ASBESTOS IN NATURAL AND ANTHROPIC OPHIOLITIC ENVIRONMENTS: A CASE STUDY OF GEOHAZARDS RELATED TO THE NORTHERN APENNINE OPHIOLITES (EASTERN LIGURIA, ITALY)

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Keywords: *Asbestos fibres, ophiolite, serpentinite quarry, Internal Ligurides. Liguria, Italy.*

ABSTRACT

Asbestos-related environmental issues include: i) the presence of natural outcrops of asbestos-bearing rocks, ii) the cycle of asbestos within natural matrixes, and iii) the quantitative assessment of asbestos fibres within large volumes of rock. The characterisation of the origin of asbestos as an exogenous agent, or during anthropogenic activity and the subsequent dispersal of fibres in neighbouring areas, allows the definition of a “fibre-cycle”, which is overall parallel to the hydric cycle. Pilot studies using microstructural and mineralogical investigations to assess the distribution and approximate volumes of asbestos minerals and their potential contribution of airborne fibres were undertaken at six quarry sites within the very-low-grade metamorphic ophiolites of the Northern Apennines in eastern Liguria, Italy. These studies also incorporated the assessment of the abundance of fibres within heaps of sedimentary debris within the same quarries; this assessment focused on heaps that were formed during natural erosion in addition to those formed during mineral extraction.

This study also tested a protocol that aimed to improve the Italian DM 16/5/1994 Release Index by addressing the issue of multi-scale analyses that are tailored for studies from outcrop scales to the microscale by integrating multiple techniques (optical microscopy, scanning electron microscopy, XR diffractometry, μ-Raman, geomechanical analysis, and modal petrographic analyses).

INTRODUCTION

The Italian national law (D.L. 257/92) prohibits the extraction, marketing, and production of asbestos in accordance with European Community directives. Nevertheless, stone quarrying, foundation constructions, the movement of rocks and stones, and the construction of tracking roads or galleries within serpentinites or metabasites all present potentials avenues whereby hazardous asbestos fibres may be released into the atmosphere.

Italian national law prescribes the same analytical protocols for industrial wastes and for environmental sampling (D.M. 06/09/1994 and, in particular, D.M. 14/05/1996), but a significant gap is present in terms of quantifying asbestos fibres. D.M. 06/09/1994 states that a mass value of releasable fibres from rocks needs to be identified, and also defines protocols for characterisation and diagnosis within buildings, and associated mitigation procedures. In addition, safety parameters have been issued for materials quarried from ophiolitic rocks, with D.M. 14/05/1996, defining suitability criteria for slabs, blocks, and breccias using an index (release index, IR) that describes the amount of fibres released by mechanical wear. However, this normative reference is unsuitable for assessing geohazards related to natural outcrops, ophiolite-bearing sediments (e.g., beach materials), landslides, stream sediments, or rock waste within quarries. The inadequacy of the IR measure as an exclusive parameter of asbestos hazard definition has also been recognised by the Italian Council of State (Sentence 315/2012), who determined that: “the release index is not and cannot be the analytical element to define the asbestos hazard in complex geological framework”. Recent studies on the potential for outcrops and rocks to release asbestos fibres (Gaggero et al., 2006; Giacomini et al., 2010) has also indicated the need for custom-tailored quantifications.

In Liguria, the Regional Law D.G.R. n° 878/06 “Criteri per l’utilizzo e la gestione di terre e rocce da scavo” identifies the need for a survey protocol for asbestos quantification in ground, soils and rocks, involving the ranking of ophiolites and metabasites into three groups (A, B, and C), as defined by the Regional D.G.R. n° 105 - 10/12/1996 (“Piano di Protezione dell’ambiente, di decontaminazione, di smaltimento e di bonifica ai fini della difesa dai pericoli derivanti dall’amianto”). In addition, D.G.R. n° 878/06 advises that excavation project documentation should include structural analyses of outcrops, particularly in terms of fracture extent and the presence of associated asbestos infill.

Asbestos-bearing rocks, chiefly serpentinites, can release significant amounts of fibres into the air, water, and soil during quarry operations, most commonly as a result of extraction procedures, including the stacking, storing, and grinding of excavated materials. This study focuses on several serpentinite outcrops within quarries in the very-low-grade metamorphic ophiolites of the Northern Apennines in the eastern Liguria region of Italy. These outcrops were used as pilot studies that used microstructural and mineralogical techniques to assess the distribution and approximate volume of asbestos minerals within these outcrops, and the potential of each outcrop to contribute fibres to the atmosphere. We also studied heaps of unconsolidated sediments within the same quarries; these sediments were formed either by natural erosion or by quarrying activity.

This study focuses on: i) the environmental issues related to naturally cropping out asbestos-bearing rocks, ii) the asbestos cycle in natural matrixes, and iii) the quantitative assessment of the amount of asbestos fibres within large volumes of rock. We focused on quarry sites and quarrying activity because the asbestos hazards related to these areas have been discussed during judicial proceedings, and because these quarry areas have total rock exposures that can be assumed to represent the worst-case scenario in terms of evaluating the global diffusion of asbestos within ophiolitic areas.

This work also aims to develop an operative protocol by addressing multi-scale analyses and integrating multiple techniques specific for geological issues in order to improve the Release Index outlined in Italian DM 16/5/1994.

REGIONAL SETTING

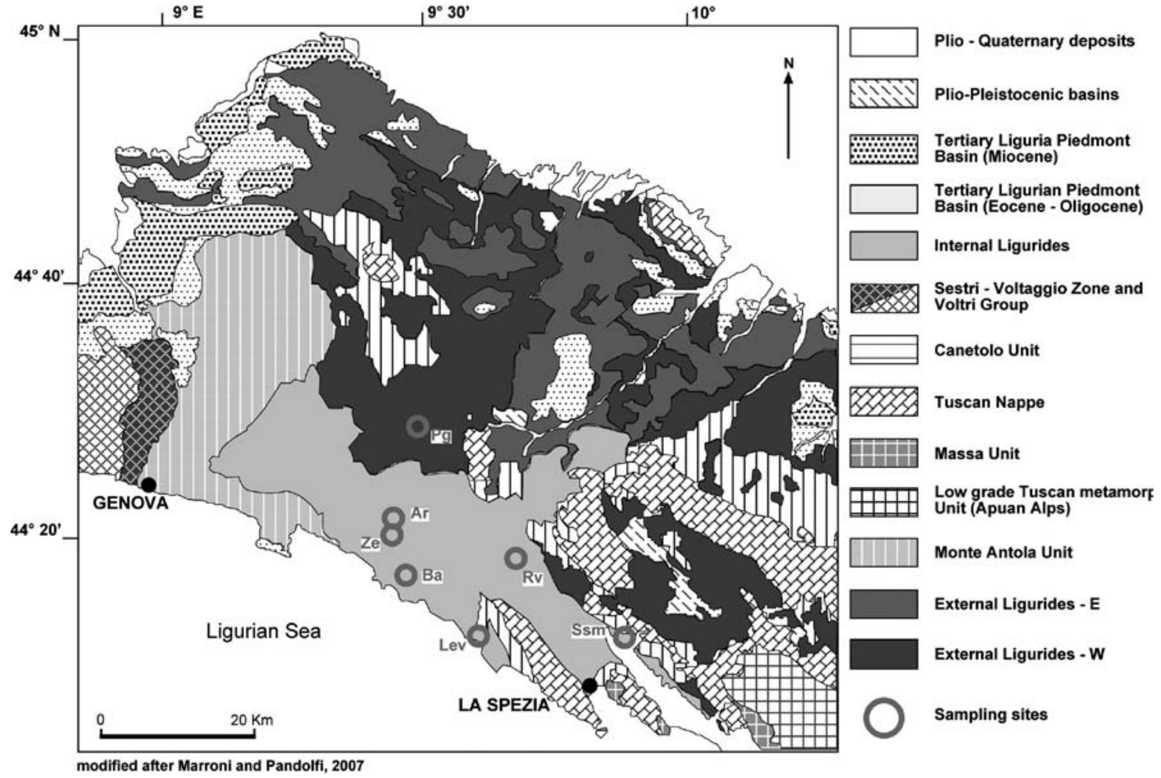
This study focuses on serpentinite units that represent the upper mantle basement of the Internal Liguride sequences, fragments of the Neotethyan Ocean that were uplifted during formation of the Apennine belt (Principi et al., 2004 and references therein).

These serpentinites formed from moderately depleted lherzolite that underwent spinel facies recrystallisation (Rampone et al., 1996) and is variably cross-cut by pyroxenite and gabbro dykes (Beccaluva et al., 1984; Rampone et al., 1998; Rampone and Piccardo, 2000; Piccardo et al., 2004). Conspicuous gabbro bodies intruded the mantle rocks, and consist of olivine gabbros and troctolites with metre-scale lenses of cumulus melatroctolites, chromitites, and plagioclasites (Cortesogno et al., 1994). A whole-rock and clinopyroxene separate Sm-Nd crystallisation age of 164±14 Ma has been obtained for these gabbros (Rampone et al., 1998), and they are cross-cut by Fe-Ti oxide gabbroic, dioritic, and polyphase plagiogranitic dykelets (Borsi et al., 1998) that yield a zircon U-Pb age of 153±0.7 Ma (Borsi et al., 1996). The gabbro-peridotite basement is cross-cut by two swarms of N-MORB affinity basalt dykes, although these dykes are more differentiated in composition than N-MORB (Cortesogno and Gaggero, 1992). The gabbro-peridotite basement is also overlain by tectonic breccias (ophicalcites) that are reworked into sedimentary breccias and intercalated with basalt flows (Cortesogno et al., 1987; Principi et al., 2004).

The metamorphic history of the ophiolite succession consists of two major phases of ocean floor polyphase metamorphism (Cortesogno et al., 1975; 1994 and references therein): i) ductile deformation and recrystallisation at granulite to greenschist facies during the period between the early intrusions of gabbros into lherzolite and the unroofing of the basement on the ocean floor; and ii) hydrothermal metasomatism of the breccias within the succession followed by thermal overprinting during the emplacement and eruption of basalt flows. This ocean floor cycle was followed by Palaeocene-Eocene pumpellyite-actinolite facies orogenic deformation (Cortesogno et al., 1994) of the basic rocks of the ophiolitic sequence and associated Late Jurassic-Early Palaeocene sedimentary cover units (Marroni and Perilli, 1990). This polyphase evolution means that the serpentinite basement contains complex ductile to brittle deformation patterns, including widespread veining and the formation of associated fibrous infill. Consequently, we used a systematic approach to the analysis of asbestos within natural outcrops, where the degree of microfracturing of a rock was correlated with other micro- and mesoscopic features.

A total of six serpentinite quarries within units of the Northern Apennines ophiolitic sequences (Val di Vara Supergroup, Bracco-Graveglia Unit) form the focus of this study; rocks from these quarries underwent detailed mineral and textural analyses in order to attain the best estimate of the abundance of asbestos within a given volume of rock. The six quarries, ranked "A" category (major asbestos risk) by the regional normative provisions, are as follows (Fig. 1):

"Arbisci": Né, near Botasi, Genoa (C.T.R. n° 232020),
"Bargonasco": Casarza Ligure, Genoa (C.T.R. n° 232100),
"Fosso delle Streghe": Levanto, La Spezia (C.T.R. n° 247040),
"Pietre Gemelle": Passo dei Ghiffi, Borzonasca, Genoa (C.T.R. n° 215100),



modified after Marroni and Pandolfi, 2007

Fig. 1 - Tectonic sketch map of the Northern Apennines, showing the location of the six serpentinite quarries that form the focus of this study: Ar- Arbisci; Ba- Bargonasco; Lev- Levanto, or Fosso delle Streghe; Pg- Pietre Gemelle; Rv- Rocchetta Vara; Ssm- Santo Stefano Magra.

"Polo di Serpentino": St. Stefano Magra, La Spezia (C.T.R. n° 248080),

"Rocchetta Vara", an outcrop along an adjacent road: Rocchetta Vara, La Spezia (C.T.R. n° 233100 - 233140). At this site serpentinite and chert were quarried in the lower Vara Valley. At present, only cherts are exploited.

"Zerli": Né, near Case Moggia, Genoa (C.T.R. n° 232060).

All of these sites are areas of former extraction of serpentinite aggregate for use in concrete.

FEATURES OF SERPENTINITES AND DERIVED SEDIMENTS

Outcrop-scale classification of serpentinites

Exposed outcrops of the six quarries (Fig. 2) have been characterised using the UNI EN ISO 14689-1 ("Indagini e prove geotecniche - Identificazione e classificazione delle rocce") scheme modified specifically for asbestos-bearing serpentinites. The quarry outcrops were classified and mapped as: A) massive, B) fractured, and C) cataclastic serpentinites (Fig. 2, Table 1).

A) Massive serpentinite

These serpentinites are massive rock bodies that contain lherzolites that originally had granular to porphyroclastic tectonised textures but were overprinted during the ocean-floor serpentinisation event, leading to the development of serpentine pseudomorphs after olivine and pyroxene, and the formation of bastite porphyroblasts. Pristine olivine is overgrown by a fine-grained mesh- and ribbon-textured aggregate dominated by lizardite with minor chrysotile and magnetite. Massive serpentinites form 20-25% of the volume of exposed faces within the quarries and are present as weakly fractured sub-spherical or irregularly shaped metre- to decametre-sized lenses. Fractures within this facies of rock are regularly distributed and have medium (200-600 mm) to wide (600-2000 mm) spaces between fractures. The main fracture systems are interconnected, forming a network that separates the massive bodies into polyhedral blocks that vary from 200 to 2000 mm in size. The fractures that separate these blocks are 10-100 mm thick and are partially or completely filled by fibrous or columnar light green to whitish serpentine minerals.

B) Fractured serpentinite

Several generations of cross-cutting fractures associated with variable amounts of fibrous phase development formed during the polyphase ocean floor and orogenic evolution of the ultramafic basement. Brittle structures without significant mineral recrystallisation within these serpentinites have been grouped into: 1) slickensides with elongate mineral fibres and intersection lineations between S-C surfaces that indicate the direction of tectonic movements, and 2) structures with stepwise fibre growth, sigmoids, and rotation of pre-existing foliations, all of which are shear sense indicators. Fracture frequency varies between < 1 and 30% of the rock volume, and fracturing is associated with recrystallisation of massive lizardite on slickensided surfaces (Fig. 3).

Fractured serpentinites, which form > 70% of the volume of exposed rock faces within the quarries analysed during this study, are developed along fault zones and enclose the massive serpentinite lenses described above. The very high degree of fracturing often forms cohesive cataclasites and, more rarely, poorly cohesive fault breccias, forming blocks that are 60-600 mm in size. These blocks are cross-cut by two main sets of conjugate fractures some 200-600 mm apart and with thicknesses of 10-100 mm, associated with further localised irregular fracture systems. The fractures are almost completely filled by whitish to light green serpentine minerals with massive and sometimes fibrous habits. The fibres are soft and friable and are released by water runoff or other erosional processes (Fig. 3).

C) Cataclastic serpentinite

Cataclastic serpentinite is ubiquitous throughout all of the quarries examined during this study, although this facies generally represents less than 5-10% of the volume of exposed rock within the study areas. This type of serpentinite occurs along anastomosing fault zones and encloses massive serpentinite lenses. Cataclasites are associated with a very high degree of fracturing that commonly forms cohesive cataclasites and locally poorly cohesive fault breccias.

The most extensive cataclastic serpentinites are located within the Bargonasco quarry. Here, massive serpentinite has been altered to a fine-grained matrix containing small relic fragments of the originally massive rock, and is associated with fractures that are partially or completely filled by massive or sometimes fibrous light green and/or whitish minerals, have narrow (60-220 mm) to very narrow (< 60 mm) spacings, and thicknesses that vary from 0.1 to 2.5 mm. The presence of conjugate chrysotile-filled fracture networks results in the ready dispersion of fibres, and, in rocks with cataclastic incoherent matrixes, have fibres that are considered free.

Serpentinite mineralogy and microstructures

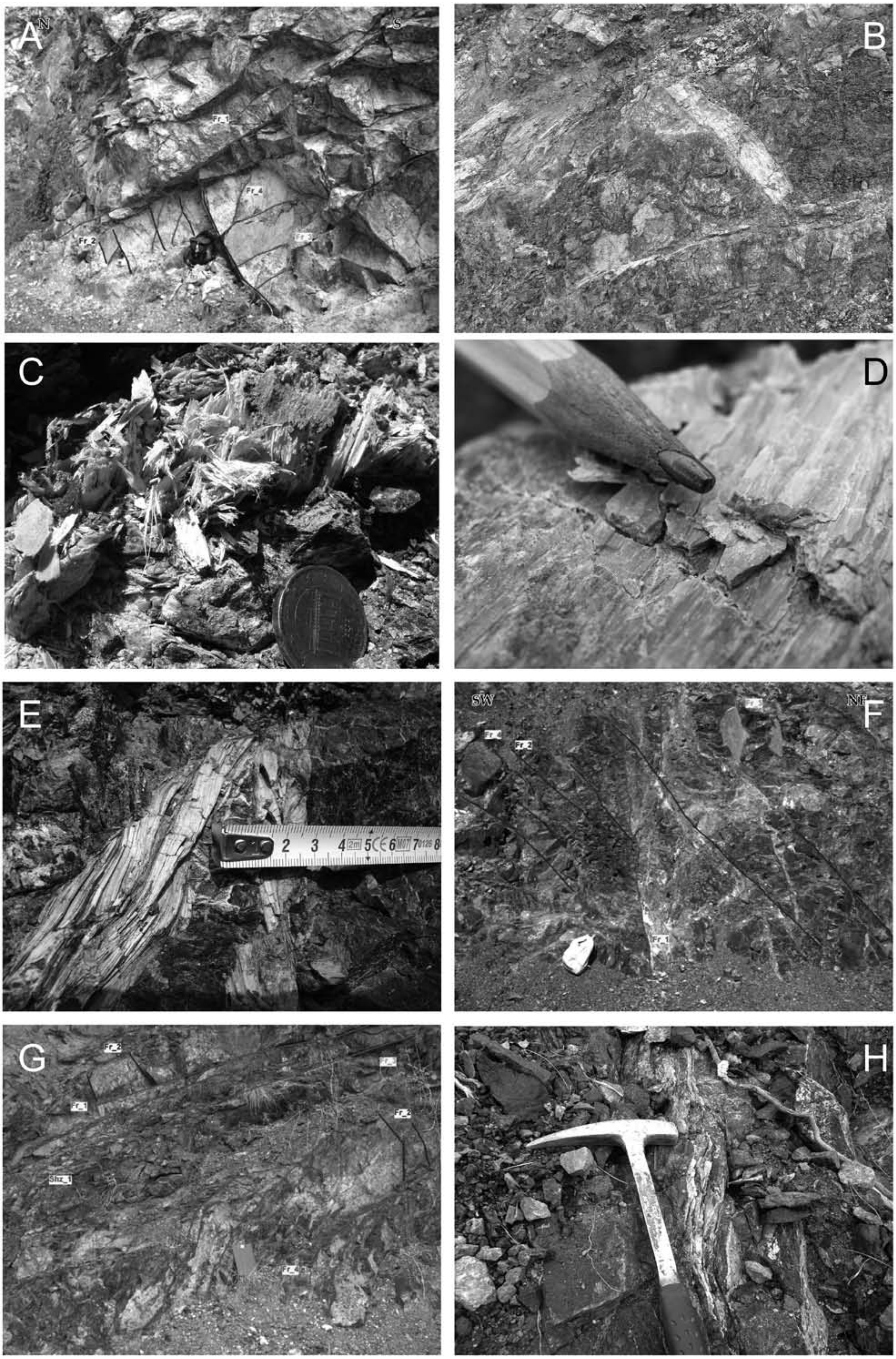
The three types of serpentinite described above all exhibit different degrees of fracturing, and have undergone different intensities and styles of deformation, but all three have homogeneous mineral compositions and retain both pristine ocean floor and orogenic textural features (Fig. 4). The main rock-forming phases are, in order of decreasing abundance, lizardite, chrysotile, magnetite and other spinels (e.g., chromite), and chlorite, with minor but ubiquitous calcite, dolomite, talc, tremolite, and clay minerals. Serpentinites are characterised by mesh-textured serpentine + magnetite pseudomorphs after olivine, and bastite pseudomorphs after orthopyroxene (Fig. 4). Serpentinites with mesh textures have fibrous chrysotile mesh rims and lizardite mesh cores, with magnetite present as elongate fine-grained aggregates along mesh rims, although some lizardite mesh cores also contain euhedral magnetite. Chrysotile fibres within mesh-textured areas are between 0.1 and 0.3 mm in length and have diameters of < 0.05 mm. These mesh textures are locally sheared, forming ribbon textures that are characterised by elongate irregular bands with lamellar lizardite cores and rims with tiny, short chrysotile fibres. Bastite pseudomorphs after orthopyroxene are present as lizardite lamellae with fibrous chrysotile (generally < 10 μm in length) along cleavage planes.

Microfractures (< 0.2 mm in thickness) are characterised by four differing types of fill: a) chrysotile; b) chrysotile + lizardite ± magnetite; c) lizardite + calcite ± chrysotile ± chlorite; and d) calcite ± dolomite. Fibrous chrysotile-filled microfractures are generally < 0.2 mm long and < 0.01 mm wide, and form > 50% of all microfractures; the overall modal abundance of fibrous chrysotile in massive-textured serpentinite and in microfractures varies from 25 to 35% (Fig. 5, Table 2).

Table 1 - Summary of vein and fracture microtextural and minealogical characteristics along the Jv lines within the six quarries analysed during this study.

Site	tot # of joint set	# of asbestos bearing sets of veins	average width [mm]	average width of asbestos bearing veins [mm]	# of asbestos filled veins	average width of asbestos-filled veins [mm]	type of fibres	type of bundles	type of fibres at the outcropping surface	% volume asbestos - bearing veins	Jv
Arbisci											
line 1	4	1	12	2	1	1.00	slickenfibres on Fr1 and cross fibres on Vn1	serrated - rigid	cessible, in the rock	6.53	22.23
line 2	4	0	2	0	2	0.50	cross fibres on Vn1 and Vn2	serrated - rigid	cessible, in the rock	9.43	47.18
Bargonasco											
line 2	6	5	5	5	0	0.00	slickenfibres	open - soft	free in the soil, cessible in the rock	80.00	39.23
line 3	5	1	3	2	0	0.00	slickenfibres	serrated - rigid	cessible, in the rock	12.12	26.75
line 4	4	3	18	5	0	0.00	slickenfibres			21.62	13.27
line 5	6	6	2	3	0	0.00	slickenfibres within fractures and on surfaces	serrated - rigid	free in the soil, cessible in the rock	100.00	22.98
Fosso delle Streghe											
line 1	4	3	2	2	0	0.00	slickenfibres	serrated and open - soft fibres	free in the soil, cessible in the rock	78.59	14.21
Pietre Gemelle	not available: quarry under environmental restoration						/	serrated and open - rigid fibres	free in the soil		n.d
Rocchetta Vara											
line 1	3	1	2	4	0	0.00	slickenfibres			69.86	15.92
line 2	3	0	11	0	3	43.00	deformed crossfibres	rigid bundles		79.12	25.72
S.Stefano Magra											
line 1	4	0	3	0	1	3.00				22.39	38.35
line 2	3	0	2	0	0	0.00				0.00	26.23
line 3	3	0	3	0	0	0.00				0.00	41.10
Zerli											
line 1	3	0	2	0	0	0.00		serrated and open - soft fibres	free in the soil, cessible in the rock	0.00	8.91
line 2	4	0	3	0	4	6.00		serrated and open - soft fibres	free in the soil, cessible in the rock	65.22	12.86
line 3	4	0	1	0	0	0.00		serrated and open - soft fibres	free in the soil, cessible in the rock	0.00	47.95

Fig. 2 - Representative examples of textures and relationships identified from outcrops. A: Fracture swarms along the Jv line within the Arbisci quarry. B: Rodingite dyke disrupted by a cataclastic band within the Bargonasco quarry. C: Bundles of soft chrysotile fibres released from an open vein within the Levanto quarry. D: Rigid fibres in a slickenside vein filling at the Pietre Gemelle quarry. E: Sheaves of deformed chrysotile fibres that formed during syntaxial growth within the Rocchetta Vara quarry. F: Jv line along the Santo Stefano Magra quarry walls. G: Cross-cutting relationships between veins along the Jv line at the Zerli quarry. H: Close-up of deformed centimetre-long rigid serpentine fibres at the Zerli quarry.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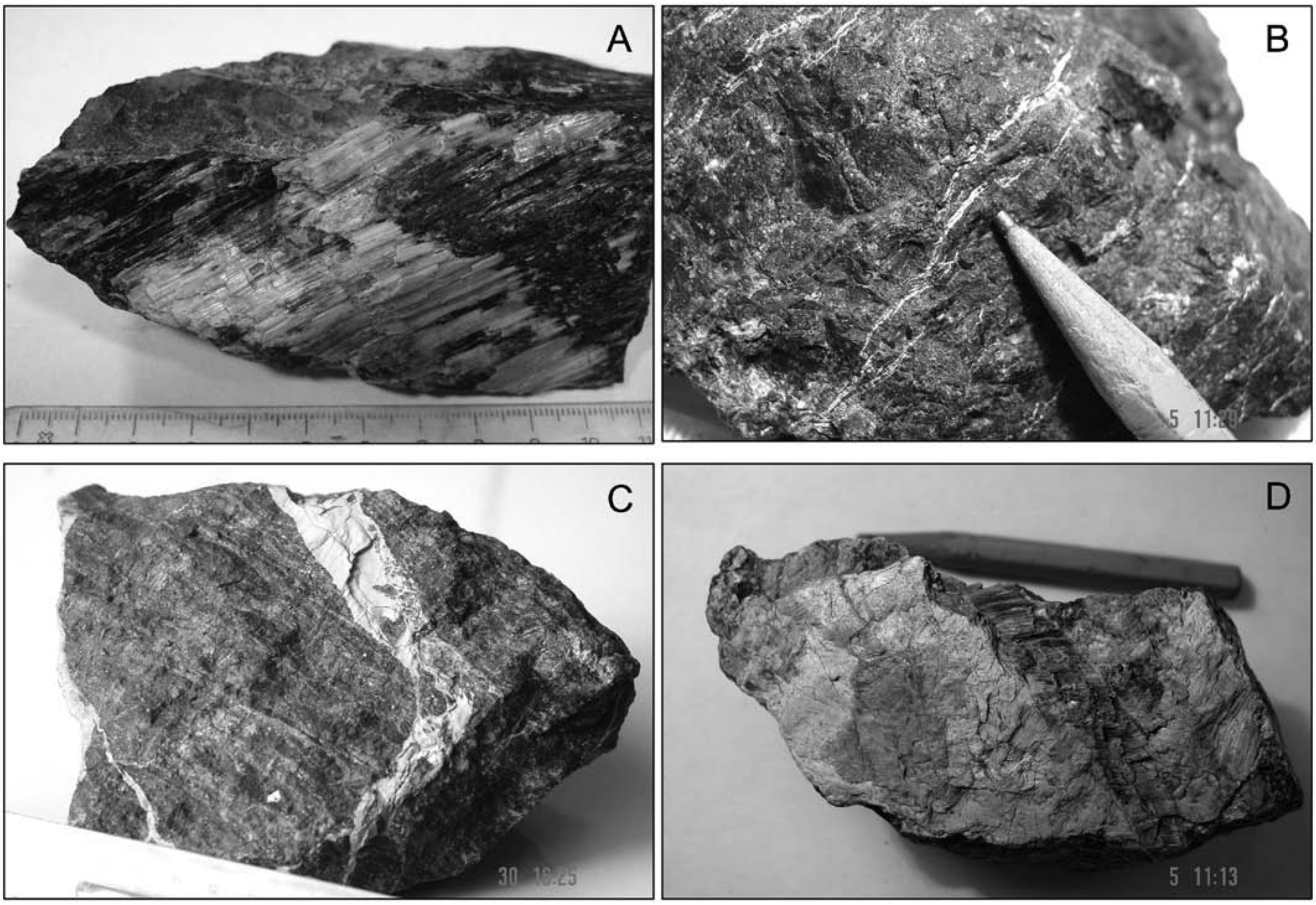

Fig. 3 - Selected mesoscopic vein textures. A: The intersection of two slickenside surfaces. B: A thin syntaxial white chrysotile vein parallel to elongate ribbon-textured serpentinite. C: Centimetre-thick composite vein filled by green chrysotile and serpentinite fragments. D: Centimetre-thick vein filled by green chrysotile cross fibres. A and B samples from the Arbisci quarry, C and D: samples from the Pietre Gemelle quarry.

Table 2 - Modal content of serpentine minerals classified by microtextural occurrences in a single sample from the Rocchetta Vara quarry.

Sample Rv_1 Rocchetta Vara quarry		
n. analysed points	Textures / phases	Volume %
110	Mesh, lizardite	11 (±2)
126	Ribbon, lizardite	12.6 (±2.3)
239	Hourglass, lizardite	23.9 (±2.8)
30	Interlocking / lizardite	3 (±1.2)
380	Bastite / lizardite	38 (±3.2)
15	Chrysotile	1.5 (±1)
24	Fracture filled by oxide / magnetite	2.4 (±1.1)
13	Fibrous veins / chrysotile	1.3 (±1)
63	Veins (without fibres)	6.3 (±1.6)
1000		100

Unconsolidated sediments

Sediments in the study area formed during erosion, landslides and rock falls, and from mineral processing after extraction. Hydraulic erosion within fractures releases fibre bundles and sheaves that are progressively deposited on the quarry floor (Fig. 3); this abundance of debris is a common by-product of quarrying activity and, as such, was examined during this study. The debris cover within the quarries consists of free-fibre bundles spread across quarry areas, and these bundles are particularly dense in locations close to vertical cuts and stockpile areas that were mapped and sampled during this study. Over one hundred samples were recovered from the three quarries at the Bargonasco site, yielding about 5 kg of sediment after quartering. Additional free or easily releasable macroscopic fibres were described, mapped, and sampled at other sites during this study.

Comparative analyses of the incoherent cover provided evidence of enrichment (up to 1-2 orders of magnitude) of free or easily releasable fibres in all sediments produced during quarry operations, and the most enriched samples were from the most recent quarry cuts and from piles of sand and gravel formed during crushing. These fibres accumulated at the base of incoherent piles and have shorter lengths than other fibres within these sediments. This is similar to the evolution of fibres observed within old ballast along disused railways; such ballast was obtained by recycling serpentinites that were tunnelled during excavations along the Ligurian coast.

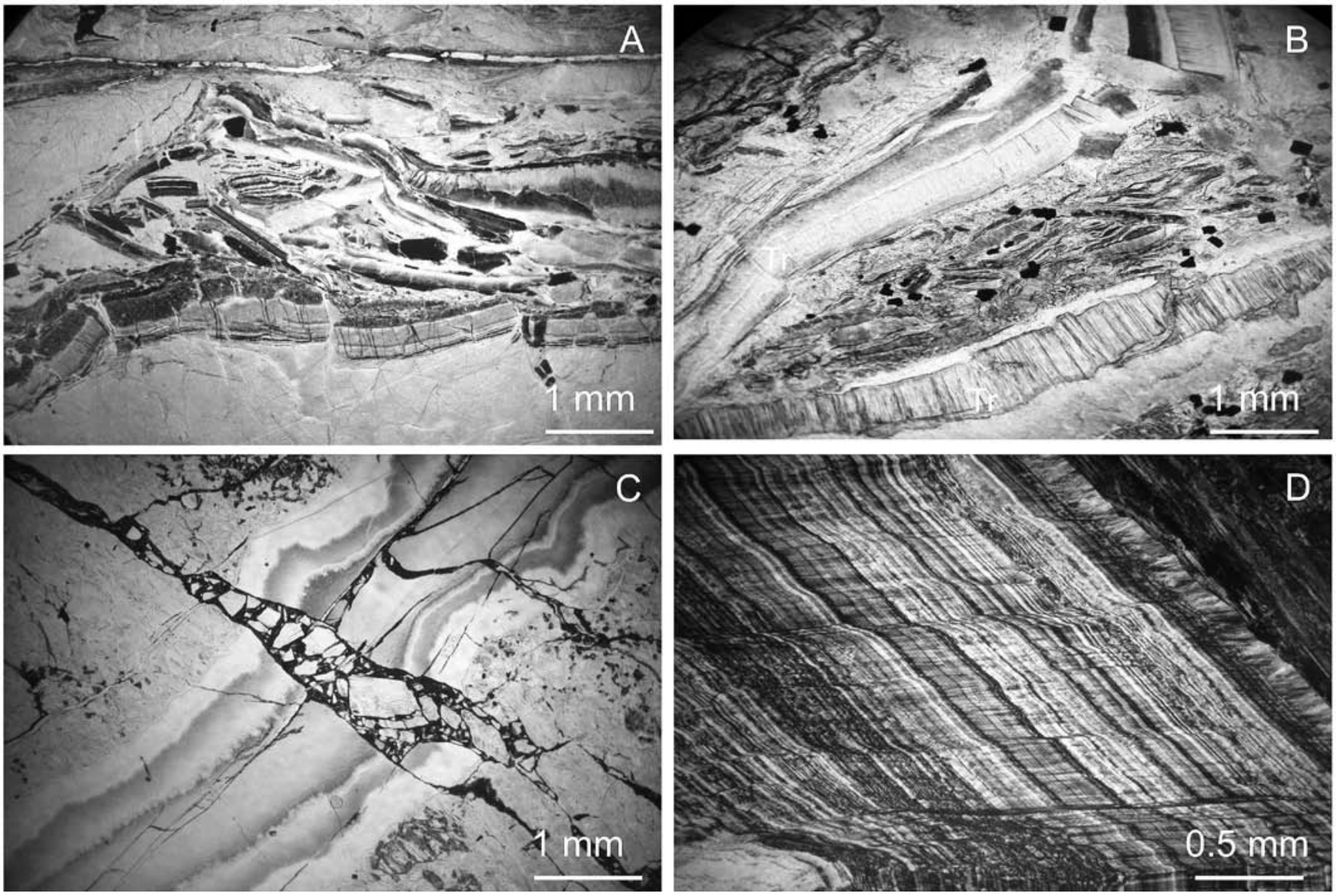

Fig. 4 - Transmitted light optical microphotographs obtained during this study. A: Brecciated composite vein including reworking of the vein selvedge (Arbisci quarry). B: Composite tremolite-chrysotile filled vein with a central disrupted and fragmented region (Pietre Gemelle quarry). C: Irregular serpentine breccia-filled vein cutting a polyphase, zoned serpentine-filled vein (Arbisci quarry). D: Polyphase syntectonic growth of banded serpentine fill within a syntaxial vein (Pietre Gemelle quarry).

It is likely that mechanical excavation and crushing are processes that are preferentially focused along vein and fracture surfaces, as evidenced by microscopic analyses that show that quarry sediments are composed almost entirely (90-95%) of serpentinite fragments. The lithic clasts within these sediments include massive serpentinite (with mesh textures and bastite pseudomorphs after orthopyroxene) and fragments of fibrous chrysotile-bearing veins. Fibrous fragments form 6-10% (by volume) of these sediments and up to 20-25% of the volume of the crushed piles.

The arenitic to pelitic sections of the cover sediments contain fibrous vein-infilling material that evolved to become free fibres that are 10-100 μm long and < 10 μm wide. Quantitative Reference Intensity Ratio (RIR) X-ray powder diffraction (XRPD) analyses identified sediments containing chrysotile concentrations between 467 mg/kg (natural sediments) and > 25,000 mg/kg (recent debris formed during extraction).

ANALYTICAL METHODS

Veined serpentinite samples were analysed by stereoscopic and transmitted light microscopy, scanning electron microscopy (SEM), micro-Raman spectroscopy, and XRPD. Prior to analysis, rocks and unconsolidated sediments were impregnated using epoxy resin and prepared as standard thin sections. Modal analysis of serpentinite (Isola, 2010) and sediment (Marescotti et al., 2006) samples was undertaken using thin sections, and both qualitative and quantitative analyses were performed using a transmitted light polarising microscope equipped with an electronic point counter. Macroscopic fibrous minerals covering sample surfaces or filling open fractures, veins, and voids were sampled using a diamond file before being manually and magnetically separated, and analysed by XRPD, yielding unambiguous mineral mixture compositions. XRPD analysis was undertaken using a Philips PW1140-XCHANGE diffractometer and CuKα radiation, employing a 30 mA current, a 40 kV voltage, a scan speed of 0.5° 2 θ/min, and a scan interval of 3-70° 2θ, interfaced with PC-APD software for data acquisition and processing.

Selected samples of very thin veins or tremolite-chrysotile mixtures were further investigated using a Philips SEM 515 scanning electron microscope equipped with an EDAX PV9100 energy dispersive spectrometer, employing a 15 kV accelerating voltage and a 2.1 nA beam current. The raw data obtained from these analyses were reduced using the ZAF algorithm and the standard EDAX PV9100 software. Further images were obtained using a Tescan Vega 3 LM scanning electron microscope equipped with an Apollo X detector and a Microanalysis TEAM energy dispersive system (EDS). Both SEM facilities were located at the DISTAV (formerly Dip.Te.Ris) at the University of Genoa, Italy. Microphotographs were acquired using graphite-sputter-coated 3D samples under high vacuum conditions with backscattered and secondary detectors.

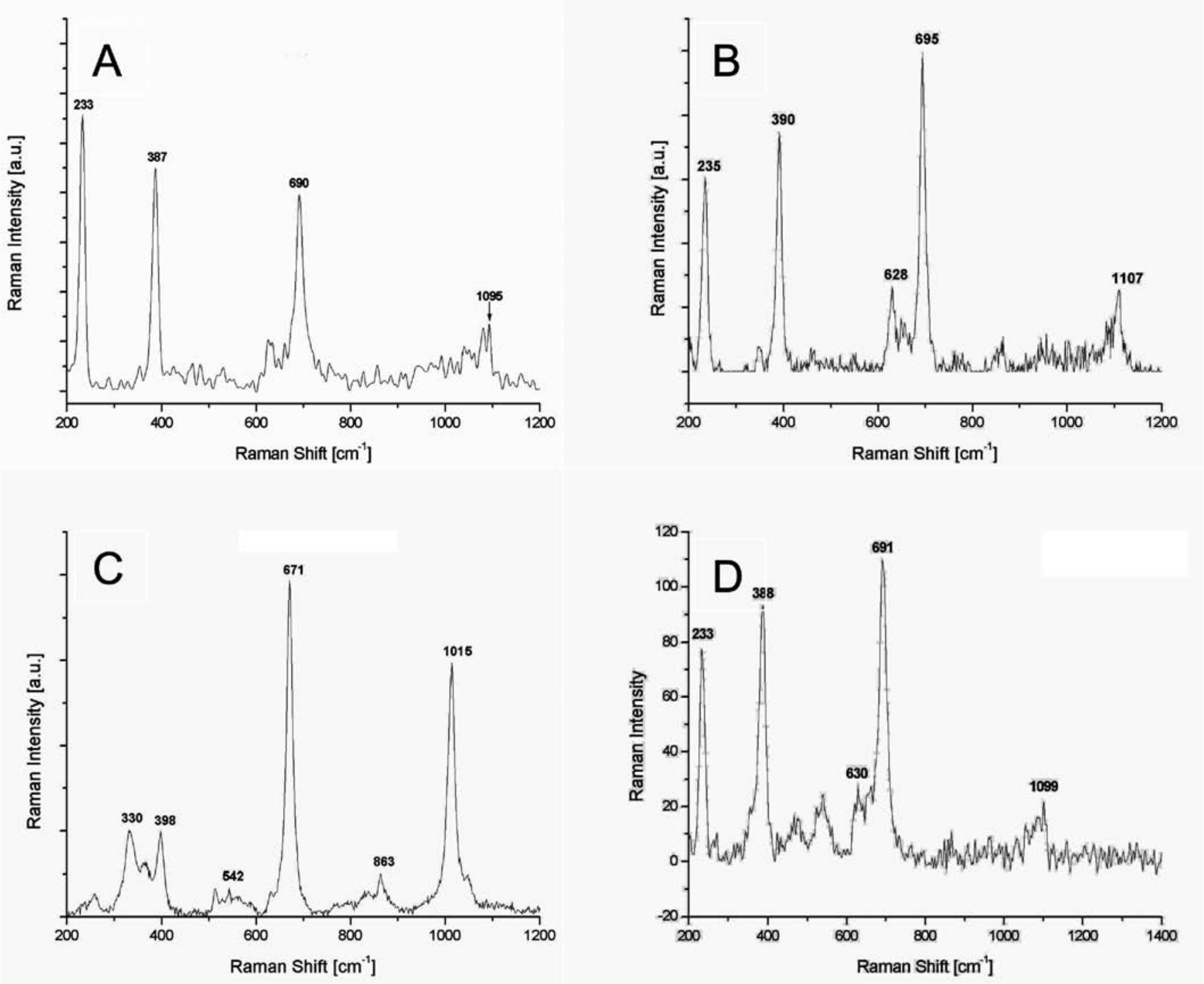

Fig. 5 - Micro-Raman analyses of significant phases within both serpentinites and veins: A: Mesh-textured lizardite and B: vein-filling chrysotile in samples from Arbisci quarry. C: Fibrous diopside from a vein fill within the Pietre Gemelle quarry. D: Bastite pseudomorphs within serpentinite from the Rocchetta Vara quarry.

Semi-quantitative electron microprobe analyses were obtained under high-vacuum conditions and were calibrated using natural standards that were initially analysed using a wavelength dispersive system (WDS) microprobe at Modena University, Italy.

High-resolution identification of mineral mixtures, the in situ mineralogy of serpentine phases with microtextural constrain were obtained using micro-Raman spectrometry and a Jobin Yvon LabRam 632.8 nm laser, at the Centro Interdipartimentale Scansetti, University of Turin, Italy.

OUTCROP-SCALE FIBRE ASSESSMENT

Chrysotile-bearing fractures and veins

Chrysotile is generally i) associated with lizardite or antigorite in massive serpentinites, ii) located in shear fractures as slip-fibres parallel to vein walls, or iii) is present as cross-fibres formed by crack-seal processes during synkinematic extension or shearing. Monomineralic veins within serpentinite can be filled by chrysotile, fibrous antigorite, diopside or tremolite, lizardite, calcite, or dolomite (Isola, 2010), and composite veins can host polyphase assemblages.

Systematic analyses were carried out to correlate the degree of micro-fracturing with micro- and mesoscopic features, and the weathering of vein-filling phases within natural outcrops. The six quarries were the field study to investigate these fracture patterns.

Geometry of vein arrays

The majority of veins within the study area are composite fibre-filled veins, but syntaxial and antitaxial fibre growth patterns (Ramsay, 1980) are also present. Vein thicknesses vary from a few millimetres to several centimetres, and some veins have developed along reactivated joint surfaces. Syntaxial veins have fibrous chrysotile fills that nucleated from the host rock, forming fibres that are perpendicular to vein walls and bend towards the centre, indicating that the oldest fibres are within the vein selvedge, and indicating that there is no compositional discontinuity between the host rock and early precipitated vein-filling minerals. Antitaxial veins have straight chrysotile fibres within vein centres that are gently bent towards the wall rock, suggesting that vein fills are externally derived with central fibres that are older than fibres at the selvedge, and indicating that a "crack-seal" mechanism (Ramsay, 1980) is responsible for this geometry. However, the majority of veins have composite fibre patterns (Fig. 4) with intersection relationships that suggest that these fractures were filled during extension (syntaxial growth) associated with shearing (crack-seal). A final extensional phase is characterised by the development of centimetre-thick veins; this phase is widespread in the Bargonasco quarries but is rare elsewhere.

Vein-filling minerals

Fig. 5 shows the results of optical analysis using transmitted light polarising microscopy, XRPD analysis on minerals extracted from veins or magnetically separated, quantitative in situ electron microprobe analysis by SEM-EDS on selected massive serpentinites samples, and in situ micro-Raman spectrometry on representative microtextures.

The local development of calcite is indicative of metastable equilibrium and stepwise fracture opening. The late veining phase is dominated by the development of centimetre-long linear chrysotile and intergrown chrysotile + tremolite fibres, whereas metamorphosed basic gabbro or basalt dykelets are represented by irregularly distributed millimetre-centimetre thick veins dominantly filled by tremolite and actinolite. Chrysotile-bearing macrofractures and veins (> 1 mm thick) are ubiquitous within exposed quarry walls and faces; these veins are single or are variably connected, ranging from branched to non-branched.

Three differing types of veins were classified based on the potential for release of chrysotile fibres, textural features, and mineral fillings: A) serrate chrysotile-bearing veins; B) composite chrysotile ± lizardite veins with soft fibre sheaves; and C) chrysotile coatings.

Serrate chrysotile veins (type A) are generally monomineralic and range in colour from white through to light and dark green, and contain aggregates of parallel rigid fibres that range in thickness from 1 mm to 1 cm. Most of these veins have both syntaxial and antitaxial filling patterns. Single fibres or fibre bundles are partially detached at the surface of these veins. In comparison, composite chrysotile ± lizardite veins (type B) are generally characterised by the presence of chrysotile fibre sheaves that are up to tens of millimetres in length and have random orientations. Centimetre-long soft and friable bundles of fibres are exposed and liable to detach when affected by quarry excavation (Fig. 3). Chrysotile coatings (type C) are widespread and are particularly frequent in fractured and cataclastic serpentinites. The majority of these coatings represent the exposed surfaces of slip-fibre veins after erosion, and are characterised by fibres that are oriented parallel to the wall rock. These veins contain rigid light green to whitish fibres that are present within elongate tabular and columnar sheaves.

The fact that asbestiform phases are generally located within vein networks means that a Jv (volumetric joint count) analysis, defined as the number of joints per m^3 and a measure of the number of joints within a given volume of rock, was applied to quarry faces and walls during this study. However, as fractures are filled by minerals other than asbestos, the Jv index was also complemented with the characterisation of mineral phases and subsequent modal analysis. These Jv index and fracture width analyses were also combined with petrographic analyses and the determination of geometric parameters using microscopy to correlate meso- and microscopic structural features.

MICROSCALE FIBRE ASSESMENT

The quantification of microfracture parameters is a tool that is used in several fields, such as geological engineering and the identification of the physico-chemical properties of ornamental stones (Irfan and Dearman, 1978; Sousa et al., 2005, and references therein), or in structural investigations of damage zones along regional shear zones (Wilson et al., 2003). Irfan and Dearman (1978) defined a micro-fracturing index "I_f" to describe classes of weathered rock using the number of cracks (identified using optical microscopy) within a 1 cm length of rock. In addition, Sousa et al. (2005) correlated the intensity of weathering of ornamental granite slabs with the degree of microfracturing by defining a "LCD index". This index represents the number of cracks (determined using SEM observation) along a linear unit (in mm). Integrating field and microscopic data during fracture analyses allow significant results to be obtained (e.g., Guerriero et al., 2010) and is a promising approach for the assessment of asbestos within rocks. The analyses of fractures within Ligurian serpentinites undertaken during this study use the following data: discontinuity type classification, fracture occurrence, fracture spacing (mm), vein continuity or persistence, vein width (mm), the presence and type of asbestos vein fills, and microtextural patterns. This approach transfers the "Jv" index (ISRM, 1993) from macro- to microscale observations and incorporates micro-aperture and micro-spacing observations undertaken on thin sections, thereby defining a new "μ-Jv" index as:

$$\mu Jv = 1/\mu S_1 + 1/\mu S_2 + 1/\mu S_3 + \ldots$$

where μS_1, μS_2,..., μS_i represent the average micro-spacing (in mm) for each fracture set. Fracture sets are defined as all of the joints within a given surface where the Jv index was recorded in the field.

Filling phases in the area previously analysed using the Jv index were further analysed by μ-Raman spectroscopy to identify serpentine polymorphs within different textural sites and mono- and poly-mineralic veins, and modal analyses were used to quantify the abundance of serpentine minerals in a given volume of rock. These modal analyses used a point counting approach and the selection of 1000 points over an average area of about 3 cm^2 within 8 samples taken from Jv lines along quarry faces that had previously been analysed by μ-Raman spectroscopy. Optical analyses and measurements were undertaken at 30x magnification under transmitted polarised light.

These microscopic observations revealed a linear correlation between μJv and Jv indexes for values ≤ 30, corresponding to a "very fractured rock" classification (Fig. 6), indicating that thin section analyses can be used as a tool to adequately describe rock volumes containing thicker joints. However, hand samples of rocks with Jv values > 30 (cataclastic rocks) cannot be used to adequately mirror the presence of all joints within the rock, indicating that mesoscopic analyses need to be used to adequately determine asbestos abundances.

DEVELOPING AN ANALYTICAL PROTOCOL

The multi-scale (from field observations to petrographic analyses at meso- and microscales) and multi-technique approach (optical microscopy, spectroscopy, and diffractometry) used during this study indicates that integrating field data

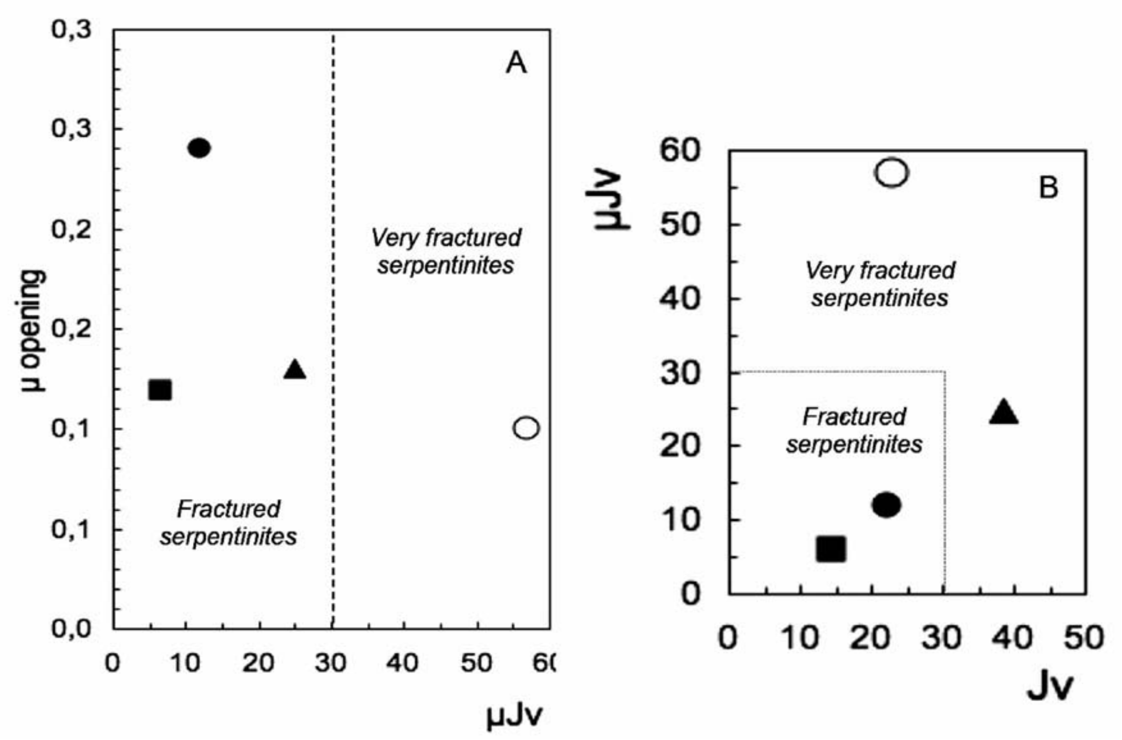

Fig. 6 - A: Aggregate data for micro-opening vs. µJv values and B: correlation between Jv and µJv values, showing a clustering of Jv and µJv values below 30. Filled circles- Arbisci quarry; squares- Levanto quarry; triangles- Santo Stefano Magra quarry; open circles- Bargonasco quarry.

with qualitative and quantitative analyses can yield a reliable estimate of the concentration and abundance of asbestos within serpentinite (as in Groppo et al., 2006; Donatio et al., 2013, this volume; Zaccagnini and Marroni, 2013, this volume).

D.M. 14/5/1996 is the reference normative in terms of evaluating the potential release of asbestos, and it stipulates the analytical procedures that should be used on synthetic materials and quarried blocks and aggregates that have already been extracted and are in use. However, the application of this normative introduces a number of major inconsistencies in terms of neglecting the environmental effects of asbestos release from natural outcrops, as follows: i) despite the final aggregate, block, or slab products having low IR values, a considerable amount of fibres may be released during processing (e.g., drilling, mining), and these fibres may enter the sediment cycle; ii) a given volume of serpentinite or metabasite does not contain 100% asbestos, but needs to be considered as a rock that contains different volumes of fibres diluted with other rock-forming minerals in associations connected with specific textural sites; and iii) the fibre host system is time-variable and natural weathering of rock surfaces or runoff over detrital stone heaps can enhance or inhibit fibre dispersion.

Our investigation integrated the following steps:

i) Field survey and characterisation according to UNI EN ISO 14689-1 (“Indagini e prove geotecniche - Identificazione e classificazione delle rocce”) as adapted for asbestos-bearing serpentinites. The direction and dip of vein families were measured over quarry faces, and were plotted on stereonets. Data on fracture frequency, width, and continuity were used to obtain mesoscale Jv index values, although further analyses of the state of the quarry faces could also be undertaken.

ii) Subsequent strategic sampling aims to obtain representative examples of vein families, as µJv values have been demonstrated to correlate with Jv values < 30. As fibrous minerals preferentially develop in fractures and veins, the fracture analyses undertaken at all of the quarries during this study were coupled with microscale mineralogical and petrographic analyses, including the description of fracture discontinuity types, spacing and width (in mm), continuity, and fibrous infill growth structures. The sampling strategy is also crucial in terms of representative analysis of unconsolidated debris. These debris piles evolve from a non-sorted detrital apron to a cover with a broadly inverse stratification formed by a combination of rainfall and gravity. Herein, fibres tend to concentrate in the pelite fraction washed at the bottom of the pile, as long as the fibre sheaves become weathered and release smaller fibres.

iii) In addition to the characterisation of in situ rocks and unconsolidated debris, vein filling phases and unconsolidated sedimentary debris were characterised using the integrated results of optical microscopy, XRPD, SEM-EDS, and µ-Raman spectroscopy on the same volume of rock or fracture material.

DISCUSSION

Serpentinites within the quarries investigated during this study are variably veined and contain abundant chrysotile (up to 20-25% of the total mineralogy of the rock) occurring in a variety of pseudomorphic and non-pseudomorphic textures. However, chrysotile fibres from massive rocks are generally not released by natural exogenous processes or quarry operations. In comparison, fibres within vein networks are liable to be released into the air, water, and soil across the entire quarry. Consequently, it is necessary to make a preliminary characterisation and quantification of the abundance of fibrous minerals within the serpentinite, as long as only a small amount of microfibrous chrysotile is associated with the serpentinite, in order to fully evaluate the hazards posed by the evolution of surfaces within the quarry. Given this, we consider lizardite-bearing, porphyroclastic, mesh- or ribbon-textured serpentinites as massive units, and releasable fibres, which represents the amount of asbestos minerals enclosed in the host rock in areas with different textures and liable to be released during natural or anthropic friction and/or comminution. The non-fibrous tremolite, actinolite, and sodic amphiboles develop few splinters or slivers with length:width ratios of > 3:1, and very few of these minerals attain the critical dimension of fibres (> 5 μm long and < 3 μm in diameter). Conversely, the milling of fibrous chrysotile increases the percentage of fibres, primarily as a function of the perfect lengthwise cleavage of these fibres. This indicates that milling, representing a size reduction of between a few millimetres to several centimetres, of lizardite-bearing serpentinite pieces releases few fibrous minerals if the material is devoid of veins with fibrous fills. Syntaxial veins contain chrysotile fibres that grew consistently with the host serpentinite and can therefore be assumed on a microscale to be a mechanically continuous material. Conversely, antitaxial and widespread composite syntaxial-antitaxial veins are characterised by marked differences between wall-rock and vein minerals, and by contrasting fibre orientations along lateral cross-sections, indicating that fibrous chrysotile within these veins is more likely to be released during mechanical disturbance. Another factor that needs to be considered is the incremental weathering of the exposed outcrops, which results in an increase in the volume of released fibres.

The modified UNI EN ISO 14689-1 ("Indagini e prove geotecniche - Identificazione e classificazione delle rocce") adapted to fractured serpentinites provides a method of measuring the geometric relationships between vein networks and the frequency of veining compared with the undisturbed rock volume. However, this approach contains significant analytical biases, including I) the fact that the approximation of the orientation of the Jv line acquired along the face of the quarry is dependent on the analyst or operator, meaning that bias may be introduced when extending modal abundances obtained in 2D from meso- to microscales to 3D rock volumes and, more importantly, II) analyses of the quarry face are operator dependent. These biases indicate that μJv values derived from microscopic and micro-structural analysis are probably a more reliable parameter for the assessment of moderately to highly fractured rocks. Vein microtextures and mineralogies were characterised and quantified at meso- and microscales.

Finally, free fibres detached from rocks or host veins are liable to enter the sedimentary cycle, hydrosphere, atmosphere, and/or biosphere. Sediments and muds derived from quarry operations that are stored after milling are highly enriched in free chrysotile fibres or fibrous bundles, and any disturbance of these fibre-rich sediments has the potential to release asbestos into the ambient air.

CONCLUSIONS

Asbestos-related environmental issues include the quantification of the natural background level of asbestos released from extensively exposed ophiolitic rocks. The determination of the origin of fibres as exogenous agents or by release associated with anthropic factors and the dispersal of fibres in neighbouring areas allows the identification and definition of a "fibre-cycle", in a similar fashion as the hydric cycle.

The massive ultramafic rocks investigated during this study are composed of fine-grained, though not fibrous, lizardite, with subordinate magnetite and chrysotile. This indicates that the general term "ophiolite", beyond the strictly defined geological and petrological terms, should also be used to indicate asbestos-bearing rocks with various levels of dilution of asbestos fibres by other rock-forming minerals.

In the rocks studied here, the blastesis of asbestiform phases occurred in a brittle deformation regime and was associated with the development of vein-filling minerals, indicating that rock fracturing is critical for the formation and concentration of asbestos. Open or filled fractures act as discontinuities and disrupt the rock body, and the earliest fracture networks are easily reactivated during late-stage cataclastic tectonic events or during quarrying. The subsequent concentration of fibres occurs by natural processes (cataclasis, detrital aprons, and pedogenesis) interacting with a veined rock body, whereas airborne fibre dispersion is caused by both natural and anthropic agents.

Fibres are unlikely to form from non fibrous mineral or mineral-bearing rock bodies (McCrone, 1987), and the crushing (i.e., quarry operations) of a massive serpentinite body to form aggregates produces only rare fibre-shaped and -sized particles, and the production of milled powder tends to dilute the initial amount of asbestos fibres within the rock. An effective evaluation of the asbestos risk before quarry authorisation should overcome the issues inherent within the analytical protocols of the Italian D.M. 14.05.1996; this evaluation should include a systematic geological, mineralogical, and petrological study, consisting of: a) geological field observations; b) definition of a sampling strategy; c) characterisation of outcrops by mineralogical, petrological, and geotechnical analyses; d) quantitative determination of the abundance of asbestos in bulk samples; and e) estimation of the amount of airborne asbestos as well the asbestos in sediments and crushing muds. Although restricted to selected areas worldwide, appropriate integration of data derived from quantitative field surveys and laboratory investigations is an effective tool that can be used to comprehensively assess the potential environmental impact and the likelihood of both quarrying-derived and natural asbestos release.

ACKNOWLEDGMENTS

This work was carried out within the PRATT 2012 University of Genoa and LIFE+ 2012 FIBERS frameworks awarded to Laura Gaggero. The authors are indebted to Laura Negretti and Antonio Cucchiara (UNIGE) for SEM-EDS and XRPD analyses. Chiara Groppo (Turin University) kindly assisted Evelina Isola during the acquisition of μ-Raman spectra, and constructive suggestions of Michele Marroni (Pisa University) are warmly acknowledged.

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Received, April 3, 2013
Accepted, June 2, 2013