ASBESTOS IN ROCKS AND ENVIRONMENTAL ISSUES: QUALITATIVE AND QUALITATIVE EVALUATION OF FIBROUS MINERALS

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INTRODUCTION

The term asbestos commonly indicates a group of silicates, characterized by fibrous habit, widely exploited for industrial and technological applications. The extraction, use and marketing of these minerals have been banned in the European Union and in the United States of America, because of the proven harmful effects that the asbestos fibres may cause, mainly affecting the respiratory system. Currently, the risks linked to the exposure to these fibres derive from the improper storage of materials that contain asbestos, still installed in working and living environments, and from the disruption of asbestos-bearing rocks.

The ophiolitic outcrops are sites where there might be fibrous minerals potentially harmful to health, some of which classified as asbestos. These minerals fill macro- and micro-fractures in the host rock. Natural processes of chemical and physical alteration or human activities can determine the release into the atmosphere of inhalable mineral fibres (Compagnoni & Groppo, 2006). In nature there are also dozens of mineral species with fibrous habit, which does not necessarily have had an industrial use and therefore are not considered asbestos by the current regulations. Several of these minerals may have environmental significance, as it has been proved that they are able to induce the same diseases attributed to exposure to asbestos fibers (Pott *et al.*, 1974; Berry, 1999).

The Italian legislation, although complies with European directives that ban the extraction, use and marketing of minerals classified as asbestos, allows the extraction and the commercialization of materials, such as ballast or blocks, from asbestos-containing rocks. The extraction of these rocks in Italy is regulated by the Ministerial Decree of May 14, 1996. This decree provides a list of rocks that may contain asbestos. It stipulates that the sites affected by mining activities should be under investigation for the evaluation of the fibrous mineral content, but clear provisions for the regulation of these investigations are lacking. This decree is the only part of Italian legislation dealing with asbestos from natural sources, but only in mining activities. However, the risks linked to natural sources of fibrous minerals are not related only to mining, but also to excavation works for the construction of infrastructures such as roads and tunnels (Bologna *et al.*, 2005).

As stated above, the ophiolitic outcrops from Apennines are sites where rocks may contain fibrous minerals, including those that are classified as asbestos. These mineral phases may have environmental significance. The potentially asbestos-containing rocks have been studied, both from the geological and health point of view, to characterize the environmental compartments in order to provide a contribution to the knowledge of this issue and to define the risk linked to the dispersion of mineral fibres in the environment. This research project intends to propose an alternative approach for the preliminary evaluation of the fibrous mineral content in ophiolitic rocks.

Aims of the PhD project

This PhD project has the aim to study the distinctive features of three ophiolitic outcrops in the Northern Apennines, where asbestos naturally occur, by conducting field and laboratory investigations in order to determine the presence, the nature, the spatial distribution and the amount of fibrous minerals, either classified or not classified as asbestos.

The three selected sites are located within the Region of Tuscany and belong to three different tectonic settings. The case studies of this research are three abandoned serpentinite quarries.

The main purposes of this work are as follows: a) assessment of the presence of fibrous minerals in rocks; b) identification of the fibrous minerals and determination of their spatial distribution within the rocks; c) analysis of the elements useful to provide a procedure for the correct quantification of potentially dangerous minerals in ophiolitic outcrops; d) use and examination of methods and analytical techniques that can provide support and validation for the quantitative analysis of fibrous minerals.

The ultimate goal of this project is to outline a procedure that could allow a correct geological survey of sites potentially containing dangerous minerals; this procedure would be useful for further assessment on the risks arising from possible rock disruption by natural agents or human impact. The need for this procedure comes from the apparent inadequacy of existing legislation and the need to thoroughly understand the environments that may pose a health risk in presence of sensitive receptors.

CASE STUDIES

Three outcrops from the Northern Apennines ophiolites (Tuscany), representative of three different tectonic settings, were identified. All these sites are abandoned serpentinite quarries. The rocks from these sites have been quarried to be used mainly for road foundations and railway ballast. The quarries were particularly suitable for this research project because they provided excellent exposures to perform detailed geological surveys. It was however difficult to find abandoned mining sites that have been subjected to an environmental restoration. Indeed not all the pits, although restored, were in good conditions. Therefore three areas with different state of preservation and accessibility were selected in order to make this study as representative as possible of the actual situation.

For each case study, the work undertaken may be summarized as follows: a) field analysis and sampling of representative lithotypes and fibrous minerals; b) petrographic and mineralogical characterization of samples; c) analysis of rock surfaces at different scales, when possible, aimed to the quantification of fibrous mineral species.

Pomaia quarry

The Pomaia quarry is a dismissed and restored borrow pit located in the Cecina Valley (Pisa). The quarry face showed good exposures of the lithotypes, consisting of lherzolites, gabbros, and cataclasites. These lithotypes belong to an ophiolitic sequence referred to the Internal Ligurian Units.

Serpentinites are almost all tectonitic lherzolites having variable degrees of serpentinization due to oceanic metamorphism, ranging from zeolite to upper amphibolite facies. These rocks are generally extremely fractured and display a network of isotropic and emerald green or fibrous and light green to white veins filled by serpentine-group minerals.

Fig. 1 - Gabbro dyke in serpentinized lherzolites from Pomaia quarry.

Gabbros are intruded in serpentinites as 5-60 cm thick dykes or 1×20 m sized stocks (Fig.1). Wide cataclastic zones cut both serpentinites and gabbros. These zones contain brownish mm-thick sheets of fibrous sepiolite.

The characterization of lithotypes in the Pomaia quarry was carried out using analyses aimed to

identify the nature of fibrous minerals, potentially harmful to health. Both in the serpentinites and cataclasites minerals characterized by fibrous morphology were identified. On the contrary, gabbros did not reveal any fibrous mineralization.

The occurrence of minerals belonging to the serpentine-group in the serpentinite veins was confirmed by X-ray powder diffraction. The micro-Raman spectroscopy is an additional technique that allowed the identification of the mineral phases and the distinction between the different kinds of serpentine (*i.e*. lizardite, antigorite, chrysotile). However, only the collection of data from different techniques and their integration allowed an unambiguous characterization of the serpentine minerals. Through the comparison between these data and those reported in the literature (Whittaker & Zussman, 1956; Wicks, 2000), antigorite, chrysotile, and lizardite were identified. It is important to stress that micro-Raman spectroscopy is useful for punctual analysis (Rinaudo *et al*. 2003), but, for the purposes of this study, the X-ray diffraction was more appropriate, because it allowed to identify the actual mineralogical composition of the veins and to collect data for quantitative analysis.

Serpentine minerals also occurred in the cataclasites and they were related to the presence of serpentinite fragments. In cataclasites with carbonatic cement, fibrous minerals were scattered in the matrix; through micro-Raman spectroscopy these fibres were identified as chrysotile. It is interesting to note that this kind of lithotypes were characterized by the presence of sepiolite, that occurred as brown fibres, thus resulting a further potential hazard to health.

The morphology of the vein samples was studied by means of SEM-EDS; in addition to the extreme fibrousness of those phases that appeared fibrous even at the meso-scale, an unexpected fibrous habit was also observed in crushed specimens that appeared compact at the meso-scale before milling.

The fibrous minerals occurring in the Pomaia quarry and identified by the petrographic and mineralogical characterization were chrysotile, antigorite, and sepiolite. Only chrysotile is a mineral classified as asbestos, whereas antigorite and sepiolite are not regulated by the current legislation, though they may lead to the same pathologies as those induced by asbestos (Wagner *et al.*, 1987; Pott *et al.*, 1990; Fitz Gerald *et al*., 2010; Cardile *et al.*, 2007; Pugnaloni *et al.*, 2010).

The quantification of the lithotype surfaces outcropping in the studied quarry was achieved through a geological survey and the collection of digital images of the studied samples. The whole quarry was divided into different sectors, taking into account the nature of the lithotypes; the limits between the different lithologies were identified using an image processing software and the outcropping surfaces were calculated as percentage. An accurate geological survey, focused on the structural features of the outcrop, pointed out the preferential orientation of the gabbro dykes, the serpentine vein systems, and the cataclastic domains. Taking into account also this additional information, an areal sampling of serpentinites was performed, processing photos of ten sampled areas by means of the image processing software, in order to quantify the distribution of the serpentine veins at the meso-scale. This kind of analysis was also applied at the micro-scale, using thin sections representative of the studied lithotypes. The thin section images were processed using the software ImageJ 1.43u (Rasband, 1997-2009). Through this multi-scale approach, it was estimated that the studied rocks contained an amount of minerals that might be potential source of free fibres, variable from 20 to 56%.

Sasso Cinturino quarry

The Sasso Cinturino quarry is a dismissed and not restored borrow pit located in Garfagnana, near to Villa Collemandina (Lucca); it was opened in serpentinite rocks belonging to the External Ligurian Units.

In the External Ligurian Units, the mafic and ultramafic rocks occur only as slide-blocks in the Santonian - Early Campanian sedimentary mélanges, known as “basal complex”. Due to the abundant detritus, the quarry shows bad exposures of rocks. The outcropping serpentinites derived from spinel-bearing sub-continental lherzolites; locally, rodingites intrude the ultramafites. These rocks are strongly tectonized and exhibit different types of veins, whose mutual relationships are also detectable at the outcrop scale. Three systems of veins were identified and their geometric relationships were measured. The veins were both massive and fibrous (cross- and slip-fibres) and they were distinguished as follow: a) mm-sized chrysotile veins, pervasively scattered in the

Fig. 2 - Tremolite-actinolite veins from Sasso Cinturino quarry.

rocks; b) mm- to cm-sized green compact or fibrous serpentine veins; c) late stage cm-sized fibrous tremolite-actinolite veins (Fig. 2). Samples of lithotypes and fibrous mineral phases were collected and they were mineralogically characterized through X-ray powder diffraction and EDS chemical analyses. The identified minerals are tremolite-actinolite and chrysotile, both classified as asbestos. The presence of an amphibole belonging to the tremolite-actinolite series is particularly important for hazard assessment of this site.

This mineral was readily identifiable at the outcrop scale and occurred in veins formed by fibres up to several cm in length, generally characterized by a growth parallel to the walls of the fracture (slip-fibres). Through the careful analysis of the cross-cutting relationships with the other vein systems, the tremolite-actinolite-bearing vein system seems to be related to a late-stage tectonic phase. This was peculiar from the geological point of view, as it might be the evidence of a correlation between the geometric relationships of veins and tectonic framework. This study is obviously not enough accurate to claim the above considerations, but offers an idea for reflection for any investigation at a regional scale aimed at verifying this assumption.

The location of the samples potentially source of mineral fibres was restricted to the image analysis on thin sections scans at the micro-scale. It was not possible to perform an image analysis to meso-scale due to the bad conditions of the outcrop. These results provided evidence that the amount of material potentially source of fibres ranged from 43% to 64%.

The examined quarry presented a moderate level of hazard, not only for the presence of fibrous serpentinite fragments in the nearby area, that testify the dispersion of fibres, but also for the most important presence of fibrous amphiboles, here represented by tremolite-actinolite (Fig. 3). Both epidemiological and cytotoxic studies showed that this kind of amphibole is more pathogenic than serpentine asbestos (Hughes *et al.*, 1987).

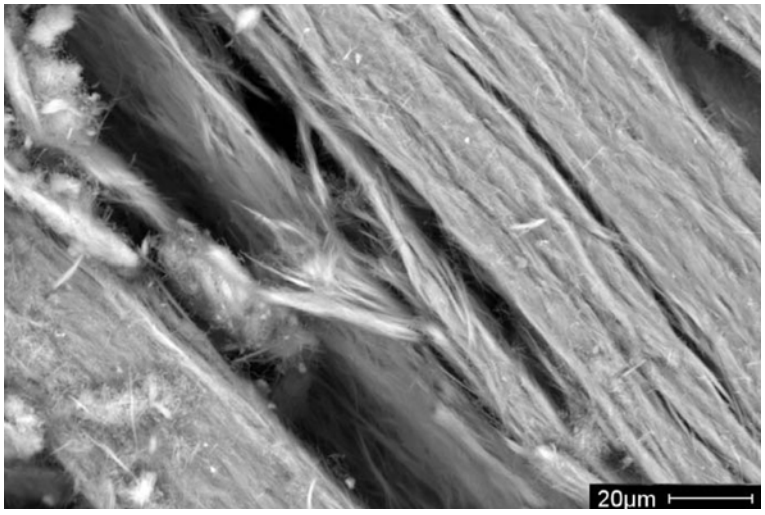

Fig. 3 - SEM-EDS image of tremolite-actinolite specimen from Sasso Cinturino quarry.

In particular, the cytotoxicity seems to be correlated with the iron content; therefore, the chemical composition of the amphibole from Sasso Cinturino suggested its potential toxicity. In addition, most studies that detected cases of disease caused by asbestos exposure from natural

sources, reported the presence of tremolite among inhalable fibres, in agreement with the studies stating that the amphiboles appear more biopersistent and therefore more dangerous for the health (Coffin *et al.*, 1992).

Monte Fico quarry

The Monte Fico quarry is a dismissed and restored borrow pit opened on the western slopes of Monte Fico, in the Elba Island, near Rio Marina (Livorno). According to Bortolotti *et al.* (2001), the serpentinized lherzolites of the Monte Fico area belong to a tectonic unit regarded as deformed during HP/LT metamorphism and thus referred to the Schistes Lustrés complex of Alpine Corsica. This quarry exhibits quite good exposure of serpentinized lherzolites.

The serpentinites from the Monte Fico quarry are tectonitic peridotites derived from sub-oceanic mantle. These rocks are locally foliated and pervasively serpentinized.

Rare dunite layers and sporadic cm-thick gabbro dykes are also present. The serpentinites are characterized by veins (Fig. 4) and coatings formed by serpentine minerals. Such phases generally display a lamellar morphology, rarely fibrous, but in both cases the morphology appears not asbestiform.

Fig. 4 - Serpentine veins in serpentinite thin section from Monte Fico quarry (parallel nicols).

The fractures filled with fibrous serpentine minerals occur close to shear zones. The geometrical relationships between vein systems show conjugate attitudes of the veins, coherent with their origin during active oriented tectonic stress.

A detailed sampling of lithotypes and veins were performed in this site. X-ray diffraction analyses confirmed the presence of serpentine minerals in the vein fillings; the specimens characterized by a lamellar morphology were composed by chrysotile and minor lizardite, whereas those with a fibrous appearance, that after crushing showed an asbestiform morphology, were composed by chrysotile, with minor talc and dolomite. In addition to the phases identified during this study, also antigorite occurrence has been reported from the Monte Fico area (Viti & Mellini, 1996). Image analysis performed at the micro-scale on thin sections of rock samples, evidenced that the percentage of minerals that potentially represent a source of fibres, ranged between 22% and 64%.

This site seems to have no clear risk factors, such as the presence of mineral species specifically suitable for fibres release. However, the geological survey highlighted that rock fractures were filled with minerals classified as asbestos. Therefore, the Monte Fico quarry is a site that, if disturbed, could be a source of dangerous mineral fibres.

DISCUSSION

The three studied quarries were in a different storage conditions and presented differences with regard to the typology of fibrous minerals and their mutual relationships. The field study allowed the identification of the lithotypes and the detection of the fibrous mineralizations at the meso-scale. In all the investigated sites, serpentinites were the dominant lithotype, usually associated with other lithotypes (gabbros, rodingites,

cataclasites). Therefore, the study was planned in order to characterize all the representative elements of the examined site, sampling the different lithotypes, vein types and associated mineralization, and discontinuities.

Petrographic and mineralogical studies were performed to characterize the collected samples. The observation of thin sections of rock samples allowed, not only to study their microstructure and composition, but also to determine the presence of fibrous phases. Indeed, not all the lithotypes in the studied quarries contain fibrous mineral species. Several analytical techniques were used. These analysis allowed to identify the minerals with fibrous morphology, and then to locate their source in the studied sites. Table 1 summarizes the characteristics of the studied sites and the results of the mineralogical and petrographic characterization.

Table 1 - Comparison between the studied sites.

	CASE STUDY 1 (POMAIA)	CASE STUDY 2 (SASSO CINTURINO)	CASE STUDY 3 (MONTE FICO)
TECTONIC SETTING	Internal Ligurian Units	External Ligurian Units	Metamorphic Ophiolites
LITHOTYPES	Serpentinites Gabbros Cataclasites	Serpentinites Rodingites	Serpentinites
ASBESTOS	Chrysotile	Chrysotile Tremolite-Actinolite	Chrysotile
OTHER ASBESTIFORM MINERALS	Antigorite Sepiolite	Not Detected	Not Detected
PERCENTAGE OF MATERIAL SOURCE OF FIBERS	20% - 56%	43% - 64%	22% - 64%

The results of the characterization of the three ophiolitic outcrops belonging to different tectonic settings, highlighted that the studied sites could be considered homogeneous (compared to dominant lithotype) by the present-day regulations, but displayed different and sometimes complex lithological assemblages, in turn containing different kinds of fibrous minerals. It was possible to suggest a relationship between the structural setting and the characteristics of fibrous mineralizations. Such hypothesis should be verified on a regional scale, by means of further field and laboratory analyses. The fibrous minerals classified as asbestos and the unregulated fibrous minerals were recognized and this had to be considered important because it highlighted the limitations of the legislative definition of asbestos. The results of the quantification of the elements that, according to the mineralogical analysis, were potential source of fibrous minerals, were comparable in all the studied sites; their amounts varied from 20% to 64% and, therefore, are high in the maximum values. This estimation did not want to be an assessment of the fibres content of a rock mass, but rather an assessment of the material that might release fibres. The high rates of materials recognized as potential source of fibres, highlighted that a procedure which includes such preliminary studies should be necessary.

CONCLUSIONS

This PhD project had the aim to study rocks containing fibrous minerals in order to contribute to the understanding of this issue, in a geological and environmental perspective, and to highlight the lack in regulations for the management of the ophiolitic areas in Italy.

A multi-scale investigation were performed in three abandoned quarries, belonging to three different tectonic settings of ophiolites from the Northern Apennines, in order to define the occurrence, the nature, the spatial distribution, and the amount of fibrous minerals within the rocks.

The procedure set out in this work, aimed to a preliminary identification and quantification of fibrous minerals in the rock mass, can be summarized as follows:

- field work:
  - identification of lithologic types;
  - identification of fibrous phases at the meso-scale;
  - identification of the geometrical features of lithologic types and veins;
  - representative sampling;
- petrographic and mineralogical characterization:
  - study of thin sections of rock samples;
  - integrated mineralogical analysis;
- quantification of minerals potentially sources of fibres:
  - multi-scale image analysis.

The key elements to make a proper characterization of the studied sites were:

- representative sampling of lithologic types in the studied sites;
- analysis of outcrops at different scales;
- accurate identification of fibrous minerals;
- integration and selection of appropriate analytical methods for properly assessing the materials that could release fibres.

The integration of these data allowed to determine the amount of materials that are potentially capable to release mineral fibres. Nevertheless, the performed method has some limitations, because quantification is the result of an assessment in two dimensions and it is difficult to reproduce. In fact, the outcrops with good exposures of rocks are rare and it is not always possible to perform an useful image analysis. The results of quantification are still valid for a preliminary characterization of rock masses, but have significance only if validated by mineralogical analysis.

Another limitation is the accessibility, both economic and technical of the research instruments for the operators in this specific field. Therefore, the preferred technique for the mineralogical analyses is the X-ray powder diffraction. This technique is among the most widely used and available, and allows an efficient and relatively inexpensive identification of mineral phases that are critical for their impact on environment and health.

The designed method was appropriate to a preliminary characterization of the asbestos content of a rock mass. The comparison with the legislation pointed out its inadequacy and the need for detailed procedures, especially for a proper sampling, aimed to assess the actual asbestos content of a rock. If the legislation, in providing criteria for the field survey, considers the rocks as homogeneous bodies, the present study showed that it is important to identify and to locate all the elements of variability, especially to perform a proper sampling.

Therefore, we can deduce how the only part of Italian legislation that concerns the management of places with asbestos-containing rocks, even if limited to the sphere of mining activities, is unsuitable to assess the risk associated with the mobilization of asbestiform fibres from natural sources. As already mentioned, the evaluation of the fibrous minerals content and their potential releasability into the environment, cannot dispense from making a preliminary and detailed study that deals with the geology of a site.

The Italian law and, specifically, the previously mentioned Ministerial Decree of May 14, 1996 lacks an efficient procedure that defines such a type of study. The methodological approach outlined in this study is intended as a contribution to improving the regulatory in the management of sites where there are rocks containing dangerous minerals. Furthermore, not only sites affected by mining activities, but also all those sites affected by infrastructural activities should be regulated.

The preliminary geological study of the areas characterized by the presence of outcropping rocks containing fibrous minerals, as the ophiolites, could be very useful for their management, either in the presence or absence of anthropogenic disturbances. Moreover, it could provide a significant help, not only for a hazard assessment of areas with dangerous minerals, but also to ensure proper land use planning.

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