



Detecting asbestos fibres and cleavage fragments produced after mechanical tests on ophiolite rocks: clues for the asbestos hazard evaluation

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ABSTRACT - The generation of particulate matter emitted by management (e.g., mining, crushing, grinding, and milling) of ophiolite rock masses induces environmental impact due to production and dispersion of fibrous particles, which can be potentially classifiable as asbestos. Accordingly, characteristics of particles generated after mechanical stress on rocks are preparatory features to evaluate the environmental impact due to the asbestos hazard. This study deals with the characteristics (in terms of size, morphology and mineral classification) of particles generated after application of three different mechanical stress procedures (i.e. crushing, micronizing, and abrasion) on five ophiolite lithotypes and a man-made material obtained from rock mixing. A petrographic investigation has been addressed to classify the rock samples in terms of their internal fabric (foliated vs massive) and to individuate textural locus of fibrous minerals within the rock mass. The application of mechanical tests reveal that all the investigated lithotypes resulted able to spread out fibres as a consequence of rock disaggregation, with a prevalent amount of liberated fibres coming from samples characterised by pervasive foliation. The combined use of transmission electron microscopy and particle size analyser has been addressed to analyse morphological properties of the particulate matter. Different counting criteria have been used to distinguish asbestos fibres and non-asbestos particles (cleavage fragments). The results show that the counting criteria adopted for the fibre classification led to divergent interpretations in differentiating asbestos fibres and cleavage fragments and to determine the amount of asbestos. It derives the importance to define univocal criteria to define particle as asbestos for supporting procedures and normatives addressed to evaluate the asbestos hazard in environmental sites.

Keywords: Asbestos; cleavage fragment; fibrous particle; rock mechanical test; counting criteria; ophiolite.

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1. INTRODUCTION

Asbestos is a generic term applied to a group of six silicate minerals belonging to the serpentine (chrysotile) and amphibole (riebeckite (crocidolite); grunerite (grunerite asbestos); anthophyllite (anthophyllite asbestos); tremolite (tremolite asbestos); and actinolite (actinolite asbestos) groups, which have crystallised in the asbestos habit (e.g., World Health Organization-WHO, 1997; Gunter et al., 2007). Notably, in addition to the six regulated asbestos minerals, about 400 minerals are known to occur, at least occasionally, with fibrous morphology (e.g., Compagnoni et al., 1985; Skinner et al., 1988; Gianfagna et al., 2003; Belluso et al., 2017).

During the 20th century, due to its peculiar thermo-mechanical characteristics (high tensile strength, flexibility, low thermal and electrical conductivity, high heat resistance and high mechanical and chemical durability), asbestos has been mined worldwide and

largely exported for international commerce (e.g., Ross and Nolan, 2003; Kazan-Allen, 2005 for a review). Asbestos mining and uses continue in many countries (e.g., USGS, 2008; Strohmeier et al., 2010), although an increasing number of epidemiological studies arises the relations between asbestos exposure and related diseases. In this regard, three principal diseases are linked to asbestos inhalation: (1) asbestosis, a non-malignant diffuse interstitial fibrosis of the lung tissue; (2) lung cancers, a bronchogenic carcinomas; (3) mesothelioma, a cancer which develops mainly in the pleura (outer lining of the lungs and internal chest wall), but it may also occur in the pericardium and peritoneum (the lining of heart and abdominal cavities, respectively) (Doll, 1955; U.S. National Research Council, 1985; Wagner, 1991; Berry and Gibbs, 2008). Accordingly, asbestos is listed as Group 1, i.e. human carcinogenic, material (IARC, 2011).

It is documented the presence of naturally occurring asbestos (NOA) as accessory mineral in ophiolite

sequences exposed in orogenic domains (Ross and Nolan, 2003; Van Gosen, 2007; Hendrickx, 2009; Vignaroli et al., 2011). The ophiolites, which represents remnants of paleo-oceanic lithosphere consisting of mafic (pillow basalts and gabbros), and ultramafic (serpentinites and basal peridotites) rocks that experienced complex tectonic and metamorphic stages during the geological events, are of economic importance since their extensive use for industrial, engineering and building activities (Marinos et al., 2006; Pereira et al., 2007). Therefore, the handling of this rock type is subjected to predictive assessment of the asbestos content for mitigating and reducing the potential environmental hazard (Rohl et al., 1977; Pacella et al., 2008; Giacomini et al., 2010; Bloise et al., 2012; 2017; Lescano et al., 2013; Vignaroli et al., 2013, 2014; Wylie and Candela, 2015). Indeed, the asbestos hazard occurs whenever both weathering processes (erosion and mobilisation) and human activity (e.g., related to the abrasion industry) can separate fibres and break them down to fibrils of sub-microscopic dimensions widely dispersed in the environment and easily respirable.

Anyway, it must be pointed out that non-asbestos minerals (amphiboles of serpentines) are more common than asbestos and can be found in many geological environments. In addition, non-asbestos crystals can break, during crushing or grinding, along preferred cleavage planes leading to splinter-like cleavage that may be mistaken for asbestos fibres. Therefore, any exploiting of rock and mineral deposits hosting non-asbestos particles may result in an exposure to airborne particles with morphology resembling asbestos. Notably, the classification of a particle as either a real asbestos mineral or a cleavage fragment (non-asbestos) has a key role in assessing a reliable asbestos hazard scenario. Furthermore, there is no epidemiological evidence of demonstrable cancer effects from exposure to cleavage particle fragments (Ilgren, 2004; Gamble and Gibbs, 2008; Williams et al., 2013), and the health effects of fibres of all lengths are still the matter of debate (e.g., Dodson et al., 2003).

The evaluation of the asbestos hazard is based on counting criteria (see the protocol in Yamate et al., 1984) used to determine the amount of “regulated fibres”, i.e. those particles having an aspect ratio (A.R., length of the particle divided by its width) greater than 3:1, a minimum length of 5 μm , and a diameter $<3\mu\text{m}$ (WHO, 1997). Nevertheless, different procedures complementing or overcoming the A.R. criterion have been proposed for refining the classification of particles as asbestos or fibres originated by preferential cleavage of particles (Wylie et al., 1985; AHERA, 1987; OSHA, 1994a, 1994b; Harper et al., 2008, 2012; Van Orden et al., 2008; National Institute for Occupational Safety and Health-NIOSH, 2011; Tab. 1). The AHERA method (Asbestos Hazardous Emergency Response Act, 1987) suggests considering a 5:1 as the minimum aspect ratio. Stanton et al. (1981) correlated the asbestos hazard to the occurrence of asbestos particles having size $>8\mu\text{m}$ in length and $<0.25\mu\text{m}$ in diameter.

Berman and Crump (2003) proposed a hazard scenario by considering particles longer than 10 μm and thinner than 0.4 μm (A.R.>25:1) (see also Berman and Crump, 2008). The method introduced by Harper et al. (2008) is based on microscopic measurements and considers all particles having width below 1 μm . Chatfield (2008) reported a procedure based on the combination of the width and the aspect ratio of particles, classifying as asbestos all particles thinner than 1.5 μm and having A.R. exceeding 20:1. Finally, Van Orden et al. (2008, 2009) proposed a multidisciplinary procedure to differentiate amphibole asbestos from non-asbestos by integrating chemical and morphological features at the scale of transmission electron microscopy (TEM).

In two previous distinct works, we faced the generation and emission of particulate matter from stone crusher industry (Belardi et al., 2013) and we qualitatively assessed the in-situ asbestos hazards in natural settings (Vignaroli et al., 2014). Anyway, how to evaluate the asbestos hazard from particulate matter emitted by industrial management of rock volumes? Our aim is to answer this question by combining minero-petrography observations, engineering mechanical tests, and morphological analyses of particles on five ophiolite lithotypes and on a man-made material obtained from rock mixing. We propose a procedure for classifying particles in terms of asbestos and non-asbestos (cleavage fragments). We show that the application of the commonly used counting criteria procedures for asbestos identification can not be exclusively based on particle dimensional characteristics (i.e. length, width, aspect ratio). We will indeed demonstrate that the asbestos identification in dust generated after mechanical stresses requires a multidisciplinary, multiscale approach, which reduces possible ambiguities in the asbestos hazard

Procedure/reference	Single particle
AHERA method (1987)	aspect ratio $\geq 5:1$
Stanton et al. (1981)	length $> 8\mu\text{m}$; diameter $<0.25\mu\text{m}$
Berman and Crump (2003)	length $>10\mu\text{m}$; diameter $< 0.4\mu\text{m}$; aspect ratio $> 25:1$
Harper et al. (2008)	diameter $< 1\mu\text{m}$
Chatfield (2008)	diameter $< 1.5\mu\text{m}$; aspect ratio $> 20:1$
Van Orden et al. (2008; 2009)	aspect ratio $> 5:1$; parallel sides; perpendicular ends; uniform diffraction contours; twinning; selected area electron diffraction (SAED) pattern: $75^\circ \leq \text{angle} \leq 90^\circ$

Tab. 1 - Counting criteria adopted for procedures on asbestos risk assessment and asbestos identification.

evaluation for environmental management of natural materials during engineering works.

2. TERMINOLOGY

Here, we report a list of definitions we attribute to some terms used in this paper, after terminology re-examination from standards and research works (e.g., AHERA, 1987; Langer et al., 1991; OSHA, 1994a; WHO, 1997; ISO-13794, 1999; Dorling and Zussman, 1987; Ilgren, 2004; Strohmeier et al., 2010; ASTM D7712-11, 2011).

Acicular is defined as a mineral habit characterised by sectional dimensions that are small relative to its length, i.e. needle-like. “The term is applied in mineralogy to straight, greatly elongated, free-standing (individual) crystals that may be bounded laterally and terminated by crystal faces. The aspect ratio of acicular crystals is in the same range as those of ‘fibre’ and ‘fibrous’, but the thickness may extend to 7 mm” (Strohmeier et al., 2010).

Asbestiform is defined as a special type of fibrous morphology, typical of asbestos, in which the fibres are separable into thinner fibres and ultimately into fibrils.

Asbestos is a term applied to six specific silicate minerals belonging to the serpentine (chrysotile) and amphibole (riebeckite (crocidolite); grunerite (grunerite asbestos); anthophyllite (anthophyllite asbestos); tremolite (tremolite asbestos); and actinolite (actinolite asbestos)) groups, which have crystallised in the asbestiform habit, causing them to be easily separated into long, thin, flexible, strong fibres when crushed or processed.

Asbestos fibre is defined as the asbestiform mineral achieving its high aspect ratio by unidirectional growth, without showing evidence for cleavage.

Cleavage fragment is defined as a particle produced by fracture along the planar surfaces dictated by the crystallographic structure of the mineral. Cleavage fragment, normally formed by comminution of minerals, is often characterised by parallel sides and a moderate aspect ratio. “Cleavage fragments do not exhibit fibrillar bundling at any level of examination” (ASTM D7712-11, 2011).

Fibre is defined as an elongate particle that is longer than 5.0 μm , with a minimum aspect ratio (length of the particle divided by its width) of 3:1, and showing parallel or stepped sides developed during growth. “Fibre dimensions may range from approximately 1 mm to the nanometre range” (Strohmeier et al., 2010).

Fibril is defined as a single fibre that cannot be further separated longitudinally into smaller components without losing its fibrous properties or appearances.

Fibrous is defined as a morphology that exhibits parallel, radiating, or matted aggregates of fibres.

Mineral habit is defined as the shape or the form that a mineral assumes during its crystallisation, including characteristic crystal growth and irregularities.

Prismatic is defined as a mineral habit characterised by elongate, prism-like predominant crystal faces parallel

to the growth axis. Prismatic particles often exhibit “aspect ratios usually below 3:1 and grading into equant (aspect ratio = 1), … a well-defined corner or edge and a crystalline termination” (Strohmeier et al., 2010).

3. MATERIALS AND METHODOLOGY

3.1. Materials

We selected five rock types (serpentinite, basalt, marble, gabbro and metagabbro) belonging to the ophiolite suites cropping out along the mountain belts of the Western Alps, the Ligurian Alps, and the Northern Apennines (Northern Italy) (Fig. 1). These lithotypes were chosen because they have been extensively processed by the stone crushing industry for the production of railway ballast and roadbed, and involved in engineering works (such as tunnelling), as like as they can be used as ornamental stones. In addition, a man-made material (sample RIC), obtained by mixing fragments of talc-schist and metagabbro in equivalent amounts, has been made for simulating man-made material designated to waste after rock management. The main meso-scale and micro-scale minero-petrographic characteristics of each investigated lithotypes are presented below and summarised in table 2, focused to textural locus of fine grain minerals (possible source of fibrous particles) within the rock mass (to compare with Belardi et al., 2013).

Serpentinite. Sample AN is characterised by a dominant dark green rock mass locally showing very thin (few millimetres in width) whitish layers (Fig. 1). The meso-structure is defined by a main schistosity, which is pervasive throughout the rock mass. The schistosity is defined by sub-mm-thick plano-parallel foliation. At the thin section scale, the schistosity mainly consists of growing of serpentine (both antigorite and chrysotile) and chlorite, wrapping around relicts of the pristine magmatic mineralogical association, such as olivine, pyroxene, and plagioclase (Fig. 2a). Serpentine crystals marking the schistosity show an elongated (acicular-to-fibrous) morphological habitus (Fig. 2b). Very thin (few micrometres) amphibole crystals (tremolite) occur within post-schistosity micro-veins, corresponding to the whitish layers evidenced at the meso-scale.

Basalt. Sample AQ is characterised by a dark grey colour, homogeneously diffused in the rock mass (Fig. 1). The meso-structure is dominantly massive; the grain size is slightly homogeneous and not visible at naked eye. Millimetre-thick layers, grey in colour, locally cut through the meso-structure. At the thin section scale, the grain size spans from very fine to fine (0.020-0.300 mm). The micro-structure mainly consists of interstitial overgrowth of plagioclase laths, often dissected by a set of prehnite-filled micro-veins, the latter corresponding to the grey layers detected at the meso-scale (Fig. 2c). Very thin grain of both amphibole (actinolite) and chlorite are dispersed within interstices between plagioclase and pyroxene grains. Fibrous amphibole develops from the massive groundmass (Fig. 2d).

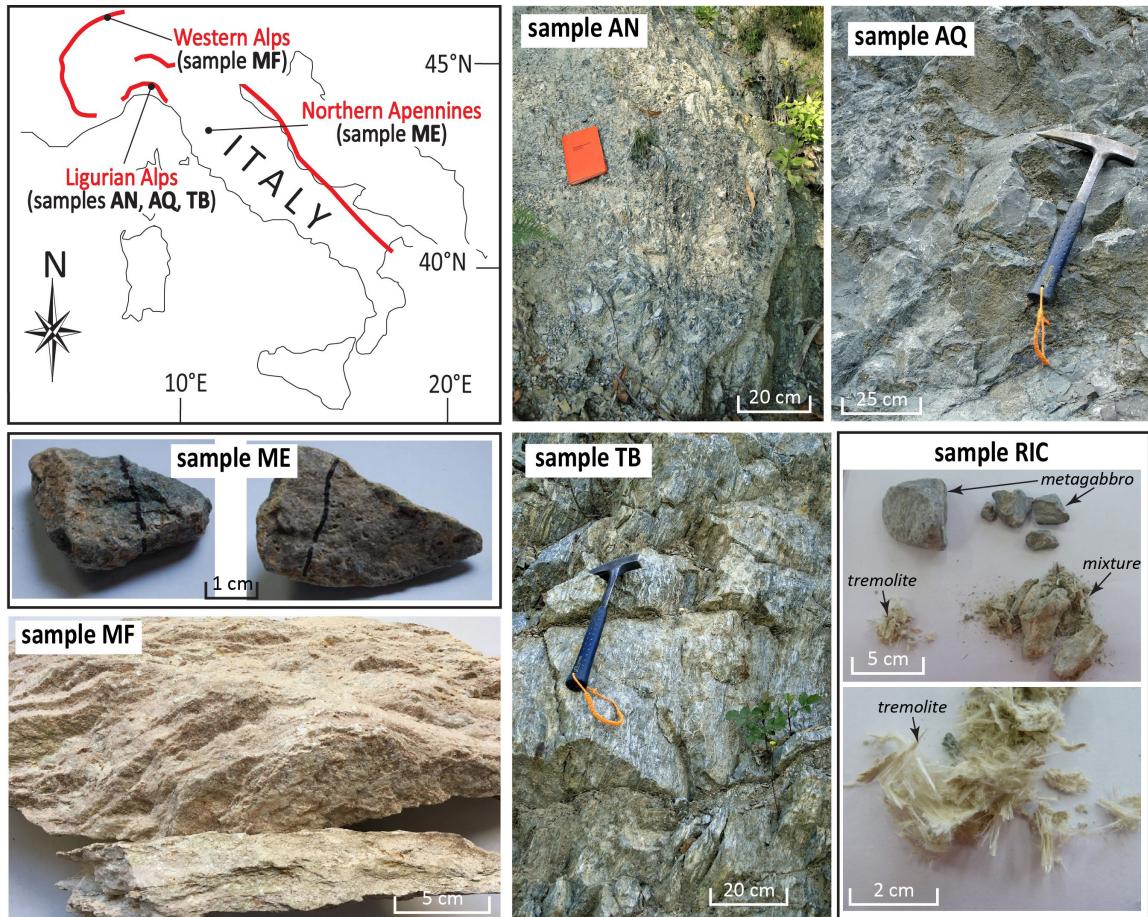


Fig. 1 - Meso-scale features of the selected rock samples. See the insert above for indicative location. Sample MF belongs to an ophiolitic sequence of the Lepontine Alps (Western Alps) and it has been collected in an outcrop located few kilometres north to Como. Samples AN and TB belong to an ophiolitic sequence named Voltri Massif, cropping out in the eastern part of the Ligurian Alps. Samples has been collected in a quarry area located northeast to Genoa. Sample AQ belong to an ophiolitic suite of the Northern Apennines and it has been collected in a quarry area located east to Sestri Levante. Sample ME belongs to an ophiolitic suite of the Northern Apennines and it has been collected in a quarry area north to Grosseto.

Gabbro. Sample ME is characterised by a dark green colour with whitish, millimetre-thick, layers (Fig. 1). The meso-structure is massive, with crystals clearly visible at naked eye. At the thin section scale, the structure mainly consists of large grains of clinopyroxene, euhedral plagioclase, and feldspar. The grain size is medium-to-coarse (0.100-2 mm) (Fig. 2e). The largest feldspar grains show diffuse alteration by the mean of clay minerals. Moreover, pyroxene grains are often rimmed by fine-grains of chlorite and green amphibole (hornblende), the latter showing prismatic morphological habitus. Amphibole is also a constituent, together with chlorite and Na-plagioclase, of micro-veins cutting through the pristine magmatic assemblage (Fig. 2f).

Marble. Sample MF is characterised by a white-to-beige colour, homogeneously distributed throughout the rock mass (Fig. 1). The meso-structure is characterised by the occurrence of a pervasive schistosity, the latter showing slightly undulated foliations around elongated crystals. At the thin section scale, the composite micro-structure consists of a sub-millimetre-thick schistosity wrapping around coarse (up to 2 mm) calcite crystals

(Fig. 2g). Schistosity surfaces are marked by alignment of white mica and green amphibole crystals. Amphibole (tremolite) grows also in flakes, with radial disposition and showing a prismatic-to-acicular morphological habitus (Fig. 2h).

Metagabbro. Sample TB shows a composite meso-structure including massive domains (greenish in colour) and weakly foliated domains (Fig. 1). The latter consists of cm-thick alternation of green-to-bluish levels and white levels. At the thin section scale, the massive domains consist of equigranular assemblage of clinopyroxene and plagioclase crystals, both of them showing a tabular morphological habitus and fine-to-medium grain size (0.020-0.100 mm) (Fig. 2i). The foliated domains, conversely, mainly consist of development of pervasive mm-thick schistosity, which is marked by alignment of thin green amphibole (actinolite-to-hornblende) in association with albite, epidote, chlorite and pumpellyite. Amphibole growing along the schistosity shows a prismatic-to-acicular morphological habitus. Very thin amphibole crystals (actinolite), having fibrous morphological habitus, occur within plagioclase-filled

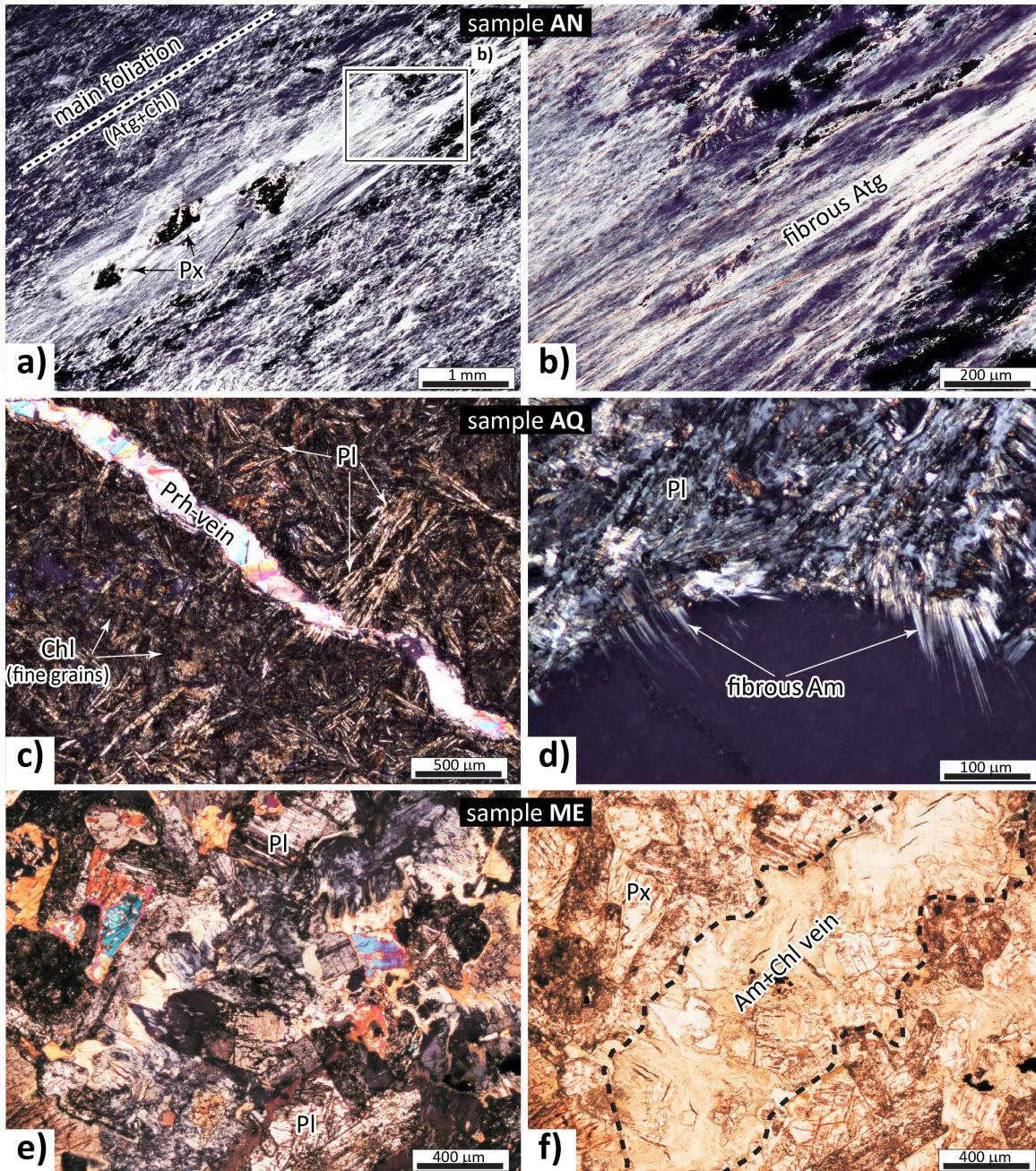


Fig. 2 - Petrographic characteristics of the selected rock samples at the thin section scale (see text for details). a-o) cross nicols; p) scanning electron microprobe image (FEI Quanta 400 MK2 model with operative conditions of 15 kV and point-beam 1-5 μm in size).

veins that cut across the schistosity (Fig. 2l).

RIC. The sample is a mixture of metagabbro fragments (equivalent to sample TB) and fragments of talc-schist, the latter containing tremolite (Fig. 1). At the thin section scale, talc-schist is characterised by a pervasive, sub-millimetre-thick foliation consisting of very thin aggregates of talc, green amphibole, and subordinate chlorite+oxides (Fig. 2m). Tremolite is mostly concentrated in high strained domains of the fabric (i.e. mylonitic shear zones). At the scale of the scanning electron microprobe (SEM), tremolite appears as fibrous agglomerates where individual fibres (having length up to 200 micrometres and width up to 10 micrometres) show cleavage and formation of separable

fibrils, the latter having length up to 200 micrometres and width of few micrometres (Fig. 2n).

3.2. Mechanical tests

Three types of mechanical stress were applied to the investigated samples, i.e. crushing, abrasion (autogenous) mill, and micronizing procedures, in order to simulate the particulate emissions by abrasion industrial activities (such as crushing, grinding, size separation, tunnelling, quarrying, etc.). Notably, in spite of these tests can only roughly simulate the generation and the release mechanisms of particles, they provide a benchmark of the mechanical stresses to which the materials are subject

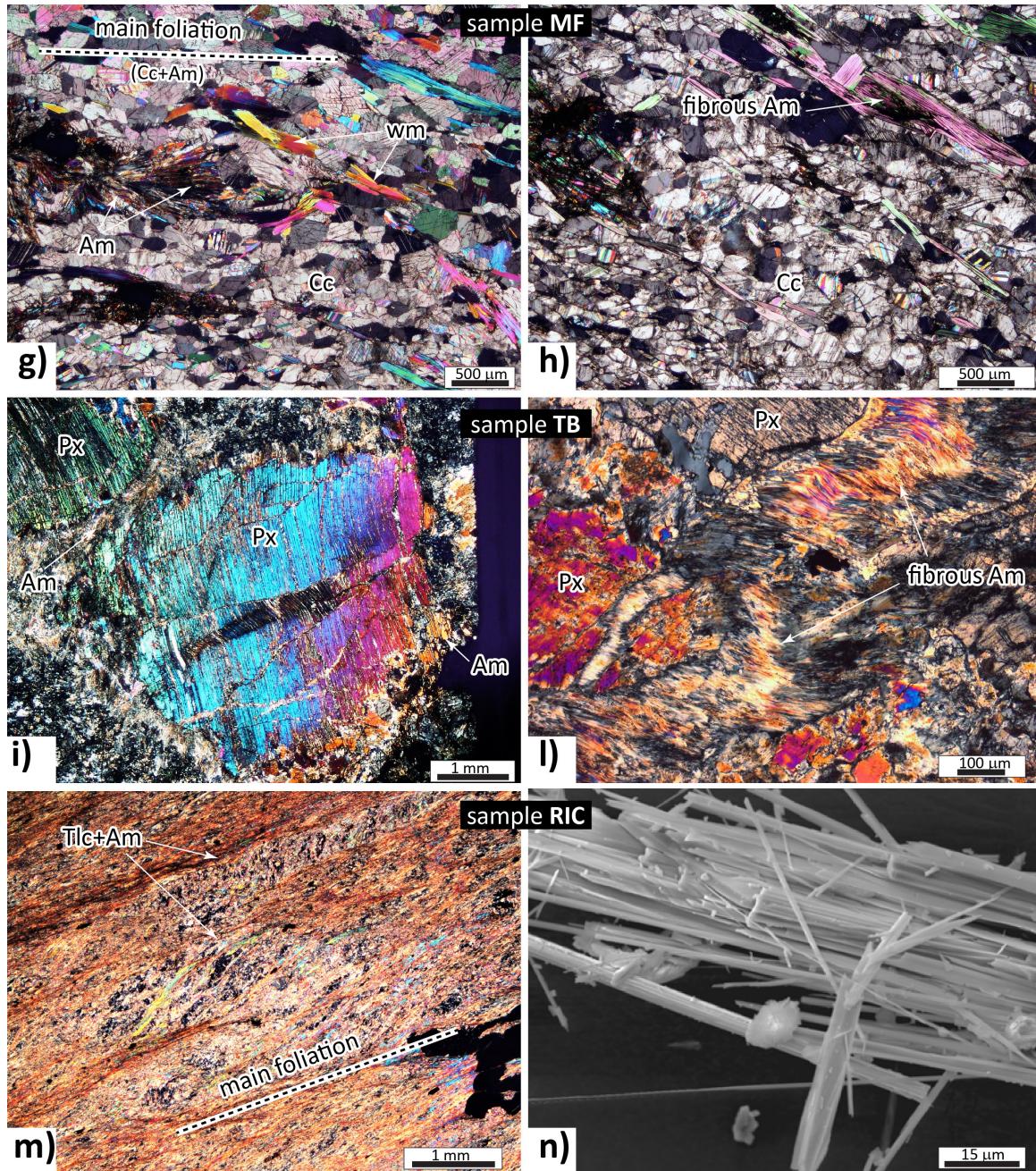


Fig. 2 - ...Continued

during industrial activities. All selected samples were subjected to the crushing test, which represents a recurrent and important industrial activity in environmental engineering. The micronizing test was applied to those samples pertaining to two distinct petrographic classes: sample having dominant foliated fabric with fibre accumulation along the foliation (sample AN) and samples having a heterogeneous fabric composed of both foliation and granular mineral association with fibre accumulation in specific microtextures (sample TB and sample RIC). Due to its peculiar petrographic properties, sample TB underwent to abrasion test in order to compare the obtained results with those of the other mechanical tests.

3.2.1. Crushing procedure

Crushing tests were carried out by a jaw crusher model Retsch BB200. In this test, the production of fine particles mainly derives from the chipping process, i.e. from rock fragmentation attaining at confined high pressure during grain-jaw and grain-grain hurts (Liu et al., 2002). The size of each sample ranged between 30 and 70 mm, which is the typical size of rock used for railroad ballast or base material for road building. A closed-side setting of 10 mm was adopted for all reduction tests. A feed rate of about 50 kg h⁻¹ was used for closed-side setting. The tests were carried out in closed circuit (Fig. 3) in order to ensure the size distribution of the product under 10 mm. The fraction over 0.250 mm was observed under optical

microscope to verify the occurrence of asbestos particles, whereas the size fraction under 0.250 mm was used for the chemical characterisation of amphibole particles released from the materials. Notably, the size fraction under 0.250 mm (bulk material) is representative, in terms of chemical composition and morphology (aspect ratio), of the airborne particles collected in the environment (Tuula and Antii, 1997; Belardi et al., 2013). Accordingly, it has been suggested that the fibrosity in bulk samples has correlation with the number and mass of respirable particles (Virta et al., 1983; Chatfield, 2008).

The adopted procedure differs from those proposed

by Harper et al. (2008) and Van Orden et al. (2012) for the reduced cutting size in order to avoid overgrinding. Moreover, none of the samples were ultrasonicated.

3.2.2. Micronizing procedure

In this procedure (Fig. 4), the samples are milled under a nominal size ranging from 30 and 70 mm. The sample preparation was designed to avoid overgrinding of the minerals, inasmuch the grinding process is repeated in successive stages, removing the smallest particles at the end of each grinding stage. This procedure should minimise the effects of grinding that may affect the

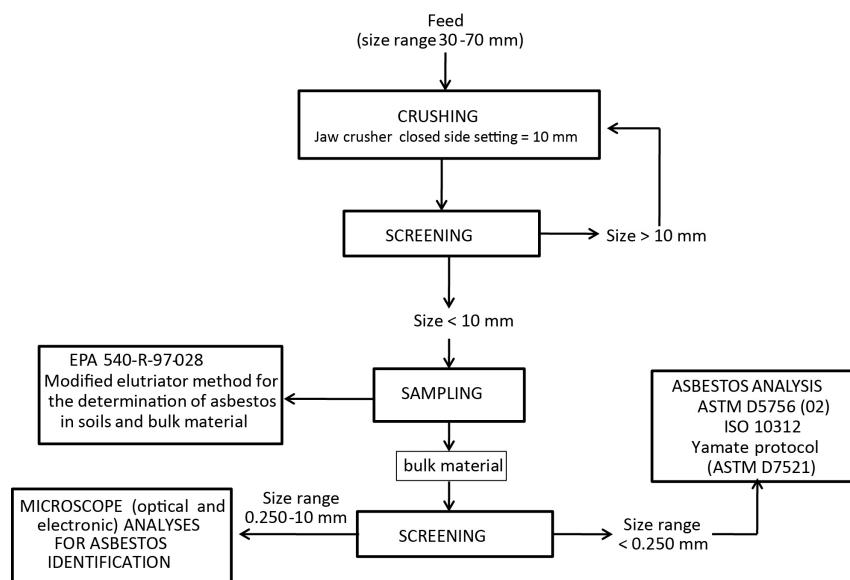


Fig. 3 - Flowchart of the crushing procedure.

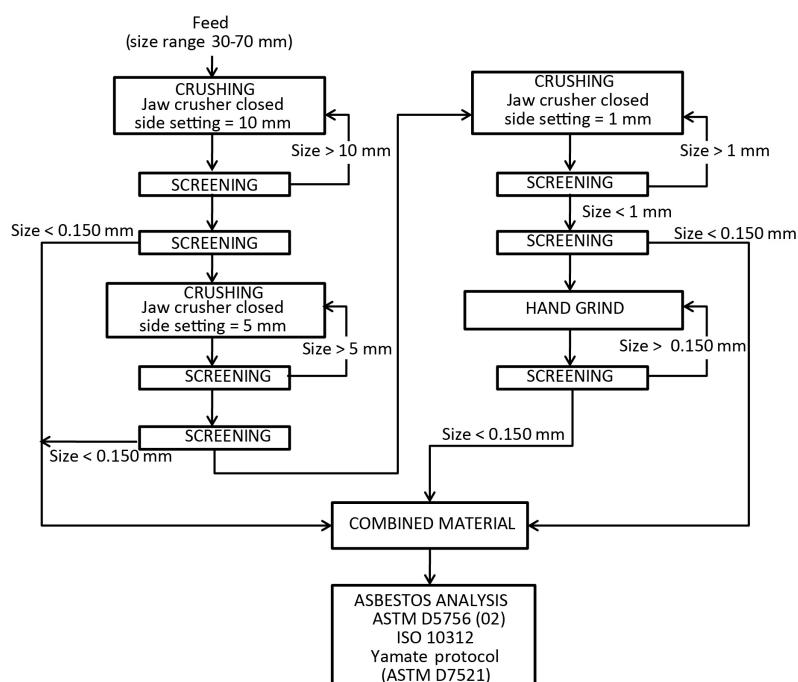


Fig. 4 - Flowchart of the micronizing procedure.

morphologies of the asbestos particles (e.g., Harper et al., 2008; Van Orden et al., 2012). The choice to analyse the micronized size fraction under 150 μm is based on the fracture mechanics (Austin et al., 1984).

3.2.3. Abrasion (autogenous) mill procedure

In this procedure (Fig. 5), the samples were put in a cylindrical steel mill, having an internal diameter of 300 mm and an axial length of 300 mm without shell lifters. Further operative conditions are: fractional test mill of about 1%, top mill load particle size of 30-70 mm, rotation speed of about 80% of critical speed, test time of 4h. The optimal operating condition is fully cascading to ensure a charge motion (Belardi et al., 2008). The production of fine particles mainly derives from the chipping and abrasion processes on the materials. The size distribution of the material produced is in general bimodal and the analyses were carried out on the smallest fraction (<0.250 mm).

3.3. Sample morphological investigation

The analyses were carried out with a Jeol 1200 and a Jeol 2000 TEM equipped with Energy-dispersive X-ray (EDX) system (EDAX Genesis microanalyser). Experimental conditions were as follow: acceleration voltage 120 kV, magnification 10-20 kX, grid opening area 910 μm^2 , grid opening 10 and 25. The 10 grid openings analyses were focused on particle with length >0.5 μm . While the 25 grid opening analyses were focused on the larger sizes (length >5.0 μm). The total area analysed (i.e. the multiplication of the grid opening area and the number of grid openings analysed) is in 0.30-0.35 mm^2 range.

Samples were prepared by suspending a small portion of each powdered samples in a beaker containing deionized water. Each suspension was settled for 1 min and an aliquot of the supernatant was withdrawn and filtered using a polycarbonate filter (porosity of 0.4 μm). For each sample, the weight of the material used was in the 150-200 mg range, placed on an effective filter area of 385 mm^2 with a dilution factor of about 0.0001. Filters

were prepared and analysed for asbestos identification following sample collection proposed by ASTM D5756-02 (2008) and in accordance with Level III of the Yamate et al. (1984) protocol.

The morphological parameters (i.e. length, width, shape, cleavage) of single fibres were extrapolated through image analysis of particles resting on filters using a stepwise TEM examination. The results for each sample and test were plotted in an aspect ratio vs. width diagram, according to the different methods for risk assessment (Stanton et al., 1981; Berman and Crump, 2003) and for asbestos identification (Chatfield, 2008; Harper et al., 2008; Figs. 6-9). In addition, the procedure of Van Orden et al. (2008) to discriminate asbestos from non-asbestos particles was adopted. In particular, differentiation between amphibole asbestos and non-asbestos was carried out by using EDX analysis, selected area electron diffraction (SAED) patterns and some physical-chemical characteristics such as phase alterations, crystal defects and surface chemical alterations.

4. RESULTS

4.1. Results from crushing test

Results showed that all particles coming from crushing of gabbro (sample ME, 3 total particles), metagabbro (sample TB, 43 total particles), basalt (sample AQ, 31 total particles), and marble (sample MF, 10 total particles) have width and A.R. falling in the range 0.1-2.50 μm and 5:1-30:1, respectively (Fig. 6). The only exception is represented by two particles belonging to metagabbro and basalt both having aspect ratio of about 65:1 and average width of 0.2 μm .

For the gabbro sample (sample ME), all particles would be identified as asbestos fibres following the criterion of Harper et al. (2008). In addition, about 67% of the particles are within the Chatfield (2008) and Berman and Crump (2003) "asbestos field". However, both the Stanton et al. (1981) hypothesis and the Van Order et al. (2008) procedure ruled out the occurrence of asbestos within

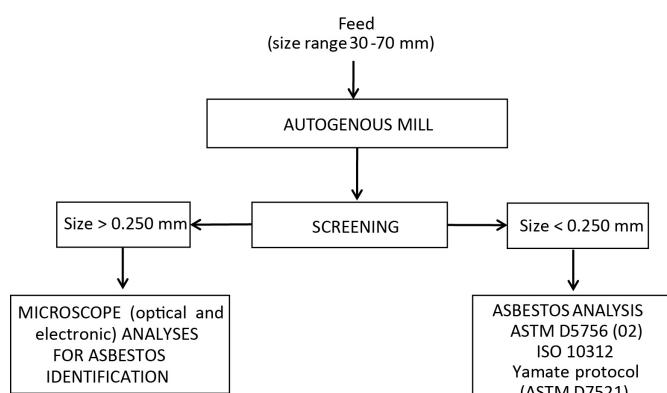


Fig. 5 - Flowchart of the abrasion mill procedure.

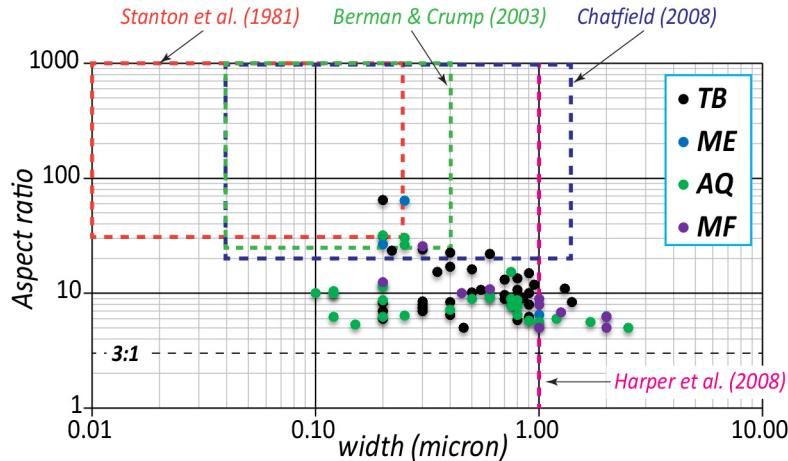


Fig. 6 - Aspect ratio vs width diagram for the analysed particles generated by crushing test belonging to: metagabbro (TB), gabbro (ME), basalt (AQ), and marble (MF) samples. Dotted boxes and dotted lines defines fields and criteria for risk assessment (Stanton et al., 1981; Berman and Crump, 2003) or asbestos identification (Chatfield, 2008; Harper et al., 2008).

this sample.

For the metagabbro sample (sample TB), about 84% of the total particles have width below 1 μm and therefore would be identified as asbestos fibres following the criterion of Harper et al. (2008). However, only 14% and 5% of the metagabbro particles are within the Chatfield (2008) and Berman and Crump (2003) "asbestos field", respectively. Only one particle having width of 0.2 μm and aspect ratio of about 65:1 falls within the box delimiting the "asbestos field" by the Stanton et al. (1981) hypothesis. Finally, the Van Order et al. (2008) procedure ruled out the occurrence of asbestos within this sample.

For the basalt sample (sample AQ), about 80% of the total particles fits with the asbestos criterion of Harper et al. (2008). This result markedly differs with that obtained using the criteria of Chatfield (2008) and Berman and Crump (2003), being only 10% of the particles falling within the "asbestos field" identified by both methods. Only one particle having width of 0.2 μm and aspect ratio of about 35:1 falls within the box delimiting the "asbestos field" by the Stanton et al. (1981) hypothesis. Finally, the Van Order et al. (2008) procedure ruled out the occurrence of asbestos within this sample.

For the marble sample (sample MF), about 88% of the total particles fits with the asbestos criterion of Harper et al. (2008). Moreover, a significant lower proportion of particles (corresponding to about 10% of the total particles) matches with the "asbestos field" following the procedures of Chatfield (2008) and Berman and Crump (2003). Notably, the analysed particles from this sample do not encounter morphological criteria for asbestos when considering either the Stanton et al. (1981) hypothesis or the procedure of Van Orden et al. (2008).

For the serpentinite sample (sample AN), particles (total number of 71) mostly have width ranging from 0.02 μm to 0.5 μm (Fig. 7), which is one order of magnitude thinner than width of particles generated by the other samples. Moreover, particle aspect ratio spans from about 5:1 to about 170:1, with an average value of 34:1, three

times higher than aspect ratio for particles obtained from crushing of the other samples (about 10:1). Notably, it was shown that the average aspect ratio of particles classified as asbestos is larger than that observed for particles classified as cleavage fragments (Harper et al., 2008; Van Orden et al., 2008). Accordingly, the Van Orden et al. (2008) procedure shows that about 94% of the produced particles is identified as asbestos (Fig. 7). In particular, all identified fibres showed a chrysotile chemical composition, except one fibre of tremolite composition. Interestingly, same results were obtained if we use the definition of asbestos of Harper et al. (2008), being 99% of the total particles characterised by widths below 1 μm . On the contrary, about 50% of the particles falls within the "asbestos field" of both classifications proposed by Chatfield (2008) and Berman and Crump (2003).

Crushing test on sample RIC (Fig. 8) produced particles (total number of 28) having width spanning from 0.3 μm to 2.0 μm , and aspect ratio spanning from 5:1 to about 180:1. Results showed that 60% of them would be classified as asbestos using the method of Harper et al. (2008). However, only 18% and 7% of the investigated particles fall within the Chatfield (2008) and Berman and Crump (2003) "asbestos field", respectively. In addition, only about 4% is within the "asbestos field" proposed by the Stanton et al. (1981) procedure. For this sample, the proportion of particles classified as asbestos fibres following the procedure of Van Orden et al. (2008) is 11% (Fig. 8).

4.2. Results from micronizing test

Micronizing test performed on metagabbro sample (sample TB) produced particles (total number of 58) with aspect ratio values ranging from 4:1 to 50:1 (Fig. 9). In addition, about 90% of the generated particles fit the asbestos criterion of Harper et al. (2008). However, only 2% of the total particles are within the "asbestos field" following the Chatfield (2008), Berman and Crump (2003), and Stanton et al. (1981) procedures. Notably,

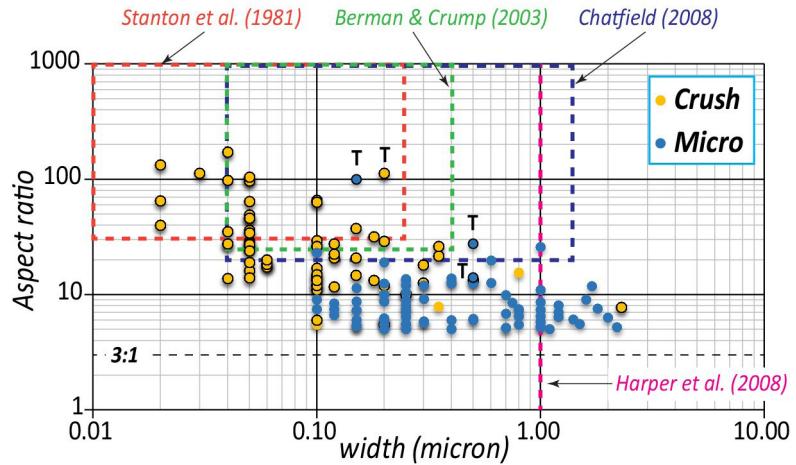


Fig. 7 - Aspect ratio vs width diagram for the analysed particles generated by different mechanical stresses (micronizing and crushing) applied to the serpentinite sample (sample AN). Dotted boxes and dotted lines defines fields and criteria for risk assessment (Stanton et al., 1981; Berman and Crump, 2003) or asbestos identification (Chatfield, 2008; Harper et al., 2008). Symbols with the black border indicate the particles classified as asbestos following the procedure of Van Orden et al. (2008). T: tremolite asbestos, whereas the remaining asbestos particles are chrysotile.

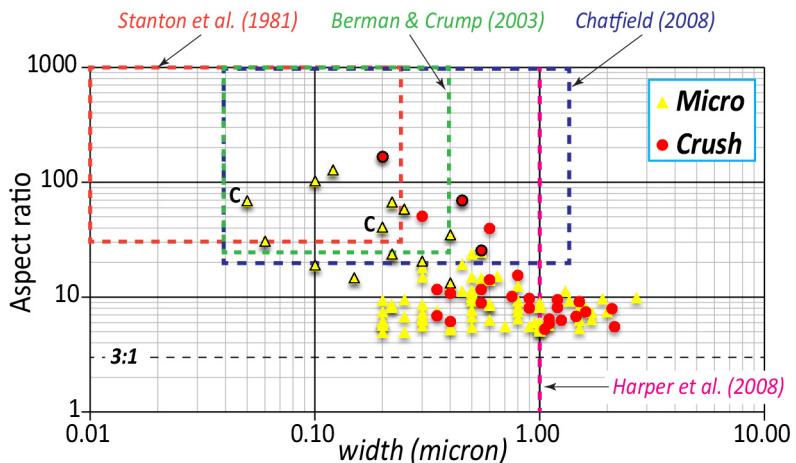


Fig. 8 - Aspect ratio vs width diagram for the analysed particles generated by different mechanical stresses (micronizing and crushing) applied to RIC sample. Dotted boxes and dotted lines defines fields and criteria for risk assessment (Stanton et al., 1981; Berman and Crump, 2003) or asbestos identification (Chatfield, 2008; Harper et al., 2008). Symbols with the black border indicate the particles classified as asbestos following the procedure of Van Orden et al. (2008). C: chrysotile, whereas the remaining asbestos particles are tremolite asbestos.

only the Van Order et al. (2008) procedure ruled out the occurrence of asbestos within the sample, in general agreement with results obtained on particles generated by crushing.

Particles generated by micronizing test on the man-made material (sample RIC; total number of 95) span in a wider range of widths (from $\sim 0.1 \mu\text{m}$ to $\sim 2.0 \mu\text{m}$) with respect to those generated by crushing test (from $\sim 0.3 \mu\text{m}$ to $\sim 2.0 \mu\text{m}$) (Fig. 8). Furthermore, for this sample the micronizing produced grains having an average size significantly smaller than that generated by crushing (length=6.6 μm , width=0.5 μm and length=11.5 μm , width=1.0 μm , respectively). In particular, about 15% of particles have aspect ratio value exceeding 20:1, with highest values up to 100:1. In spite of this, the proportion of particles encountering the asbestos definition by Harper

et al. (2008) is about 70%. The criterion of Chatfield (2008), Berman and Crump (2003), and Stanton et al. (1981) would identify 14%, 8%, and 6% of the particles as falling within the “asbestos field”, respectively. The 14% of the RIC particles are asbestos following the procedure of Van Orden et al. (2008).

Particles generated by micronizing test on serpentinite sample (sample AN; total number of 87) show a range of widths spanning from $\sim 0.1 \mu\text{m}$ to $\sim 2.0 \mu\text{m}$ (Fig. 7), as already observed for sample RIC. However, for the serpentinite sample the retrieved aspect ratio values span in a narrower range (from 5:1 to 30:1, except for one particle with aspect ratio of about 100:1) with respect to that observed for particles of RIC sample (aspect ratio values up to 100:1). About 80% of the particles fit with the asbestos definition by Harper et al. (2008). In addition,

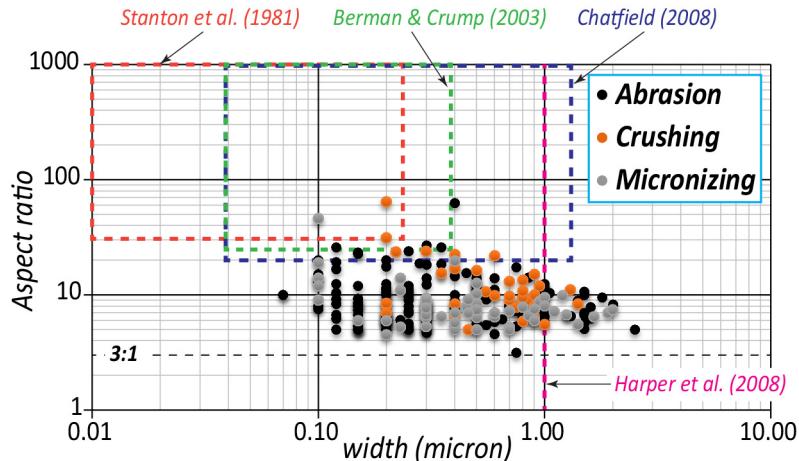


Fig. 9 - Aspect ratio vs width diagram for the analysed particles generated by different mechanical stresses applied to metagabbro (sample TB). Dotted boxes and dotted lines defines fields and criteria for risk assessment (Stanton et al., 1981; Berman and Crump, 2003) or asbestos identification (Chatfield, 2008; Harper et al., 2008).

the percentage of particles falling within the “asbestos field” is 5% following Chatfield (2008) or even lower (1%) following both Berman and Crump (2003) and Stanton et al. (1981) criteria. Notably, this result fairly agrees with that obtained following the procedure of Van Orden et al. (2008) that classifies 3% of the serpentinite particles as asbestos (classified as tremolite).

4.3. Results from abrasion test

Abrasion test performed on metagabbro sample (sample TB) produced particles (total number of 179) with aspect ratio ranging from 4:1 to 27:1, except for two particles having ratio values of 3:1 and 65:1 (Fig. 9). In addition, the majority of the particles (about 85%) have diameter $<1.00 \mu\text{m}$, fitting with the asbestos criterion proposed by Harper et al. (2008). Differently, only the 4% and 2% of the total particles falls within the morphological criterion for asbestos whenever considering the procedures by Chatfield (2008) and Berman and Crump (2003), respectively. On the contrary, both the application of the Stanton et al. (1981) and the Van Orden et al. (2008) procedures allows classifying all the particles as non-asbestos.

5. DISCUSSION

Origin of rock textures, the shape of the rock-forming minerals, and the characteristics of particles generated after mechanical stress on rocks are essential aspects for discussing the environmental impact due to the presence of naturally occurring asbestos (NOA).

Main fabric heterogeneity for our selected ophiolite lithotypes is due to the occurrence or absence of planar anisotropic features (i.e. foliation), leading to either foliated fabric (samples AN and MF), or massive fabric (samples AQ and ME), or fabric composed of both foliation and granular mineral association (samples TB and RIC). The occurrence of millimetric and sub-millimetric thick foliation is characterised by a penetrative and organised

distribution of minerals showing acicular-to-fibrous mineral habit. This is evident for natural samples AN, MF, TB and for the man-made sample RIC, everyone showing the presence of fibrous amphibole disposed along (and forming) the main foliation. Serpentine (both antigorite and chrysotile) and talc represent additional fibrous mineral specimens crystallising along the main foliation of samples AN and RIC, respectively. Accordingly, we suggest that foliation produced at ductile rheological regime is considered a feasible shearing structure for promoting and enhancing fibrous mineralisation in the selected ophiolitic rocks (e.g., Karkanas, 1995; Andreani et al., 2005; Hirauchi and Yamaguchi, 2007; Vignaroli et al., 2011 and references therein).

Then, we reassess the fibrous mineralisation in terms of asbestos fibre or cleavage fragment as unravelled by the means of the counting criteria. Our mechanical tests highlight that four of the selected ophiolite lithotypes (basalt, marble, gabbro, and metagabbro) do not produce particles classified as asbestos following the multi-analytical procedure of Van Orden et al. (2008) (Tab. 1). Besides, about 5% of particles misidentified as asbestos fibres generated by metagabbro (sample TB) after crushing test falls within the overall error rate estimated for this procedure (below 10%, see Van Orden et al., 2008). On the contrary, applying the Harper et al. (2008) procedure an amount of particles spanning from 40% to 90% would be classified as asbestos, therefore leading to a significant error in asbestos fibre identification. In addition, using the Chatfield (2008) and Berman and Crump (2003) criteria the majority of the particles are properly classified as non-asbestos, being the non-asbestos particles of the investigated samples misidentified as asbestos up to 15% for both procedures (except for the gabbro ME sample where the particle misidentification reaches about 70%). Moreover, results obtained on the sample RIC show that the application of the Chatfield (2008) and Berman and Crump (2003) procedures misidentify only from 4% to 7% of the asbestos fibres as non-asbestos. Notably, these errors

are in good agreement with those previously estimated on the two procedures by Van Orden et al. (2008). However, concerning the serpentinite (sample AN), our results showed that both the Chatfield (2008) and Berman and Crump (2003) criteria would misidentify up to about 50% of the particles as non-asbestos. Interestingly, in this case the method of Harper et al. (2008) leads to a correct identification of the asbestos proportion in the sample.

Summarising, the application of the Harper et al. (2008) produced the highest error rates in the most of the cases, providing therefore a significant overestimation of the asbestos hazard. Conversely, the Chatfield (2008) and Berman and Crump (2003) procedures resulted more appropriate in the "asbestos identification". Nevertheless, while both these criteria led to a slight overestimation of asbestos hazard for lithotypes that actually do not release asbestos particles (basalt, marble, gabbro, and metagabbro; Figs. 6 and 9) under mechanical stress, they may markedly underestimate the asbestos hazard of lithotypes able to release asbestos fibres (serpentinite; Fig. 7). These misidentifications are due to overlap in dimensions between cleavage fragments and true asbestos fibres that makes their discrimination very tricky. The method of Van Orden et al. (2008), taking into account of additional morphological features of the investigated particles, today represents the most rigorous criterion for the proper asbestos identification. In particular, cleavage fragments may be identified by using TEM images because they are characterised by an irregular shape with a variable diameter measured along the particle length, no parallel surfaces, tapered or ledged terminations (Fig. 10). On the contrary, asbestosiform fibres show parallel sides, nearly constant diameter along the length, regular terminations, and straight shapes (Fig. 11).

6. CONCLUSIONS

We applied three different mechanical tests (i.e. crushing, micronizing, and abrasion) on six materials (five ophiolite lithotypes and a man-made material) to evaluate the asbestos hazard of rocks mined for industrial application or civil work. The starting material shows heterogeneities in terms of rock fabric, as both samples showing foliated fabric and massive-granular fabric were investigated. We documented the main occurrence of fibrous mineralisation along millimetre and sub-millimetre thick foliation in foliated rock fabric. In order to determine the amount of fibres regulated by the asbestos normative, we applied different counting criteria. Among the rocks belonging to the ophiolite suite here investigated, our results highlighted divergent interpretations in assessing the asbestos content. The counting methods dominantly based on the fibre dimensional criteria allow considering all the investigated lithotypes are able to release asbestos particles, with a prevalent amount of asbestos particles coming from samples characterised by pervasive foliation. The application of a multi-analytical approach (based on both chemical and morphological

features of the individual particles) revealed that samples characterised by a strongly foliated fabric (serpentinite and talc-schist lithotypes) are able to release asbestos (in particular tremolite and chrysotile).

Finally:

The use of dimensional criteria based only on particle width and aspect ratio is not appropriate to avoid misidentification between asbestos particles and cleavage fragments. Additional morphological, structural, and chemical features of the analysed particulate matter are recommended to be incorporate into the counting procedures.

As scientific studies indicate that cleavage fragments are not biologically similar to the regulated asbestos minerals, it is important that the scientific community converges on univocal and shared criteria to define particle as asbestos, recommending a critical review of the counting criteria commonly used for the asbestos particle identification.

Refining the counting criteria procedures is a prerequisite for assessing the presence of NOA in rocks and, therefore, for reducing ambiguities (overestimations or underestimations) in asbestos hazard due to rock management.

Multidisciplinary and multiscale approaches, starting from the characterisation of the rocks properties (the natural source) to the amount of airborne asbestos (the induced product), should support strategies and normatives aimed at evaluating and mitigating the asbestos hazard in environmental sites.

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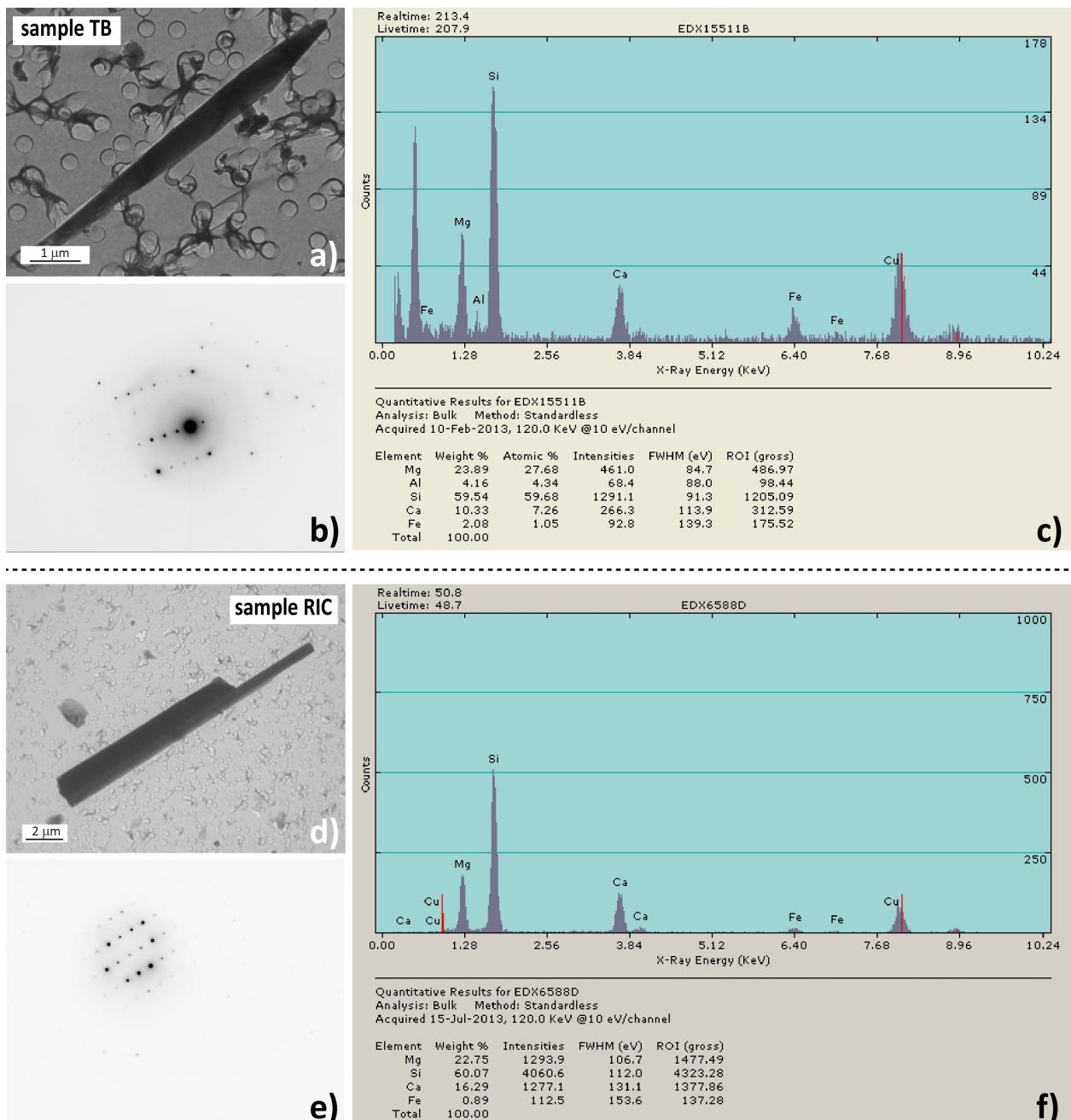


Fig. 10 - Cleavage fragments. Sample TB: a) TEM image, b) SAED pattern, and c) EDX spectra for a non-asbestiform amphibole particle generated by micronizing test. Sample RIC: d) TEM image, e) SAED pattern, and f) EDX spectra for a non-asbestiform amphibole particle generated by micronizing test.

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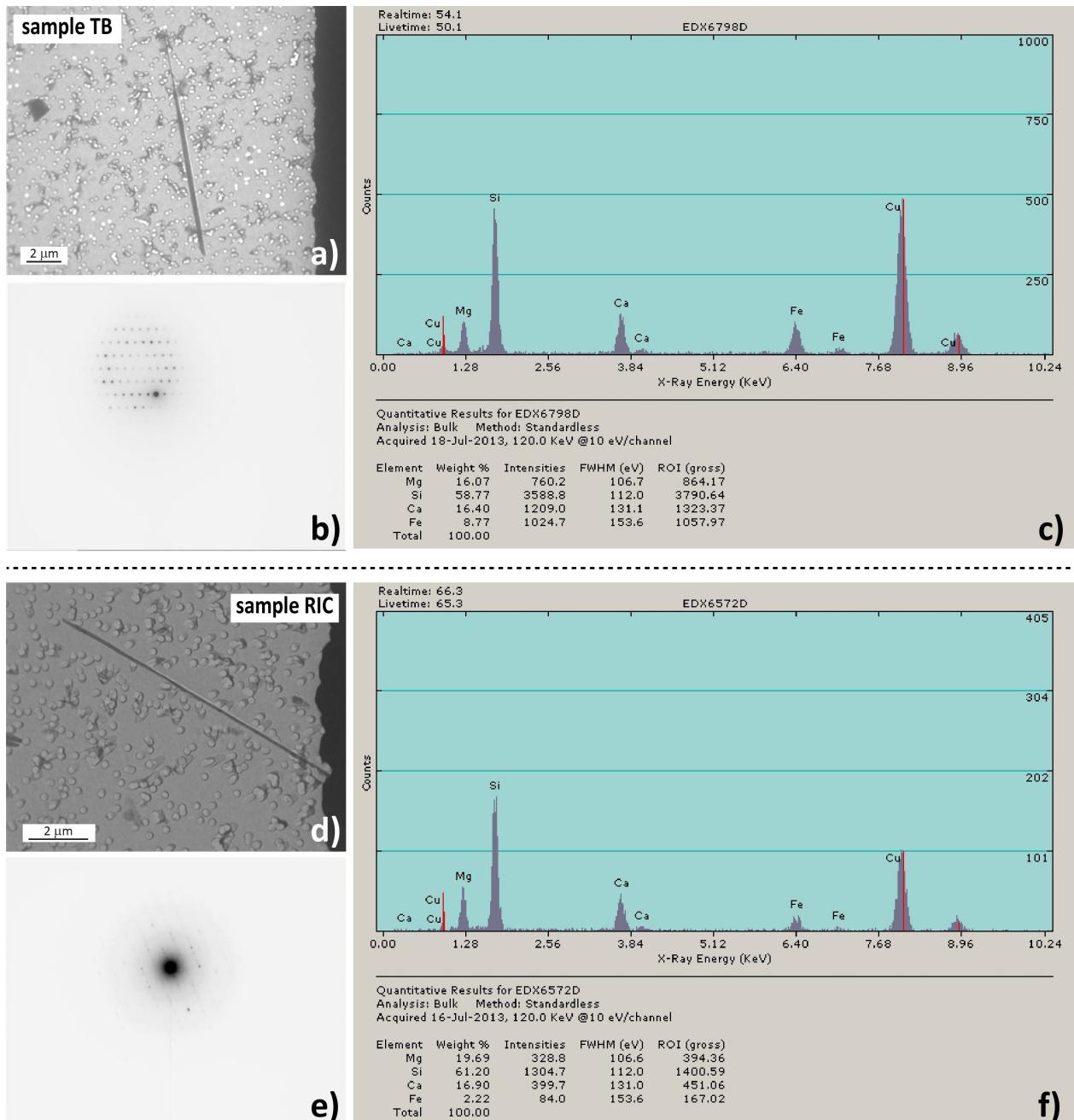


Fig. 11 - Asbestiform particles. Sample TB: a) TEM image, b) SAED pattern, and c) EDX spectra for a tremolite asbestos generated by crushing test. Sample RIC: c) TEM image, d) SAED pattern, and e) EDX spectra for an asbestiform tremolite generated by crushing test.

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