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X-ray microtomography: a new tool for investigating mineral fibres in geo-matrices

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Abstract

Over the last decades, many studies have been carried out on rocks containing Naturally Occurrences of Asbestos (NOA) with the aim of determining the potential health risks to human health. The recognition of NOA fibres in geo-matrices, in most cases requires the combined use of various analytical techniques (e.g., OM, SEM/EDS, TEM/EDS, XRPD) and therefore a specific preparation of the samples. However, the preparation procedure may disturb the specimens under study thus compromising the final results. X-ray microtomography (SR X-ray μ CT), is a non-destructive technique that allows the observation of the fibres arrangement in three-dimensional space, thus avoiding any morphological variation of the sample as a result of comminution.

Keywords: X-ray microtomography; natural occurrences of asbestos; serpentinite; marbles; metabasite

1. Introduction

Today, it is widely accepted by the scientific community that the exposure to asbestos may cause the development of health issues (e.g., mesothelioma, lung cancer, asbestosis;

Baumann et al., 2015; Bloise et al., 2019; Colombino et al., 2019; Harper, 2008; Petriglieri et al., 2019; Punturo et al., 2019a). Asbestos minerals are the main constituents of ophiolites (i.e. serpentinite and metabasite rocks); however, asbestos deposits have been also associated to ultramafic intrusion, serpentinitized carbonate rocks, marbles, as well as soils (Ross, 1981; Ross & Virta, 2001; Punturo et al., 2019b; Ricchiuti et al., 2020). Many studies focused on the mineralogical and geochemical characterization of asbestos-containing rocks by using various conventional analytical techniques, such as optical microscopy (OM), scanning electron microscopy with microanalysis (SEM/EDS), transmission electron microscopy with microanalysis (TEM/EDS), Raman spectroscopy and X-ray powders diffractometry (XRPD). Nevertheless, it is difficult to accurately characterize the asbestos fibres contained within the rocks since conventional techniques require a specific preparation procedure that might disturb the sample under study, thus affecting the final result. It is worth noting that, in order to avoid errors and/or misevaluations of asbestos findings, the preliminary step for the preparation of the samples according to the methods is regulated by law (e.g., Italian Ministerial Decree No. 06/09/1994; International Standardization Organization ISO/DIS 22262-2).

In recent years, the three-dimensional (3D) fabric analysis of rocks, using synchrotron radiation X-ray microtomography (SR- μ CT), has proved to be a useful tool for determining their properties (e.g., crystal size distributions, porosity and connectivity) through a non-destructive characterization (Militello et al., 2019; Punturo et al., 2019b).

2. Methods and material

In this work, we report some recent case studies that explore and adopt new techniques to determine the characteristics (i.e. size and geometric shape ratios) of asbestos minerals. In particular, we present results from synchrotron radiation X-ray microtomography applications for imaging asbestos fibres and vein arrangement within various host rock types.

2.1 SR- μ CT investigation and three-dimensional image analysis

The three-dimensional study of the rock samples was performed by synchrotron radiation X ray microtomography (SR- μ CT) measurements in phase-contrast mode (Cloetens et al., 1997) at the SYRMEP beamline of the Elettra synchrotron laboratory (Trieste, Italy). Each specimen was shaped into parallelepiped with size of about $4 \times 4 \times 20$ mm. Using a white beam configuration (Baker et al., 2012), a filtered (1 mm Si + 1 mm Al) polychromatic X-ray beam delivered by a bending magnet source illuminated the sample in transmission geometry. For each experiment, sample-to-detector distance was set to 200 mm and 1800 projections were acquired over a total scan angle of 180° with an exposure time/projection of 2 s. The employed detector was a 16 bit, aircooled, sCMOS camera (Hamamatsu C11440 22C) with a 2048×2048 pixels chip. The effective pixel size of the detector was set at $1.95 \times 1.95 \mu\text{m}^2$, yielding a maximum field of view of ca. 4 mm^2 . Since the lateral size of the samples was larger than the detector field of view, the microtomographic scans were acquired in local or region-of-interest mode (Maire and Withers, 2014). A single distance phase retrieval-preprocessing algorithm (Paganin et al.,

2002) was applied to the white beam projections in order to improve the reliability of the quantitative morphological analysis and enhance the image contrast.

The obtained 3D volumes were then imported in VGStudio Max 2.2 (Volume Graphics, Charlotte, NC, USA) for the 3D rendering and segmentation by manual thresholding.

3. Results and discussion

3.1 Mineralogical and Microstructural Features of Namibia Marbles: Insights about Tremolite Related to Natural Asbestos Occurrences

The Mg-rich marbles of Namibia are widely exploited and marketed abroad for ornamental purposes. In particular, Karibib marbles, commercially known as “White Rino Marble”, are characterized by the occurrence of tremolite-rich veins and therefore they represent an interesting case of study. Punturo et al. (2019b) describe in detail the mineralogical and petrographic characteristics of the main commercial marble in the Karibib area (Namibia, Africa). They investigated some selected marble samples by using various analytical techniques such as optical microscopy (OM), scanning electron microscopy (SEM/EDS), X-ray diffractometry (XRD), micro-Raman spectrometry, and synchrotron radiation X-ray microtomography (SR X-ray μ CT). Results revealed that tremolite occurs both in the matrix, with non-asbestiform habit, and in the vein as fibrous aggregates (Fig. 1a). Special attention was paid to X-ray microtomography results that evidenced the arrangement of fibres in the three-dimensional space. In particular, this technique allowed to image the three-dimensional network and intergrowth of nematoblastic (i.e. constituted of tremolite) and granoblastic (i.e. with dominant calcite and minor dolomite) levels as well as the geometry and reciprocal arrangement of constituting minerals into the marble samples, with special regard to the spatial relationship between calcite and tremolite (Fig. 1b).

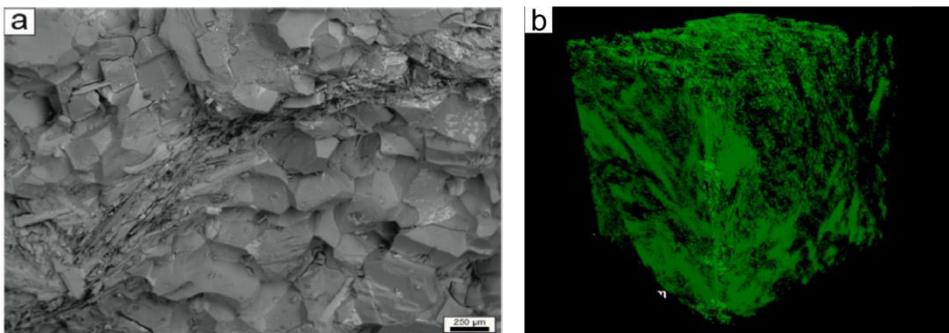


Fig. 1. a) scanning electron photomicrographs showing calcite-rich granoblastic bands cut by tremolite veins; b) 3D rendering of a selected part of analysed specimen; the green colour represents the highest-density phase (i.e. tremolite). Modified after Punturo et al. (2019b)

3.2 Multi-Analytical Approach for Asbestos Minerals and Their Non-Asbestiform Analogues: Inferences from Host Rock Textural Constraints

Militello et al. (2019), compared at different observation scales, by a multi-instrumental approach (OM, μ -Raman, SEM/EDS, TEM/EDS and SR X-ray μ CT), the morphological features and the influence of fabric constraints in several massive samples which determine the origin of fibrous and asbestiform or fibrous but non-asbestiform products, or rather the Elongated Mineral Particles (EMP) both from amphibole and serpentine groups. These EMP therefore comprise cleavage fragments of minerals belonging by composition, but not necessarily by morphology, to the group of asbestos.

Figure 2 shows an unpublished example on which morpho/mineralogical studies and bioassays are in progress. This is an amphibolite vein from Ligurian Alps (Italy), characterized by an intense presence of very elongated acicular amphiboles belonging to the actinolite-tremolite serie. In figure 2b, the three-dimensional network of the fibers can be clearly seen, thanks to the fact that this technique does not foresee the grinding of the sample and therefore preserves the original morphologies. The mineral near the top right vertex was included in the rendering due to the fact that density is similar to that of amphiboles.

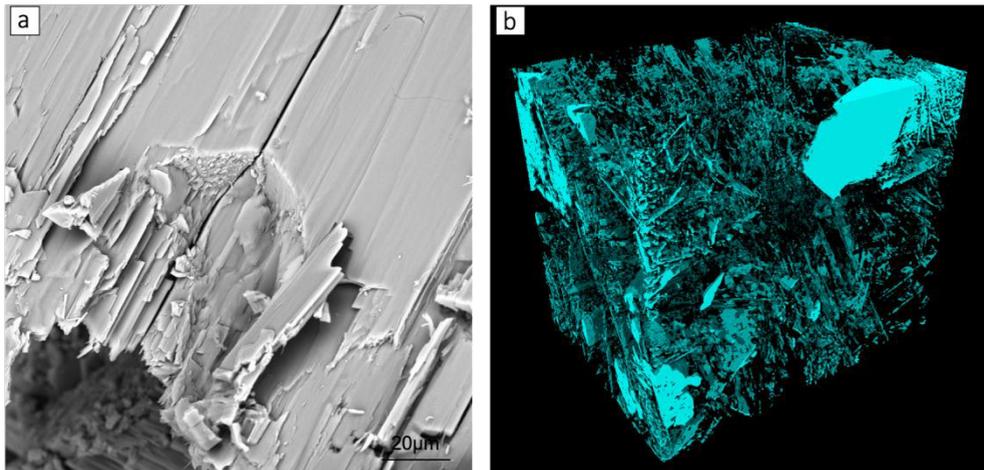


Fig. 2. a) SEM image of non-asbestiform tremolite (HV: 20 kV; Det: BSE); b) Volume rendering (7.7 mm^3) of amphibolite sample. The light blue represents the 3D distribution of the amphiboles of the tremolite-actinolite series

3.3 Synchrotron radiation X-ray microtomography: a new technique for characterizing chrysotile asbestos

In Bloise et al. (2020), synchrotron radiation X-ray microtomography (SR- μ CT) implemented with polarized light microscope (PLM), scanning electron microscopy

analysis combined with energy dispersive spectrometry (SEM/EDS), electron probe micro-analysis (EPMA) were used for identifying asbestos fibres in a mineral matrix of serpentinite rock samples. As a case study, Bloise et al. (2020), analysed a representative set of veins and fibrous chrysotile that fills in the veins, taken from massive serpentinite outcrops (Southern Italy). In particular, SEM morphological observations showed that most of the fibres are flexible and they were identified as chrysotile by means of EDS chemical analyses (figure 3a), whereas lizardite with lamellar morphology characterizes the massive serpentinite. Thanks to SR- μ CT, serpentine veins could be discriminated, and 3D imaged for the first time in massive serpentinite rocks. More specifically, a vein network of various shape and size types without any preferred orientation characterizes the analysed samples. Moreover, 3D images have been used to determine the size (i.e. width, length) of asbestos fibres, thus minimizing the disturb due to the sample preparation procedure.

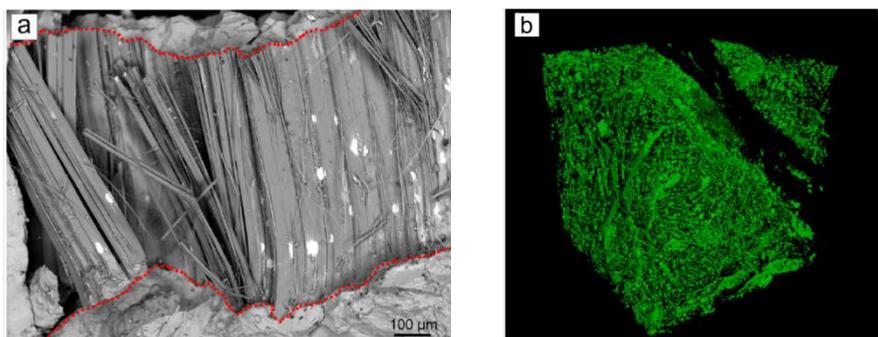


Fig. 3. a) SEM images of vein infill by chrysotile fibres bundles b) 3D rendering of serpentinite sample. The spatial distribution of the veins is shown as empty spaces between the matrix (in green). Modified after Bloise et al. (2020)

4. Conclusion

On the basis of the reported case studies, synchrotron radiation X-ray microtomography revealed to be a technique that offers the possibility to observe and image the 3D morphology and the spatial relationship between the mineral phases that constitute the investigated geologic matrices. Furthermore, it is a semi-destructive technique which allows the analysis of samples under high magnification without any grinding and/or the loss of their morphology. It is worth specifying that it provides also qualitative and volumetric information; therefore, it proved to be a complementary technique to other conventional ones, useful to implement the research, even though it is not actually listed in the existing legislative protocols in force environmental monitoring for quantitative data restitution (Gaggero et al., 2017; Militello et al., 2020).

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References

- Baker D.R., Mancini L., Polacci M., Higgins M.D., Gualda G.A.R., Hill R.J., Rivers M.L. (2012). An introduction to the application of X-ray microtomography to the three-dimensional study of igneous rocks. *Lithos* 148, 262–276. doi.org/10.1016/j.lithos.2012.06.008.
- Baumann F., Buck B.J., Metcalf R.V., McLaurin B.T., Merkler D.J., Carbone M. (2015). The presence of asbestos in the natural environment is likely related to mesothelioma in young individuals and women from Southern Nevada. *Journal of Thoracic Oncology* 10 (5), 731–737. doi.org/10.1097/jto.0000000000000506.
- Bloise A., Punturo R., Kusiorowski R., Pereira Gómez D. (2019). Editorial for special issue “mineral fibres”. *Fibres* 7, 54. doi.org/10.3390/fib7060054.
- Bloise A., Ricchiuti C., Lanzafame G., Punturo R. (2020). X-ray synchrotron microtomography: a new technique for characterizing chrysotile asbestos. *Science of the Total Environment* 703, 135675. doi.org/10.1016/j.scitotenv.2019.135675.
- Cloetens P., Pateyron-Salome M., Buffiere J.Y., Peix G., Baruchel, J., Peyrin F., Schlenker M. (1997). Observation of microstructure and damage in materials by phase sensitive radiography and tomography. *Journal of Applied Physics* 81. doi.org/10.1063/1.364374.
- Colombino E., Capella S., Casalnuovo F., Racco R., Pruiti F., Volante M., Di Marco Lo Presti V., Belluso E., Capucchio M.T. (2019). Malignant peritoneal mesothelioma in a boar who lived in Calabria (Italy): Wild animal as sentinel system of human health. *Science of the Total Environment* 683, 267–274. doi.org/10.1016/j.scitotenv.2019.05.254.
- Gaggero L., Sanguineti E., Yus González A., Militello G.M., Scuderi A., Parisi G. (2017). Airborne asbestos fibres monitoring in tunnel excavation. *Journal of Environmental Management* 196, 583–593. doi.org/10.1016/j.jenvman.2017.03.055.
- Harper M. (2008). 10th anniversary critical review: naturally occurring asbestos. *Journal of Environmental Monitoring* 10 (12), 1394–1408. doi.org/10.1039/b810541n.
- Maire E., Withers P.J. (2014). Quantitative X-ray tomography. *Int. Mat. Rev.* 59, 1–43. doi.org/10.1179/1743280413Y.0000000023.
- Militello G.M., Bloise A., Gaggero L., Lanzafame G., Punturo R. (2019). Multi-Analytical Approach for Asbestos Minerals and Their Non-Asbestiform Analogues: Inferences from Host Rock Textural Constraints. *Fibres*, 7, 42. doi.org/10.3390/fib7050042.
- Militello G.M., Sanguineti E., Yus González A., Gaggero L. (2020). Asbestos amphiboles: effects of comminution on tremolite and actinolite regulated and unregulated fibres. *Episodes* 43(3), 909-918. doi.org/10.18814/epiugs/2020/0200s09.
- Paganin D., Mayo S.C., Gureyev T.E., Miller P.R., Wilkins S.W. (2002). Simultaneous phase and amplitude extraction from a single defocused image of a homogeneous object. *Journal of Microscopy* 206, 33–40. doi.org/10.1046/j.1365-2818.2002.01010.x.
- Petriglieri J.R., Laporte-Magoni C., Gunkel-Grillon P., Tribaudino M., Bersani D., Sala O., Salvioli-Mariani E., (2019). Mineral fibres and environmental monitoring: a comparison of different analytical strategies in New Caledonia. *Geoscience Frontiers* in press. doi.org/10.1016/j.gsf.2018.11.006.
- Punturo R., Ricchiuti C., Bloise A. (2019a). Assessment of serpentine group minerals in soils: a case study from the village of San Severino Lucano (Basilicata, Southern Italy). *Fibres* 7, 18. doi.org/10.3390/fib7020018.
- Punturo R., Ricchiuti C., Rizzo M., Marrocchino, E. (2019b). Mineralogical and microstructural features of Namibia marbles: insights about tremolite related to natural asbestos occurrences. *Fibres* 7, 31. doi.org/10.3390/fib7040031.
- Ricchiuti C., Bloise A., Punturo R. (2020). Occurrence of asbestos in soils: state of the art. *Episodes* 43, 881-891. doi.org/10.18814/epiugs/2020/0200s06.
- Ross M. (1981). The geologic occurrences and health hazards of amphibole and serpentine asbestos. In: D.R. Veblen, (Eds). *Amphiboles and other hydrous pyriboles-mineralogy*. Reviews in Mineralogy, v. 9A, Washington, D.C., Mineralogical Society of America, p. 279-323.
- Ross M., Virta R.L. (2001). Occurrence, production and uses of asbestos. In: R.P. Noland, A.M. Langer, M. Ross, F.J. Wicks and R.F. Martin (Eds). *The health effects of chrysotile asbestos: Contribution of science to risk-management decisions*, The Canadian Mineralogist, Special Publication 5, Part 2, Exposure to commercial chrysotile – mineralogy, modern products and exposures, p. 79-88.