that concentrations of $0.002\ f\ ml^{-1}$ detected through scanning electron microscopy (SEM) must be considered a sign of pollution; it is of exceptional concern when concentrations are higher than $0.05\ f\ ml^{-1}$. The occupational exposure limit (OEL) for airborne asbestos in workplaces in EU countries, Directive 83/477/EC and 2003/18/EU,²⁶ is determined at $0.1\ f\ ml^{-1}$, as a time-weighted average concentration over an 8 hours work time, whereas the Italian environmental exposure limit is $0.002\ f\ ml^{-1}$.

Airborne asbestos contamination can occur during the extraction and processing cycle of the Valmalenco serpentinite, therefore it is essential to locate and quantify asbestos in the rock mass. The serpentinites have been extracted for hundreds

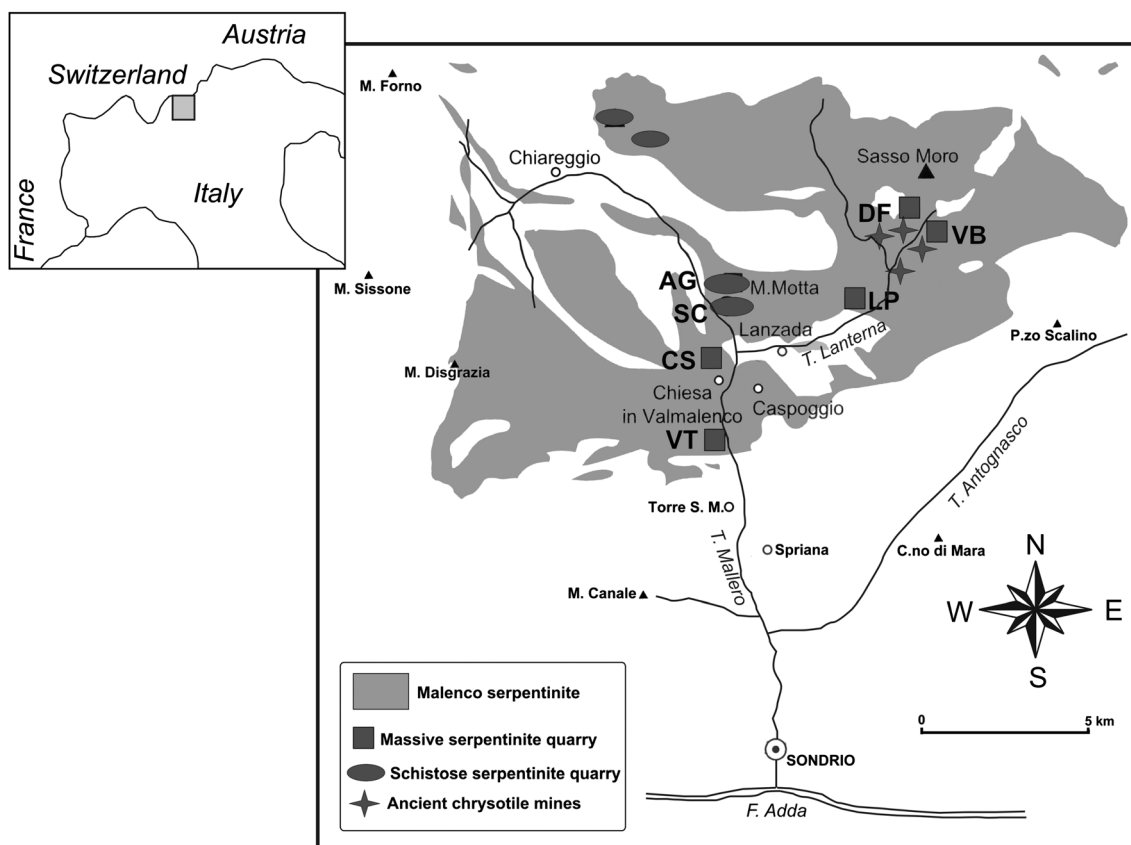


Fig. 1 Sketch map of the Valmalenco area, showing the location of the serpentinite quarries and the main abandoned chrysotile mines.

of years, and fortunately the incidence of asbestos-related diseases is below the national average,²⁷ with interesting considerations about exposure to pure chrysotile²⁸ and fibrous antigorite.^{29,30} INAIL (Italian Workers' Compensation Authority) of Lombardia – supported by the Central Offices, and in cooperation with the University of Milan-Bicocca – carried out extensive monitoring campaigns both in quarries and in processing laboratories, taking into account the rock mass, commercial stones, mineralized veins and airborne asbestos.

2 The Malenco serpentinite and the asbestos problem

The Valmalenco serpentinite derives from the Malenco unit (Fig. 1), a huge ultramafic body exposed over an area of 130 km², at the Penninic to Austroalpine boundary zone.^{31,32} Most of the Malenco ultramafics consists of schistose antigorite–olivine–diopside–chlorite–magnetite rocks, showing various degrees of deformation, serpentinization and metamorphic recrystallization.

The serpentinite has been used since the Middle Ages in Northern Italy in buildings such as churches and cathedrals, exposed for more than 10 centuries to unfavourable climatic conditions, and is still in good repair. At the present time the Malenco serpentinite is commercialized in two commercial varieties: schistose serpentinite (SS), mainly split into thin slabs for roof covering, and massive serpentinite (MS), processed in many ways, to produce valuable products like stoves, funeral monuments and designer home appliances.

2.1 Abandoned chrysotile asbestos mines and active serpentinite quarries

Italy hosted until 1992 the main European chrysotile asbestos mine in Balangero, Piedmont. Good quality chrysotile was also produced in Valmalenco, occurring in exceptionally long fibres,³³ from a few cm up to 2 m, in slip fibre veins, rarely in cross-fibre veins. In the former, the fibre axes are parallel to the walls of narrow openings in the host rock; in the latter, they are perpendicular. Structural and petrographic evidence suggests that chrysotile occurrences are essentially related to the late phases of the orogenic event, with low to very low temperature and high-fluid activity recrystallization conditions.^{34,35}

Asbestos in the past gave rise to widespread mining activity, particularly between the end of the XIX century and 1975, and was used mainly for weaving tablecloths or for wicks. A big boost to the mining activity occurred during World War II and the immediately following years,³⁶ with annual production up to 669 tons, until it ended completely in 1975.

At the present time, only serpentinite extraction occurs, in relatively small open-cast mountain quarries (Fig. 2), opened on slopes or sometimes on peaks. Certain climatic restrictions (ice, snowfall) are at times important and may introduce long periods of inactivity. The quarries are worked by means of horizontal beds and large banks, and the extraction technologies are based on a combined use of diamond wire cutters and



Fig. 2 Typical layout of a schistose (on the left) and massive serpentinite quarry (on the right, where also some tunnels of the abandoned chrysotile mines can be seen).

drilling with explosives (“dynamic splitting” using detonating fuse and gunpowder).

In the SS quarries, the primary cut is made by dynamic splitting, exploiting two important discontinuity surfaces of the rock mass; rarely must a lateral separation surface be created, in this case a diamond wire cutter is used. The MS varieties are quarried prevalently using diamond wire cutters.

About 30 enterprises in the valley perform quarrying and processing of the serpentinite, with more than 180 workers involved. The production of the single quarries is highly variable, from few hundreds to 10 000 m³ per year. The total volume extracted is assessed around 70 000 m³ per year and the resulting commercial blocks and products can be estimated as around 40–50% of the extracted raw material.¹⁵

2.2 Problems in serpentine minerals identification

Serpentinites show a great textural diversity,^{37,38} but they all mainly consist of the serpentine-group minerals antigorite, lizardite and chrysotile. Each of the three main serpentine polymorphs may occur with different crystal structures, originating from a common T–O structural configuration, with 7 Å spaced TO layers and very similar chemical compositions.^{39–41}

The analytical determination of bulk asbestos in rocks and soils is a very complex issue, especially in massive and very fine grained rocks with the simultaneous presence of non-asbestiform polymorphs, not comparable with asbestos containing materials. Because of the common T–O structural configuration of serpentine minerals, there is a strong superposition of the main diffraction peaks of the different polymorphs, and their identification by means of X-ray powder diffraction (XRPD) is not always possible, as well as the distinction of different morphologies.^{37,42} Electron microscopy, both scanning (SEM) and transmission (TEM), has been widely used for the qualitative and quantitative determination of asbestos,^{43–45} however, the small amount of the analyzed sample is not always representative. Microchemical approaches, like electron microprobe analyses (EMPA) and energy dispersive spectroscopy (EDS), are not useful in discrimination of serpentine minerals, due to the very similar chemical composition.^{11,13,46} Vibrational spectroscopies, especially micro-infrared (IR) and micro-Raman,^{47,48} reveal significant differences among the different serpentine polymorphs, but this approach is hardly applicable to bulk serpentinites, due to the interference among different serpentine polymorphs and other accessory phases. Recently, thermal

analysis (DTA) has been suggested as a possible method for both qualitative and quantitative determination of chrysotile in massive serpentinites,⁴⁹ but the results are preliminary, and the presence of chlorite hampers the attainment of reliable determinations. Thus, TEM appears to be the most accurate method for serpentine minerals identification, but it is poorly applicable to bulk determinations, due to experimental issues (*i.e.* expensive and time-consuming, poorly representative).

3 Materials and methods

We have investigated a total of seven quarries (Fig. 1), five of MS (VT, CS, LP, VB, DF) and two of SS (SC, AG). At the same time, both personal and environmental airborne asbestos sampling was performed at quarries, at the quarry property border and at the closest villages.

3.1 Quarries – geological surveys

We carried out a detailed geomechanical, petrographic and structural survey of each quarry according to ISRM,⁵⁰ in order to characterize the main discontinuities (frequency and distribution of fracture systems, orientation, spacing, linear persistence, opening, filling), with special attention to key areas for asbestos (veins, fillings, fault gouges, mylonitic bands). The surveys were followed by extensive sampling of commercial quality rocks, mineralized veins and cutting sludge (produced by drilling and/or diamond wire cutting).

We collected a total of 74 rock, 85 mineralized vein and 21 cutting sludge samples; as the contact zone between the mineralized veins and the host rock was frequently characterized by hydrothermal alteration selvages, samples were taken respectively at 1 and 10 cm from the vein contact, in order to assess possible asbestos contamination along the selvage. Representative samples of cutting sludge were taken because they cover a large part of the quarry floor, and they are representative of the mineralogical composition of large areas of the rock-mass (up to 50 m²). Moreover, cutting occurs usually along natural discontinuity surfaces (fractures, veins, faults), the most likely to bear asbestos veins.

3.2 Rocks and mineralized veins

Rock and mineralized vein samples were characterized by combined use of polarized light microscopy (PLM) on thin sections, XRPD and SEM-EDS; cutting sludge samples were analyzed only by SEM-EDS.

The PLM analyses (Leica DME 13595 microscope), both in transmitted and reflected light mode, allowed the characterization of rock mineralogy and microstructures.

The XRPD analyses were performed using a PANalytical X'Pert PRO PW3040/60 X-ray diffractometer with Ni-filtered Cu K α radiation at 40 kV and 40 mA, 1/2° divergence and receiving slits, and step scan of 0.02° 2 θ , in the 3–80° 2 θ range. The limit of detection (LOD) of XRPD depends on the mineral phase, and is generally comprised between 0.1 wt% for highly crystalline phases and 5 wt%; for serpentine minerals it is usually 1 wt%.

The qualitative XRPD analysis was performed running the PANalytical X'Pert High-Score software, using the ICSD PDF2 database. A semi-quantitative evaluation of the relative abundance of single minerals was obtained with the internal standard technique (by adding 20 wt% of corundum powder) and the reference intensity ratio (RIR) method.^{51,52} This approach is based on a least squares minimisation, like the Rietveld method, which however is not recommended on minerals with high structural disorder, like phyllosilicates.

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, to identify and chemically characterize the different minerals. To evaluate the maximum amount of potentially releasable fibres from each sample, a fine grinding was performed (crushing with hydraulic press and short grinding with agate mortar). The quantification of fibres in rock and vein samples was performed on the grain-size fraction comprised between 10 and 125 μ m of powdered and sieved samples, filtered on polycarbonate filters with a 0.6 μ m mesh (25 mm diameter), working at 2000–4000 \times magnification. The sample preparation and analytical procedure are thoroughly described in the Italian law D.M. 06.09.94 (ref. 22). The technique is based on point-counting statistics, and the occurrence, number, dimensions and chemical composition of asbestos fibres in each measured point are reported. The volume of the single fibre is approximated to that of a cylinder, and the weight is calculated assuming an average density of 2.6 g cm⁻³ for chrysotile and 3.0 g cm⁻³ for amphibole. Due to the small amount of detected fibres, the experimental error (1 σ value) reported in the data represents only the error related to the counting statistics: assuming a Poisson distribution of the fibres on the filter, the error ($\Delta N/N$) is calculated as 1/ \sqrt{N} . 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.

3.3 Air samples

Airborne asbestos was analyzed in 204 personal (41 PCM and 163 SEM-EDS) and 28 environmental air samples (SEM-EDS), collected from different quarrying activities, at quarry property borders and at the closest villages (1–5 km radius). In each quarry, 2 to 3 persons were working during sampling; tasks are periodically alternated for organizational reasons. The air samples were collected mainly in the summer season, from September 2004 to October 2011, in order to get the best meteorological conditions, as the quarries are located at an elevation between 870 m and 2020 m above sea level. Personal sampling was performed for the following activities:

- drilling (pneumatic power hammers and down the hole hammers);
- diamond wire cutting;
- moving (includes hoisting, loading, unloading, movement and transport with excavator).

Analyses were carried out using prevalently SEM-EDS (a total of 181 samples); in VB and DF quarries, where higher fibre concentrations were expected (sites of ancient chrysotile mines), personal sampling was performed mounting two

pumps on each worker, in order to obtain one sample for PCM and one for SEM-EDS analysis.

Workers' exposure to airborne asbestos was assessed according to national and UE legislation:²⁶ the WHO method⁵³ was the reference method for sampling and PCM analysis, whereas SEM-EDS analysis was performed according to national legislation²² and ISO Method 14966 (ref. 54); the fibre-definition criteria are those cited in the rules above (length > 5 μm , diameter < 3 μm and aspect ratio > 3).

Cellulose nitrate filters (25 mm diameter, porosity 0.8–1.2 μm) were used for PCM, whereas polycarbonate filters (Osmonics 25 mm diameter, porosity 0.8 μm) for SEM-EDS analyses.

Personal sampling (Aircheck-SKC; Analitica Strumenti) was performed in occupational settings, and the total volume sampled was limited between 100 and 500 l, due to high dust presence. Personal samples were taken in the breathing zone by an open-faced filter holder fitted with an electrically conducting cowl, and flow rates were generally set at 2 l min^{-1} , except for drilling sampling, where pumps were operated at 1 l min^{-1} .

Environmental sampling was carried out with a high flow portable pump (ZB2, Zambelli), placing the filter at breathing zone height (160 cm above floor level), at a flow rate of 5 l min^{-1} ; the volume sampled was between 800 and 3200 l, depending on dust concentration.

The PCM analyses (ZEISS Axioplan 451889) were performed at the INAIL-CONTARP laboratory in Rome, whereas SEM-EDS analyses (after carbon or gold coating) were carried out both at the INAIL-CONTARP laboratory (Leica Cambridge Stereoscan 260 SEM – Link Analytical eXL EDS spectrometer) and at the University of Milano-Bicocca (Vega TS Tescan 5163 XM SEM – EDAX Genesis 400 EDX spectrometer). SEM-EDS analyses were performed at 4000 \times magnification (instead of 2000 \times standard); in the case of very thin or short fibres, counting was performed at 10 000 \times .

The LOD of the PCM analyses was enhanced by increasing the number of analyzed fields (range 300–600), at approximately 0.005 f ml^{-1} ; the investigated filter area was increased for SEM-EDS as well (up to 6 mm^2), in order to reach a LOD of 0.0005–0.008 f ml^{-1} (depending on sampled volumes) and 0.0003 f ml^{-1} for personal and environmental samples respectively (calculated on the basis of ISO Method 14966 (ref. 54)). Data below the LOD were considered as LOD/2 and included in the analysis.

4 Results and discussion

4.1 Quarries and asbestos veins

The structural setting of all quarries is favourable, ensuring the compliance of the minimum commercial volume of extracted blocks. Data are reported in Table 1 for each quarry: the Ks surfaces correspond to the main schistosity, whereas K1, K2, and K3 are the discontinuity families with progressively minor rank. The fractures show a remarkable regularity in spacing, linear persistence and orientation; areas with stronger fracturing are rather rare, and are constituted by cataclastic or mylonitic bands (faults), generally less than 50 cm thick. The

regularity of fracture systems has important effects on the disposition of fissure and vein minerals, which are concentrated into regular discrete levels, and not “scattered” as in the case of cataclastic rock masses. The most significant chrysotile veins are associated to an important ENE–WSW striking fracture system, especially in VB and DF quarries, just where the most important abandoned mines are located. These veins occur in the form of discrete slip-fibre (rarely cross-fibre) fissure fillings and lenses, with a thickness from 2–3 mm up to 50–60 mm, generally with small linear extension (from less than 10 cm up to 1.5 m). The thickest veins are characterized by hydrothermal alteration selvages (Fig. 3a), affecting the wall rock up to 50 mm, with widespread micro-fractures and chrysotile veinlets. The most important asbestos veins are found in the MS quarries (especially DF and VB, thickness up to 60 mm), whereas in SS quarries (SC and AG) these veins are definitely less abundant.

It is important to note that chrysotile mineralization occurs almost exclusively in thin veins and lenses along the main fracture systems, and that these small volumes are not useful portions of the serpentinite deposit. Moreover, most of the asbestos volume has been removed by the previous mining activity, leaving now the old mine tunnels and non-mineable veins. On the other hand, these fractures are exploited for the serpentinite block extraction, so they are critical for the dispersion of airborne fibres. Chrysotile “coatings” and “encrustations” on the surface of extracted blocks (Fig. 4b), in the form of poorly adhering “beards”, are rather frequent, and inevitably accumulate on the quarry floor (Fig. 4a).

The total asbestos content in each quarry (Table 1) has been estimated with a simple volumetric calculation, considering the geostructural properties of the rock mass (three main discontinuities, mean vein filling width, spacing and linear persistence) and the quantitative mineralogical composition of the veins (XRPD and SEM-EDS analyses). Assuming an average density of 2.6 g cm^{-3} for chrysotile and 2.8 g cm^{-3} for the serpentinite, the estimated average asbestos content of the quarries is between 0.32 (DF) and 0.01 wt% (SC), very small non-mineable concentrations.

4.2 Rocks and mineralized veins

The paragenesis of the serpentinites (PLM on thin sections) is characterized by two main generations of antigorite, olivine and clinopyroxene (diopside), with minor amounts of Cr-rich chlorite, magnetite, brucite, chromite, Ti-clinohumite, Fe–Ni alloys and sulfides. The antigorite amount is variable, and the spectrum ranges from completely serpentinitized rocks to serpentinites with considerable amounts of olivine and diopside (up to 40–45 vol%). Except for a few pseudomorphic textures, the majority of the sampled serpentinites exhibit interpenetrating and interlocking non-pseudomorphic textures. The SS varieties frequently display mylonitic foliation, with interlocking equigranular texture, whereas olivine and diopside form mosaic textures. The MS varieties have a coarser grain size, a wider spaced foliation and interpenetrating textures.

Table 1 Rock mass properties of the quarries, main vein minerals and estimated average chrysotile asbestos content. Abbreviations: Cal, calcite; Chl, chlorite; Ctl, chrysotile; Grt, garnet; Liz, lizardite; Qtz, quartz; Tlc, talc. For chrysotile bearing veins, mean vein filling thickness, linear extension and mean chrysotile content (wt%, XRPD and/or SEM-EDS analysis) are reported. Symbols: (–) = mm to sub mm vein filling, linear extension < 10 cm; (O) = vein filling up to 3 mm, linear extension up to 30 cm; (+) = vein filling up to 25 mm, linear extension up to 1.5 m

Quarry area	Extracted material	Main fracture systems				Average asbestos estimate (wt%)
		Strike/dip (°), vein filling width (mean, range, mm), linear persistence (%), vein minerals ^a				
VT	Massive serpentinite	Ks	K1	K2	K3	0.03
		185/76 0.5 (0–2) >90 Chl, Cal, Liz, Ctl (–; 5%)	280/70 1 (0–4) >90 Chl, Cal, Ctl (–; 11%)	025/50 1 (0–3) 50–90 Cal, Ctl (–; 14%)	080/70 2 (0–4) 30–50 Cal, Ctl (–; 15%)	
CS	Massive serpentinite	330/25	155/70	080/70	125/55	0.09
		0.5 (0–1) >90 Cal, Ctl (–; 11%)	1 (0–3) >90 Cal, Liz, Qtz, Ctl (O; 29%)	1 (0–5) 50–90 Liz, Cal, Chl, Ctl (–; 18%)	2 (0–5) 50–90 Cal, Ctl (O; 12%)	
LP	Massive serpentinite	060/65	154/70	248/50	040/45	0.07
		0.5 (0–15) 50–90 Liz, Cal, Chl, Ctl (–; 6%)	0.5 (0–1) >90 Cal, Chl, Liz, Ctl (O; 26%)	1 (0–3) 50–90 Cal, Chl, Ctl (–; 15%)	1 (0–3) 50–70 Cal, Liz, Ctl (–; 19%)	
VB	Massive serpentinite	030/25	154/88	225/60	330/85	0.13
		0.5 (0–1) 50–90 Cal, Chl, Ctl (–; 8%)	4 (0–18) >90 Tlc, Cal, Liz, Chl, Ctl (+; 63%)	1 (0–2) 50–90 Cal, Chl, Liz, Ctl (–; 20%)	2 (0–5) >90 Tlc, Cal, Chl, Ctl (O; 32%)	
DF	Massive serpentinite	020/35	245/68	150/76	270/70	0.32
		0.5 (0–1) >90 Cal, Ctl (–; 10%)	5 (0–20) >90 Cal, Grt, Chl, Ctl (–; 12%)	4 (0–16) >90 Cal, Grt, Chl, Ctl (+; 78%)	4 (0–15) 50–90 Cal, Grt, Chl, Ctl (+; 45%)	
SC	Schistose serpentinite	280/30	145/65	010/48	170/84	0.01
		0.5 (0–1) 50–90 Cal, Liz	1 (0–3) 50–90 Cal, Liz, Ctl (–; 16%)	1 (0–3) 50–90 Cal, Ctl (–; 8%)	2 (0–6) >90 Cal, Liz, Chl, Ctl (–; 10%)	
AG	Schistose serpentinite	012/28	190/88	088/80	—	0.05
		0.5 (0–1) >90 Cal, Liz	0.5 (0–1) 50–90 Cal, Ctl (–; 16%)	0.5 (0–2) 50–90 Cal, Chl, Ctl (O; 24%)		

^a For chrysotile (Ctl) bearing veins, mean vein thickness, linear extension and chrysotile content are reported.

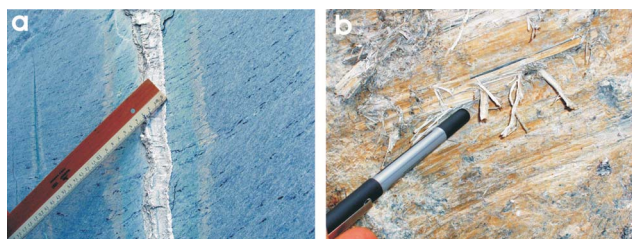


Fig. 3 Chrysotile asbestos veins: (a) cross-fibre vein with hydrothermal selvage; (b) slip fibre vein.



Fig. 4 (a) Quarry floor contaminated by chrysotile aggregates; (b) serpentinite block surface with chrysotile "beards".

The XRPD analysis of commercial stone material was in good agreement with PLM, confirming the sole presence of antigorite (pattern 7-417 of the ICSD PDF2 database) among serpentine polymorphs. The XRPD analysis of mineralized veins (a mean of 3 samples for each main discontinuity, see Table 1) showed a wide mineralogical variety: the most common minerals are

carbonates (mostly calcite, rarely magnesite, dolomite and aragonite), chrysotile [clinochrysotile polytype, discriminated on the pattern 10-380 ICSD PDF2 (ref. 55)], clinocllore, k ammererite, garnet (andradite), forsterite, magnetite, lizardite (pattern 11-386 ICSD PDF2), talc, brucite, chromite, Cr-diopside

Table 2 Chrysotile asbestos content of rock samples (taken at 10 cm and 1 cm from the veins respectively) and quarry sludge, measured by means of SEM-EDS after filtration on polycarbonate filters, according to Italian law DM 06.09.94. Mean values and range + 1 σ (experimental error related to counting statistics) are reported; main phases were identified by XRPD. Abbreviations: Atg, antigorite; Chl, chlorite; Ctl, chrysotile; Ol, olivine; Cpx, clinopyroxene; Mag, magnetite

Quarry area	Extracted material	Rock samples – 10 cm from vein – fibre concentration (Ctl, ppm)	Rock samples – 1 cm from Ctl vein – fibre concentration (Ctl, ppm)	Quarry sludge (diamond wire or drilling) – fibre concentration (Ctl, ppm)
		Mean (range + 1 σ); main phases (XRPD)	Mean (range + 1 σ)	Mean (range + 1 σ)
VT	Massive serpentinite	<100 <i>Atg, Ol, Chl, Mag</i>	<100	117 (<100–220)
CS	Massive serpentinite	123 (<100–248) <i>Atg, Cpx, Chl, Ol, Mag</i>	227 (<100–477)	246 (<100–642)
LP	Massive serpentinite	106 (<100–177) <i>Atg, Chl, Ol, Cpx, Mag</i>	285 (120–398)	170 (<100–322)
VB	Massive serpentinite	139 (<100–222) <i>Atg, Ol, Mag, Chl</i>	612 (130–1298)	850 (125–1870)
DF	Massive serpentinite	188 (<100–344) <i>Atg, Ol, Cpx, Chl, Mag</i>	786 (244–1890)	1029 (265–2350)
SC	Schistose serpentinite	<100 <i>Atg, Ol, Cpx, Chl, Mag</i>	<100 (<100–120)	<100 (<100–230)
AG	Schistose serpentinite	<100 (<100–123) <i>Atg, Ol, Chl, Cpx, Mag</i>	160 (<100–322)	262 (<100–590)

and artinite. The chrysotile content of the veins is highly variable, from nearly pure chrysotile to less than 10 wt%.

The SEM-EDS analysis was performed on commercial stone materials (no visible fractures and veins, at least 10 cm from vein selvages), mineralized veins, serpentinite close to vein selvage (1 cm) and cutting sludge (Table 2). Vein samples with high chrysotile content (revealed by XRPD), underwent only qualitative SEM-EDS analysis, to confirm the actual presence of the asbestiform polymorph (Fig. 5). Since all the samples were very rich in acicular – pseudo-fibrous antigorite cleavage fragments, the distinction from chrysotile was based on morphological criteria, operating at high magnification (up to $\times 12\,000$). All commercial stone samples can be considered virtually asbestos-free, largely below the critical value of 1000 ppm. On the contrary, there is a slight chrysotile contamination (sometimes exceeding the 1000 ppm threshold) close to the vein selvages (1 cm), due to micro-fractures and chrysotile filled micro-veins; the biggest veins (VB and DF quarries) generate the highest contamination, also in cutting sludge (Table 2). Amphibole asbestos was never detected, although this cannot be excluded completely, especially close to talc veins, where fibrous tremolite was reported.³⁶

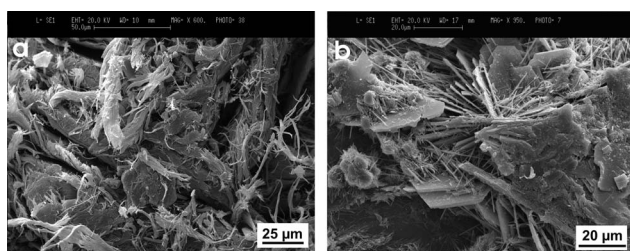


Fig. 5 SE micrographs of chrysotile bearing veins: (a) pure chrysotile; (b) chrysotile and calcite.

4.3 Airborne asbestos

The analysis of airborne asbestos showed a complex environment, with significant analytical difficulties. Compared to samples taken during industrial reclamation or in ACM settings, in a NOA context there are sometimes many cleavage fragments (falling into the fibre definition criteria) of non-asbestiform polymorphs. Considering the nature of the extracted rock, very rich in lamellar antigorite, filters were always full of splintery and acicular particles.

In the collected airborne samples, only chrysotile and pseudo-fibrous antigorite cleavage fragments were detected. Pseudo-fibrous antigorite has rectilinear, splintery acicular

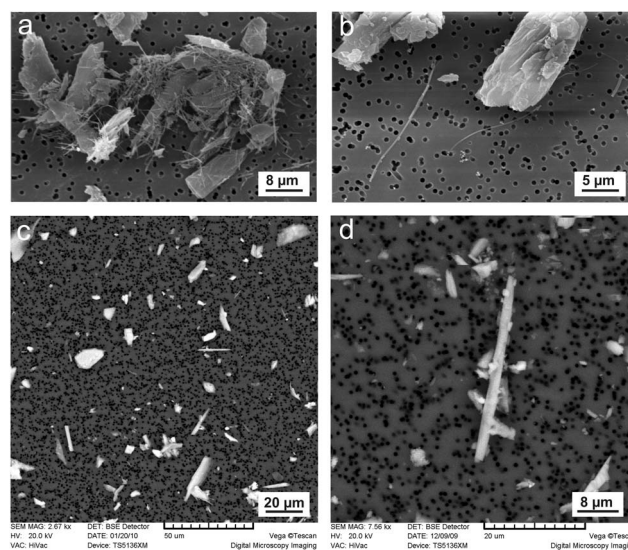


Fig. 6 BSE micrographs of polycarbonate filters: (a) aggregates of chrysotile fibrils; (b) very thin chrysotile fibrils; (c) and (d) pseudo-fibrous cleavage fragments of lamellar serpentine (antigorite).

habit, plane-parallel cleavage surfaces, diameter > 0.3 μm (typically >0.5 μm), and never forms fibril bundles (Fig. 6c and d). The length of antigorite “fibrils” was generally between 5 and 24 μm ; these “fibrils” were more abundant in SS quarries (SC and AG), where high aspect ratio antigorite grows in mylonitic bands. The concentrations of these not regulated “fibrils” are not reported, but they were always higher (up to four times) than chrysotile.

On the contrary, chrysotile occurs in long, thin, curved tubular fibrils, with fringed and splayed ends, frequently in curly aggregates or in bundles of fibrils, diameter < 0.2 microns, in agreement with the cut-off diameter indicated by Cattaneo *et al.*²⁰ Chrysotile was found generally in form of isolated fibrils with a length between 4.5 and 22 μm , or as fibre bundles. Due to the mechanical fragmentation and grinding (diamond wire cutting, drilling), many chrysotile fibrils had only a length of about 5 μm or less, a rectilinear morphology, an extremely small diameter (<0.1 μm , *e.g.* Fig. 6a and b), and were hardly visible at 2000 \times standard magnification. Frequently, the fibrils stuck to particles, or formed agglomerates (Fig. 6a), especially in the presence of aerosol (*i.e.* diamond wire cutting).

PCM and SEM-EDS personal sampling data (expressed as f ml^{-1}) are reported in Tables 3 and 4 respectively: for each activity we report the range, the arithmetic and geometric mean values, the log-normal distribution and the number of measurements.

The assessed occupational exposure levels were mainly below the OEL, except for 6 localized cases. In general, the chrysotile concentrations found in MS quarries were higher than in SS quarries, which is in good agreement with the increased frequency and thickness of chrysotile veins in the MS quarries. However, the airborne asbestos concentrations were always distributed over a wide range, and the peaks were

reasonably related to the occasional interception of chrysotile veins. Even in the case of tasks that require the use of water (diamond wire cutting), occasional high values were found (up to 0.2074 f ml^{-1}). Also handling activities showed appreciable exposure levels, presumably due to the strong contamination of the quarry floor, with continuous accumulation of chrysotile-rich waste, crushed by the incessant passage of dumpers and excavators. OEL was not exceeded during the drilling operation: this can be explained by the discrete occurrence of asbestos veins in the quarries, without disturbing them, there is virtually no risk of asbestos dispersion. Our data related to MS quarries are quite comparable with those of Cattaneo *et al.*,²⁰ whereas our values of SS quarries are definitely higher. The chrysotile concentrations at quarry property borders and at nearest villages (Table 4) were always below the Italian environmental exposure limit (0.002 f ml^{-1}), except for 2 values with no statistical significance.

SEM-EDS and PCM results show no agreement, with PCM data mostly lower than SEM-EDS, because of the abundance of extremely thin chrysotile fibrils (<0.1 μm), undetectable by PCM. This is particularly true, and for this reason very critical for risk assessment, for activities where we found overexposures in SEM-EDS: when the maximum value of 0.2074 f ml^{-1} was found for diamond wire cutting, the corresponding value (coupled sample) in PCM was only 0.025 f ml^{-1} . The problem is that UE directives and national legislation recommend the WHO method (PCM) for measuring asbestos in workplaces. Based on the experience acquired over 8 years in Valmalenco, INAIL has recently released a protocol for measuring NOA in the workplace by SEM-EDS.⁵⁶

5 Conclusions

The measurement and quantification of asbestos in natural environments is much more complex than in industrial or reclamation settings. The combination of field surveys and mineralogical investigations revealed that chrysotile asbestos was concentrated almost exclusively in discrete, well defined horizons, that coincide with the main discontinuities of the rock mass. The average asbestos amount in the quarries was very low; however, this study does not consider the possible asbestos occurrence in the form of micro-veins and micro-

Table 3 Airborne chrysotile fibre concentrations (f ml^{-1}) sorted by extracted material and working activity, obtained by personal sampling (PCM analysis) in massive serpentinite quarries. Abbreviation: AM, arithmetic mean

Activity	Extracted material	<i>n</i>	AM	Range
Drilling	Massive serpentinite	16	0.016	<0.005–0.093
Diamond wire cutting	Massive serpentinite	20	0.012	<0.005–0.066
Handling	Massive serpentinite	5	0.005	<0.005–0.007

Table 4 Airborne chrysotile fibre concentrations (f ml^{-1}) sorted by extracted material and working activity, obtained by personal sampling (P) and fixed environmental (E) sampling (SEM-EDS analysis), both in massive and schistose serpentinite quarries. Abbreviations: AM, arithmetic mean; GM, geometric mean; log *n*, log-normal distribution

Activity or location	Extracted material	<i>n</i>	AM	GM	log <i>n</i>	Range
Drilling (P)	Massive serpentinite	37	0.0166	0.0062	Yes	<0.0005–0.0674
Diamond wire cutting (P)	Massive serpentinite	52	0.0212	0.0042	Yes	<0.0005–0.2074
Handling (P)	Massive serpentinite	22	0.0224	0.0111	No	<0.0005–0.0672
Quarry property border (E)	Massive serpentinite	14	0.0005	0.0002	Yes	<0.0003–0.0025
Drilling (P)	Schistose serpentinite	17	0.0240	0.0130	No	0.0005–0.0433
Diamond wire cutting (P)	Schistose serpentinite	22	0.0092	0.0030	No	<0.0005–0.0184
Handling (P)	Schistose serpentinite	13	0.0120	0.0090	Yes	0.0028–0.0323
Quarry property border (E)	Schistose serpentinite	11	0.0006	0.0002	No	<0.0003–0.0053
Nearest town (E)	—	13	0.0002	0.0001	Yes	<0.0003–0.0005

fractures, outside of the main discontinuities, and cannot be fully applied to highly fractured rock masses.

The asbestos determination in bulk rocks requires a combined analytical approach, always in conjunction with electron microscopy, for the distinction of asbestiform and non-asbestiform polymorphs. Commercial stones without fractures and veins were practically asbestos free, whereas there was a slight contamination close to hydrothermal selvages.

The airborne asbestos concentrations were distributed over a wide range, but generally higher in the MS quarries than in SS ones, consistent with the geological-structural set up; on the other hand, there was no evidence of pollution outside the quarries. The extreme thinness of the chrysotile fibrils and clusters, within the wide range of exposure levels detected, and the abundance of pseudo-fibrous antigorite proved the SEM-EDS analytical procedure (specific protocol released by INAIL) to be the most suitable to evaluate contamination.

To reduce the exposure risk as much as possible, it is of crucial importance to avoid the interception of veins during quarrying (especially drilling and diamond wire cutting); a key issue is the continuous structural and petrographic survey of quarry fronts.

The quarry floors were generally contaminated with the chrysotile “beards” of the extracted blocks: the only way to reduce this contamination is to square-off the blocks in the quarry (e.g. with a stationary diamond wire plant), removing all visible asbestos and accumulating it in a safe area of the quarry, for subsequent disposal. The block should not be allowed to leave the quarry for further processing without serious quality control: carrying a “clean” block to processing facilities is indispensable for reducing following contamination.

Prevention actions were planned on the basis of the analytical results, and are still in progress, under coordinated supervision of the local authorities. Procedural and organizational solutions are implemented both in the quarries and in the processing facilities; employers and workers are trained appropriately, using the correct personal protective equipment.

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