MICROSTRUCTURAL AND CHEMICAL CHARACTERIZATION OF MINERAL FIBRES OF HIGH IMPACT FOR ENVIRONMENTAL POLLUTION

CLAUDIA RICCHIUTI
Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Catania, Corso Italia 57, 95129 Catania

It is now accepted by the scientific community that the exposure to asbestos may lead to the development of health issues. Chrysotile, tremolite, actinolite, amosite, crocidolite, and anthophyllite, are the six silicate minerals belonging to the asbestos group and, due to their physical properties, they have been widely exploited worldwide to produce Asbestos-Containing Materials (ACMs).

To date, according to the Italian law (L. 257/92), the extraction, the use and marketing of asbestos in Italy is currently banned, whereas only in the 34% of the countries in the world the use of regulated asbestos is restricted. Although the existing restriction, the human health is still endangered due to the exposure to the natural occurrence of asbestos (NOA) which represents a big concern. The term NOA refers to asbestos present in geological deposits (*i.e.*, rocks and soils) that, due to human activities (*e.g.*, road construction, excavation) or weathering processes (*e.g.*, erosion), may be disturbed and release asbestos fibres into the environment thus representing a source of fibres dispersion. The risk to human health consists of the potential inhalation of asbestos fibres which may penetrate the lungs thus causing cancer pathologies (IARC, 2009). The World Health Organization (WHO) established that respirable fibres have length > 5µm, width < 3 µm and aspect ratio ≥ 3 (WHO, 1986).

Rocks from the ophiolite complexes (*i.e.*, metabasite and serpentinite) are the main lithotypes associated with asbestos, since asbestos minerals are the major constituents of these rocks, and they have been of great interest to the scientific community for years. Much less literature studies refer to asbestos-bearing soils whose examination is extremely important as well (Ricchiuti *et al.,* 2020). Derived soils may contain hazardous fibres, since they inherit the mineralogical and geochemical characteristics of the bed rock (Chesworth, 1992); that could be released into the air (for instance because of agricultural activities) thus representing a source of risk to human health.

In addition to the morphometric features (*e.g.*, morphology, size, surface area, density) of the fibres, the geochemical composition of the fibres is another aspect that should not be underestimated. As a matter of fact, asbestos fibres are capable to host potentially toxic elements (PTEs) in their structure that, once inhaled, can be released into the lungs due to the dissolution processes and they may induce lung cancer (Schereier *et al.,* 1987; Wei *et al.,* 2014).

The present work is focused on the mineralogical and geochemical characterization of serpentinite rocks and derivative soils occurring in Southern Apennines (Calabria and Basilicata region) as well as on chemical characterization of three asbestos fibres types (chrysotile, tremolite, actinolite) extracted from serpentinites samples.

Due to the high impact of naturally occurring asbestos (NOA) on human health, the study areas are of great scientific interest. As a matter of fact, 70 mesothelioma deaths caused by asbestos exposure have been recorded by the Italian National Mesothelioma Register in the Calabria region between 1993 and 2015 (INAIL, 2015). Similarly, relevant excess of negative health effects NOA-correlated cases has been highlighted by epidemiological studies conducted on twelve villages of the Basilicata region (Caputo *et al.,* 2018).

The main goals of the present study were the definition of i) asbestos minerals occurrence in the study area, ii) the morphometric parameters (*e.g.*, morphology, size) of the fibres to identify the respirable ones, potentially dangerous to human health, iii) the concentration of potentially toxic elements (PTEs) firstly in asbestos-containing rocks and soils, and secondly in isolated fibres.

Results of the multidisciplinary investigation allowed to make significant considerations to asbestos-related hazard. Specifically, the mineralogical investigation of serpentinite rocks and derivative agricultural soils occurring in the Gimigliano Mount-Reventino Unit (GMRU; Calabria region) and Pollino Massif (Episcopia and San Severino Lucano villages, Basilicata region), revealed that among the six asbestos minerals, chrysotile, tremolite and actinolite fibres occur in the studied samples (Punturo *et al.,* 2018, 2019; Bloise *et al.,* 2019). Moreover, asbestiform mineral species such as polygonal serpentine and fibrous antigorite have been detected. In serpentinite samples, asbestos fibres were mainly found inside the veins rather than the massive portion with an orientation mainly perpendicular (cross-fibres) to the vein elongation directions. A broad characterization of the veins and their infill has been conducted on serpentinites from GMRU (Bloise *et al.,* 2020a). In these samples, vein systems with various size and shape crosscutting the rock were well visible even at the mesoscopic scale and those ones with average width ranging between 0.3 mm to 1 mm represents the most abundant vein type. As shown by microscopic observations, the veins were filled by chrysotile fibres whose dimensions (*i.e*., width, length) match with those of regulated asbestos and therefore classified as asbestos under European law (Directive 2003/18/CE, 2003). Accordingly, asbestos fibres (chrysotile, tremolite, actinolite) detected in serpentinite samples and derivative soils from Pollino Massif, occur with dimensions of regulated asbestos (length > 5 µm, width < 3 µm; WHO, 1986).

In addition to the mineralogical composition, the geochemical characteristics of serpentinite rocks and derived soils inherited from the mother rock revealed significant information related to the presence of potentially toxic elements (PTEs) harmful to human health. As a matter of fact, analyzed bulk rocks and derived soils showed concentration of Cr, V, Co, and Ni exceeding the maximum admissible contents established by the Italian law (Italian Legislative Decree No. 152/2006) for public, private, and residential green use (Co, V) as for industrial and commercial use (Cr, Ni). These results represent significant fundings since heavy metals can be mobilized and discharged into various environmental matrixes (*e.g*., water, soils) thus expanding the contamination source and the potential interaction with human body. Scientific studies conducted in the GMRU area, revealed that water interacting with ophiolite rocks is characterized by high amounts of PTEs (*i.e*., Cr, Ni, Cu, Zn, Pb) due to the dissolution of primary phases such as serpentine and amphiboles thus emphasizing the importance of asbestos minerals characterization for assessing contaminated groundwater and soil in ophiolitic outcrops.

The quantification of PTEs in asbestos fibres extracted from serpentinites rocks from GMRU (chrysotile, tremolite, actinolite; Bloise *et al.,* 2020b) and Pollino Massif (tremolite from Episcopia and San Severino villages, respectively; Ricchiuti *et al.,* 2021) revealed high concentrations of toxic elements (Cr, Ni, Co, Cu, Zn, V, As, Ti) as well. Specifically, Cr and Ni were the most abundant trace elements detected in the samples and, among the three asbestos species from GMRU, tremolite showed the highest content of trace metals followed by actinolite and chrysotile. It is worth mentioning, that potentially toxic minor elements such as Fe and Mn influence the balance content of toxic metals. If we wanted to suppose which fibre is more potentially dangerous based on the PTEs total amount, we would assume that tremolite is the most hazardous one due to the highest content of heavy metals. However, other important factors such as the biodurability influence the toxic potential of the fibres. For instance, chrysotile, which is considered by many countries less toxic than amphiboles, due to its shorter bio-persistence into the lungs, can quickly release its PTEs high content into the body thus causing negative effects. If this condition is exact, the toxic potential of metal-rich chrysotile asbestos should be reevaluated (Gualtieri *et al*., 2017).

As for the two tremolite from Pollino Massif, the concentrations of PTEs were even higher than those ones found in asbestos fibres from GMRU. Specifically, tremolite from Episcopia revealed the highest amounts of trace elements. In this case, other conditions being equal (*e.g*., biodurability, surface activity), among the two tremolite asbestos investigated it is possible to assume that based on PTEs content, tremolite from Episcopia is more dangerous than tremolite from San Severino Lucano village.

Therefore, what comes out from the present work, is that population living within serpentinite rich geological context could be exposed to health risks due to the presence of asbestos mineral species as well as that of high concentrations of potentially toxic elements in rocks and soils and individual fibres. In this context, local maps indicating areas with environmental concern should be published by the institutions thus avoiding hazardous exposures.

REFERENCES

Bloise, A., Ricchiuti, A., Giorno, E., Zumpano, P., Miriello, D., Apollaro, C., Crispini, A., De Rosa, R., Punturo, R. (2019): Assessment of Naturally Occurring Asbestos in the area of Episcopia (Lucania, Southern Italy). *Fibers*, **7**, 703.

Bloise, A., Ricchiuti, C., Lanzafame, G., Punturo, R. (2020a): X-ray synchrotron microtomography: a new technique for characterizing chrysotile asbestos. *Sci. Total Environ*., **703**, 135675.

Bloise, A., Ricchiuti, C., Punturo, R., Pereira, D. (2020b): Potentially toxic elements (PTEs) associated with asbestos chrysotile, tremolite and actinolite in the Calabria region (Italy). *Chem. Geol*., **558**, 119896.

Caputo, A., De Santis, M., Manno, V., Cauzillo, G., Bruni, B.M., Palumbo, L., Conti, S., Comba, P. (2018): Impatto sulla salute delle fibre di amianto presenti in affioramenti naturali nell'area del Pollino (Basilicata). *Epidemiol. Prev.*, **42**, 142-150.

Chesworth, W. (1992): Weathering systems. *In*: "Weathering, soils and paleosols", I.P. Martini & W. Chesworth, eds. Elsevier, Amsterdam, 19-39.

Directive 2003/18/CE (2003): Directive 2003/18/EC of the European Parliament and of the Council of 27 March 2003 amending Council Directive 83/477/EEC on the protection of workers from the risks related to exposure to asbestos at work (Text with EEA relevance). *Official Journal L 097*, 48-52.

Gualtieri, A., Mossman, B.T., Roggli, V.L. (2017): Towards a general model for predicting the toxicity and pathogenicity of mineral fibres. *In*: "Mineral Fibres: Crystal Chemistry, Chemical-Physical Properties, Biological Interaction and Toxicity", A.F. Gualtieri, ed. European Mineralogical Union, **18**.

IARC (2009): Asbestos (chrysotile, amosite, crocidolite, tremolite, actinolite, and anthophyllite). *In*: "Arsenic, Metals, fibres and dusts", IARC Monographs, International Agency for Research on Cancer, Lyon, **100 C**, 147-167.

INAIL (2015): Il Registro Nazionale Mesoteliomi - V Rapporto. Ed. Istituto Nazionale Assicurazione Infortuni sul Lavoro, https://www.inail.it/cs/internet/comunicazione/pubblicazioni/catalogo-generale/il-registro-nazionale-dei-mesoteliomi-v-rapporto.html.

Italian Legislative Decree n. 152/2006 (2006): Norme in materia ambientale. *G.U. Serie Gen. n. 88 del 14-04-2006 - Suppl. Ord. n. 96*. Available online: https://www.gazzettaufficiale.it/dettaglio/codici/materiaAmbientale.

L. 257/92 (1992): Norme relative alla cessazione dell'impiego dell'amianto. *G.U. Serie Gen. n. 87 del 13-04-1992 - Suppl. Ord. n. 64*. Available online: https://www.gazzettaufficiale.it/eli/id/1992/04/13/092G0295/sg.

Punturo, R., Ricchiuti, C., Mengel, K., Apollaro, C., De Rosa, R., Bloise, A. (2018): Serpentinite-derived soils in southern Italy: potential for hazardous exposure. *J. Mediterr. Earth Sci*., **10**.

Punturo, R., Ricchiuti, C., Bloise, A. (2019): Assessment of Serpentine Group Minerals in Soils: A Case Study from The Village of San Severino Lucano (Basilicata, Southern Italy). *Fibers*, **7**, 18.

Ricchiuti, C., Bloise, A., Punturo, R. (2020): Occurrence of asbestos in soils: state of the art. *Episodes*, **43**, 881-891.

Ricchiuti, C., Pereira, D., Punturo, R., Giorno, E., Miriello, D., Bloise, A. (2021): Hazardous Elements in Asbestos Tremolite from the Basilicata Region, Southern Italy: A First Step. *Fibers*, **9**, 47.

Schereier, H., Northcote, T.G., Hall, K. (1987): Trace metals in fish exposed to asbestos rich sediments. *Water Air Soil Pollut.*, **35**, 279-291.

Wei, B., Yang, L., Zhu, O., Yu, J., Jia, X. (2014): Multivariate analysis of trace elements distribution in hair of pleural plaques patients and health group in a rural area from China. *Hair Ther. Transplant.*, **4**, 2167-3118.

WHO (1986): Asbestos and other natural mineral fibres. Programme on Chemical Safety. World Health Organization, Environmental Health Criteria 53, Geneva.