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Naturally occurring asbestos (NOA) in Albania

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Abstract

Naturally occurring asbestos (NOA) and possible health risk has not been studied in Albania during the last 20 years, though unwanted „mineral resources" are large due to the frequence of ophiolites. This study evaluates earlier exploration findings in terms of modern (local) mineral identification, environmental occurrence, behavior in the host environment and transport towards a risk assessment on asbestos exposure. At NOA outcrops soil, sediment, air and rock samples were collected. Optical microscopy, XPD, Raman spectroscopy and SEM-EDS were used to identify fibers. Asbestos was found at all outcrop locations, but not at all outcrop-distanced locations. Chrysotile was present at all locations; tremolite was found only in Boboshticë. Not all fibrous materials were regulated asbestos, so only macroscopic observations may result in the overestimation of health hazard. A multiple approach on the identification of asbestiform minerals is essential towards a correct risk assessment and successful prevention of human disease and life-threatening events.

Keywords: Asbestos; fibers; multiple approach; NOA; Albania

1. Introduction

The minerals defined as asbestos, including fibrous varieties belonging to the serpentine group and amphibole group are declared carcinogenic, and all mineral species of it can cause cancer (IARC 2012; World Health Organisation 2011), mainly affecting the

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respiratory system. Even if commercial asbestos fibers remain a serious problem, the recently recognised sources as 'Naturally Occurring Asbestos' also present serious risk (Case & Marinaccio, 2017). Possible exposure in the latter case is mainly related to human activities such as construction works (large objects: dam, tunnel or road affecting asbestos-bearing rocks; Marrocchino et al., 2020), agriculture in asbestos-containing soil(Ricchiuti et al., 2020), mining (asbestos-bearing other raw materials; Monterrubio et al., 2020). Even natural processes as weathering and erosion should be identified, evaluated and managed.

Naturally occurring asbestos (NOA) are reported to occur as accompanying minerals in ophiolitic environment, which consists of mafic and ultramafic rocks that previously underwent metamorphic and tectonic stages (Van Gosen 2007; Vignaroli et al., 2011). Since these rocks are used for several purposes as industrial and construction materials, it is essential that the risk assessment of asbestos exposure is taken into consideration and is managed (Pacella et al., 2010; Wylie & Candela, 2015).

Correct identification of asbestos fibers is crucial in the whole process of assessment and regulatory decisions. A proper differentiation should be applied in the case of asbestiform habit minerals and non-asbestiform varieties (cleavage fragment), in order to make a realistic evaluation (Belardi et al., 2018; Militello et al., 2020). Transportation path is also important when it comes to possible exposure evaluation. Asbestos fibers can be transported from the host rock to the soil, water or air.

1.1 Geologic setting of NOA in Albania

In Albania, mineralized outcrops are related to ultrabasic serpentinised rocks, concentrated in two ultrabasic rock belts, eastern and western (Tremblay et al., 2015), which are outcropping on a surface of 3000 km^2 (Fig. 1). Asbestos mineralization is found in five different geological settings in transformed ultramafic rocks (Mullaj, 1998).

Mineralization is usually related to serpentinites, intensively serpentinised peridotites that come from the alteration of peridotites (harzburgite, less frequently lherzolite). Serpentine minerals are mostly chrysotile (Buces, Shullan, Kaftallë-Gomsiqe, Boboshticë, Qafa e Trezhnjevës, etc.), and to a lesser extent antigorite.

Mullaj (1998) identified both chrysotile and amphibole asbestos. The latter (actinolite, tremolite) is of limited occurrences (Dishnice, Nikolicë and Qafa e Boboshticës).

Asbestos mineralization is mainly located in the structural-facial zone of the Mirdita ophiolite belt, which is characterized by a great extent of magmatic rocks, belonging to Middle to Late Triassic and Jurassic. In these zones, asbestos mineralization is usually located near the tectonic fault zones (Albanian Geological Survey report 1996). In some of the locations, the mineralized zone is described to be a hundred meters long and 50-150 meters deep. The average concentration of asbestos fibers is around 5%, and the average fiber length is in the range of 1-3 mm. Examples of these natural sources are the deposits of Qarrishtë, Gegaj, Boboshticë, and Korthpulë (Albanian Geological Survey report 1996).

In this paper we use the following asbestos-related terms in accordance to the general asbestos literature: ***fiber, fibrous, asbestiform, cleavage fragment, slip fiber, cross fiber.*** (World Health Organization, 2011; NIOSH, 2011)

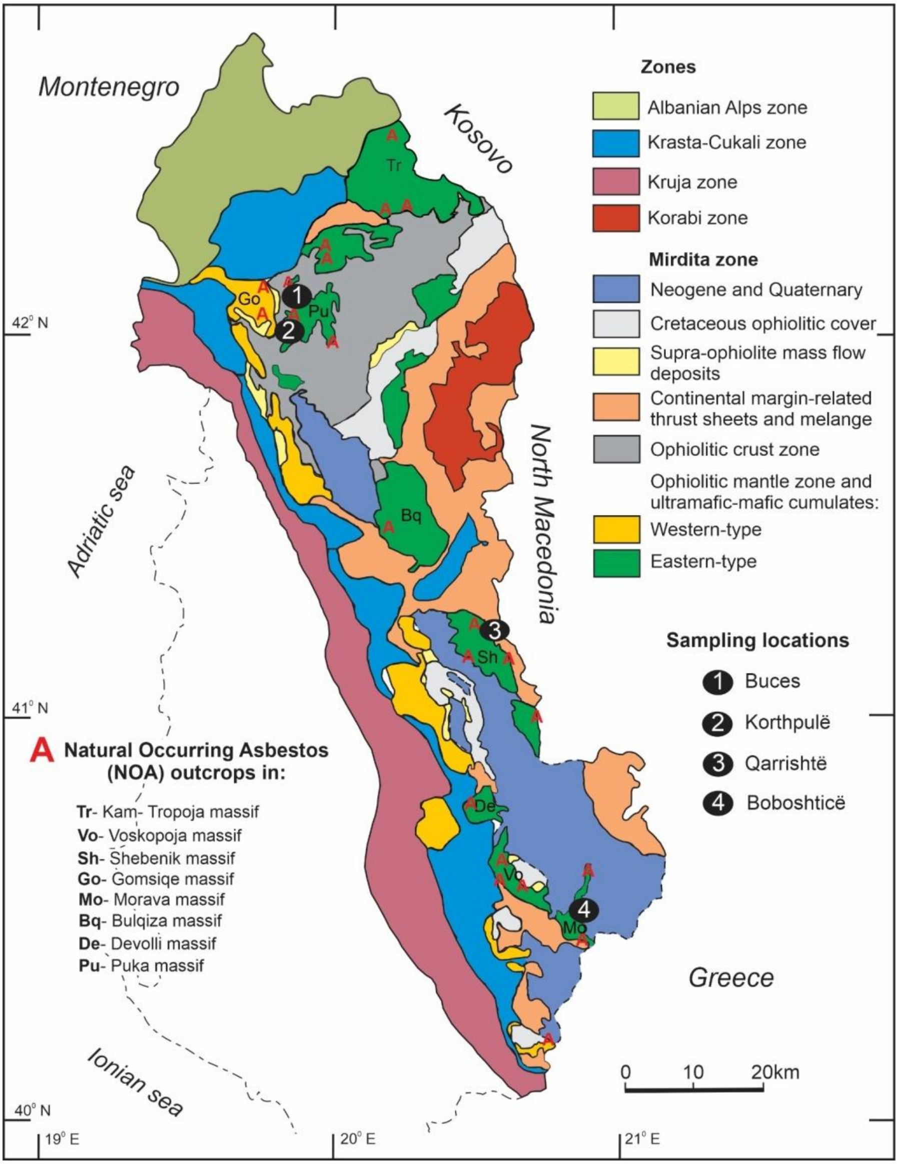

Fig. 1. Simplified geological map of Albania (modified from Tremblay et al., 2015).
Naturally Occurring Asbestos (NOA) localities (based on Mullaj, 1998) and sampling locations are shown

2. Materials and methods

There were four locations with surface outcrop presence of asbestos where samples were collected. These locations were chosen based on previous literature results, ability to reach the outcrop and the possibility to have samples from different massifs in Albania (Fig. 1). In total there were 20 samples (soil, rock, sediment and air) collected (Table 1), from which 18 of the samples were analyzed.

Table 1. Sample locations and types

Massif	Location	Sample Type			
		Rock	Soil	Sediment	Air
Puka massif	Korthpulë	3	2	4	1
	Buces	1	1	1	1
Devolli massif	Boboshticë	2	1	1	-
Shebenik massif	Qarrishtë	1	-	1	-

Rock samples were collected at the outcrop whereas soil, sediment and air samples were collected in different distances from the outcrop, aiming to understand the possible transport paths of asbestos fibers. While collecting the soil, sediment, and rock samples, precautions were taken to avoid dust creation and any kind of fiber contact in the field. A Gilian AIRCON-2 High Volume Air Sampler was used to collect the air samples (gold-coated filter: d = 25 mm, 0.8 μm pore diameter; 10 l/min flow rate; 20 minutes).

2.1 Sample preparation and analytical techniques

In order to have proper identification of asbestos fibers, a combination of various analytical techniques was applied (optical microscopy, X-ray powder diffraction - XPD, Raman spectroscopy, analytical scanning electron microscopy - SEM/EDS).

Soils and sediments were subjected to wet sieving. Grain size fractions <63 μm, 63–125 μm, 125–250 μm, 250–500 μm, and 500–1000 μm were studied separately.

XPD data were obtained at the Department of Mineralogy of the Eötvös L. University (SIEMENS D5000, Bragg-Brentano geometry, Cu Kα, secondary pyrolytic graphite monochromator, 2–65° 2Θ range, counting time: 2 seconds/step, step size 0.05°).

Raman spectroscopywas performed on selected grains and fiber bundles (from rocks, sieved sediment and soil samples), mounted on carbon glue (for later SEM microscopy). A confocal HORIBA JobinYvon LabRAM HR spectrometer was used (Nd:YAG laser (λ = 532 nm), 600 grooves/mm optical grating, 100 μm confocal hole, 1-24 s exposition time, 100× long working distance objective; 130 mW laser power at the source). Spectrum acquisition times (6-120 s) were adjusted to the maximum of the measured intensities and were repeated at least twice to avoid accidental counts (spikes).

Phase identification was based on RRUFF database (http://rruff.info). Visualization and evaluation of the spectra was realized by Spectragryph software (version 1.2.11; 2016-19).

SEM/EDS was used to study the shape of fibrous materials (hand-picked grains from sediments and solid rock fragments; both carbon coated and non-coated), as well as to analyze the fiber content of air filters (non-coated). Two scanning electron microscopes were used: 1) AMRAY 1830I + EDAX PW9800 + Moran multichannel analyserunit (acceleration voltage 20 kV, beam current 1 nA); 2) Hitachi TM4000 Plus + Quantax 75 SDD EDS system (acceleration voltage 15 kV, beamcurrent 0.8 nA (Mode 3), scan speed 20 seconds, environmental (low-vacuum) mode, back-scattered electron detector; EDX spectra collection: 1-15 keV; acquisition time 30s).

The SEM/ED Scounting of the fibrous particles on gold-coated air filters was doneon a virtual grid of 10x10 squares, each square (0.0154 mm^2, 143 μm x 108 μm, 2500 x magnification) was checked for fiber content. Counted fiber content was then normalized to the total surface area (415 mm^2) of the filter and the sampled air volume to calculate the fiber concentration of the air (ISO 14966:2019 Ambient air – Determination of numerical concentration of inorganic fibrous particles – Scanning electron microscopy).

3. Results and discussion

From the field study in the outcrops, serpentinite rocks were identified. The fibrous-asbestiform type of chrysotile was present in the rock samples collected at each of the four NOA outcrops (Figs. 2a, 2a2). The rocks were dark green (Fig. 2a) with silky-lustre white fibrous phases in cross-fiber arrangement, and occasionally hadbrownish-green, weathered appearance, too (Fig. 2a2).

The average macroscopic length of chrysotile fibers (Fig. 2a), identified in the Buces rock reached 2.5 mm. The diameter of the fibers/fiber bunches ranged from <1 μm to 3 μm (Fig. 2a1, 2a2). SEM/EDS data of the fiber bunches gave magnesium silicate composition. Raman spectroscopy was used for identifying chrysotile and excluding other potentially asbestiform magnesium silicates (serpentine: lizardite, antigorite; amphibole: anthophyllite - end-member formula $Mg_7[Si_8O_{22}](OH)_2$).

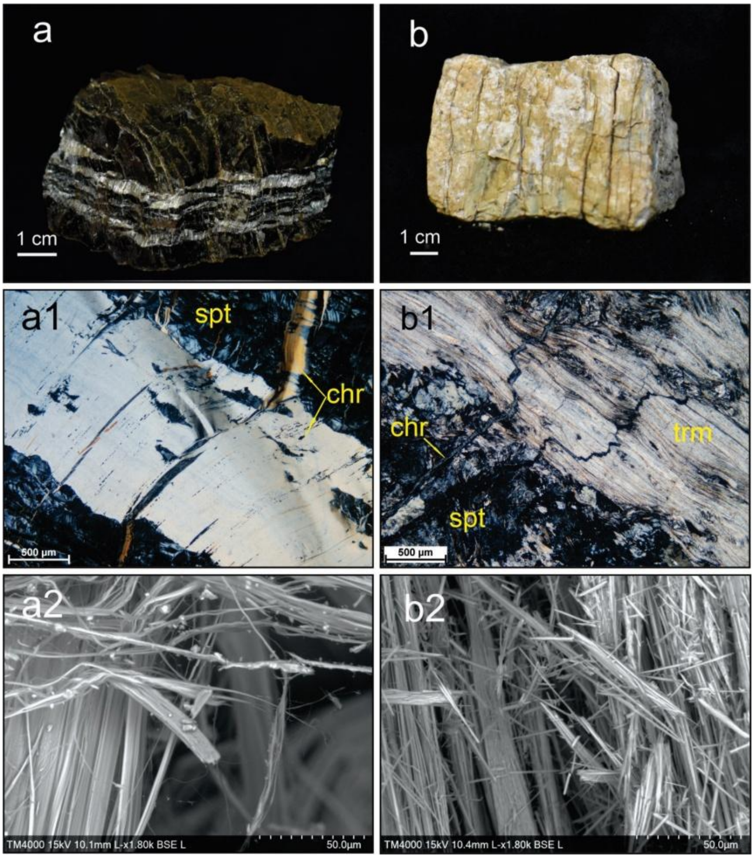

Fig. 2. a) White shiny chrysotile fibers in parallel layers, typical cross-fiber arrangement (Buces outcrop). Fibrous veins are hosted by dark green serpentinite. a1) Thin section photomicrograph of chrysotile cross fibers (chr) in the serpentinite (spt) host rock in cross-polarized light a2) SEM BSE image of the same asbestiform chrysotile, the curly appearance is a diagnostic feature. b) White asbestiform tremolite at the surface (slip fibers) of the serpentinite rock sample (Boboshticë outcrop). b1) Thin section photomicrographs of tremolite slip fiber vein (trm) in the serpentinite (spt) host rock, crosscut by asbestiform chrysotile (chr) in cross-polarized light. b2) SEM BSE image of asbestiform tremolite, showing stiff straight fibers, typical of amphibole asbestos

Fibrous material with slip-fiber texture was found in one case (Fig. 2b, 2b1, 2b2), identified as tremolite by Raman spectroscopy, and confirmedbySEM/EDS spectra, yielding Ca-Mg-silicate composition. This rock sample found in Boboshticë outcrop was the only rock sample with fibrous amphibole-group mineral. The asbestiform habit of tremolite was confirmed by SEM-BSE image, too (Fig. 2b2)

Table 2. Occurrence of asbestiform minerals present in the samples analysed

Location	***Sample type***			
	Rock	**Soil**	**Sediment**	**Air**
Korthpulë	chrysotile	-	chrysotile, antigorite, amphibole*	
Qarrishtë	chrysotile	-	chrysotile, antigorite**	
Buces	chrysotile	chrysotile, antigorite**	chrysotile, antigorite**, tremolite	chrysotile
Boboshticë	chrysotile, tremolite	-	-	-

*amphibole mineral identified but no asbestiform habit was found
** antigorite detected with fibers/laths having a diameter/width of <1 μm

In the sediment samples, apart from chlorite, quartz, talc, olivine and pyroxene, amphibole-group mineral (visually non-asbestiform) and serpentine group minerals (antigorite and chrysotile) were identified by X-ray powder diffraction and Raman spectroscopy. In soil samples asbestiform chrysotile was found in Buces, mostly in the size range 125–63 μm. In the same outcrop, lamellar aggregates were found, too, identified as antigorite by Raman spectroscopy. The lamellar morphology was evident in the SEM secondary electron image showing fibers/laths with diameter/width of <1 μm (Fig. 3a). The physical degradation of these particles would clearly yield WHO fibers (Fig. 3a1).

In the Buces air sample (Fig. 3b) 5 fibers have been counted, yielding a fiber concentration of 6.7 fibers/l. Even if further fiber bunches were identified as asbestiform chrysotile (Fig. 3b) none of them was countable fiber based on analysis protocols (ISO 14966:2019). This 6.7 fibers/l fiber concentration is below the permissible exposure limit (PEL) for asbestos workers (0.1 fibers/cm^3, i.e., 100 fibers/l on an 8-hour time-weighted average, 2009/148/EC Directive). It shall be noted that only above the 100 fibers/l concentration wouldprotective wear (breathing equipment) be necessary in the case of workers in asbestos removal projects. The Korthpulë air sample was free of fibers.

In one of the Korthpulë rock samples, slip fibers were identified apart from the common cross fibers. Together with the serpentine group minerals, the presence of brucite (Mg(OH)2; 4.74 Å; occasionally fibrous – variety nemalite) and pyroaurite-2H (Mg6Fe3+2 (OH)16(CO3) 4H2O; usually reported to be lamellar) were indicated (Fig. 3c, 3d) by X-ray powder diffraction. The fibers were easily powdered in the agate mortar, already suggesting the presence of non-typical asbestos fibers (these are difficult to powder). So far, the three phases have not yet been resolved spatially, they appear together in the Raman spectra (Fig. 3e).

Referring to the mineralogical and legal definition point of view, which classifies asbestos minerals into chrysotile and amphibole asbestos, we can say that at all studied locations asbestos minerals were found (Table 2).

4. Conclusions

Asbestos minerals were found in four natural outcrops were asbestos was previously detected. In rock samples chrysotile asbestos was identified in all four locations, while tremolite asbestos was found only in Boboshticë. Chrysotile asbestos was mostly present in a cross-fiber texture, while tremolite asbestos was found as slip-fiber. In a rock sample with slip-fiber texture at Korthpulë, brucite and pyroaurite-2H were associated with serpentine-group minerals. In sediment samples antigorite was found as lamellar aggregates. At this case, physical degradation of the laths will on the long term yield WHO fibers.

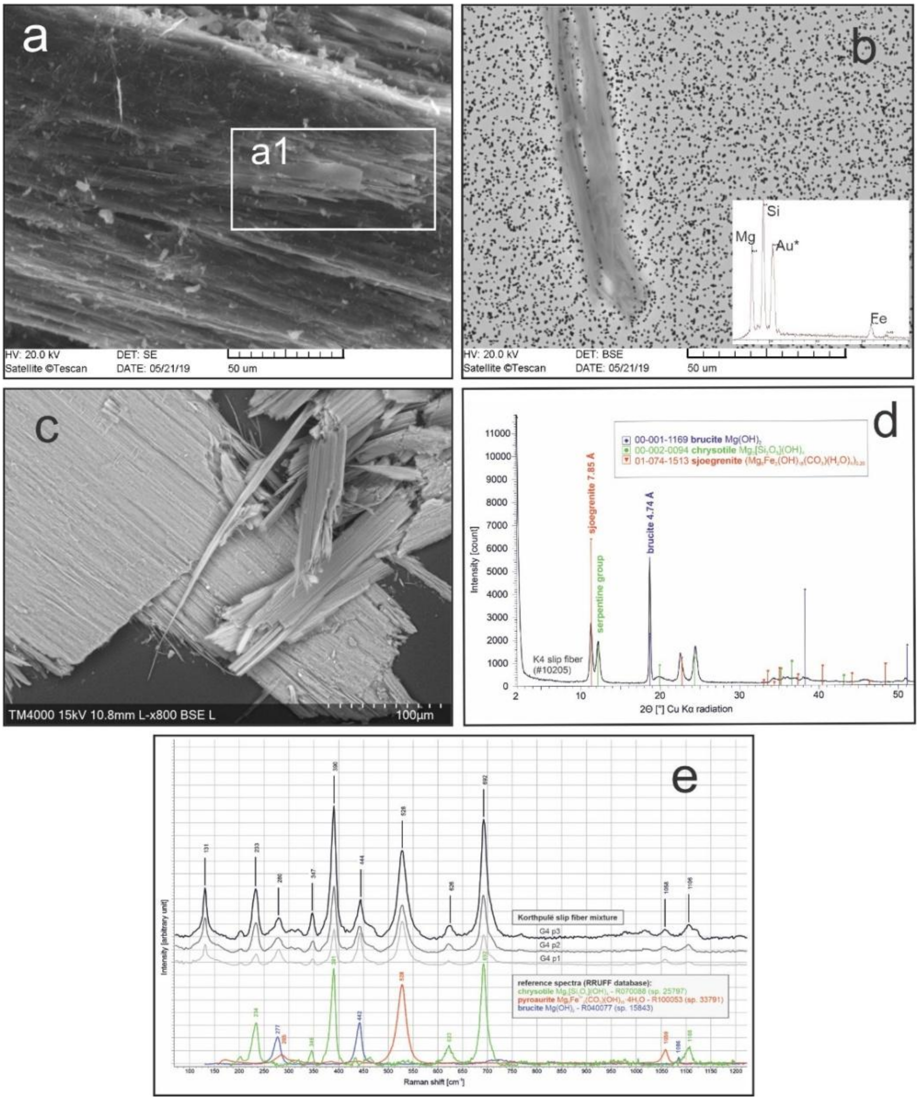

Fig. 3. a) Secondary electron image of a lamellar aggregate of antigorite, a1) degrading part with visible fibers/laths. b) Back-scattered electron image and EDX spectrum of a chrysotile fiber bunch in air sample. The fiber bunch in its present form exceeds the WHO fiber size criteria, though it is evident it may physically degrade to smaller WHO fibers in air. c) Back-scattered electron image of slip fibers in a rock sample from Korthpulë, where besides chrysotile, pyroaurite-2H (sjoegrenite is a synonym of pyroaurite-2H) and brucite were identified, too (d). e) Raman spectra of the slip fiber mixture, showing the same components in varying proportions. Although microscopically not distinguishable, pyroaurite-2H and brucite are major phases besides chrysotile. Au* Due to the gold coating of the filter and the small size of the particles, Au was always present at the EDX spectrum of the particles

No asbestiform materials were found to be transported to longer distance from the natural outcrops of asbestos-hosting rocks. In soil samples chrysotile fibers and lamellar antigorite were found only in Buces, where further investigation is needed regarding the use of the soil near the outcrop.

In addition to the abundant contamination of soil in Buces, countable fibers were found in one air sample, indicating a possible exposure risk to asbestos fibers spread in the environment around the natural outcrop, with fiber concentration being 6.7 fibers/l. Still, a standard protocol for the determination of numerical concentration of inorganic fibrous materials needs to be followed in order to give realistic estimations on the presence of asbestos particles in the air. Together with such procedures it is always important to include various analytical techniques in order to avoid overestimation (see, e.g., the presence of non-asbestos fibers) while having results based only on macroscopic observations.

The natural asbestos occurrences in Albania need further study in order to give proper estimations for the possible health risk from NOA exposure. The airborne exposure due to human activities or natural processes poses health risk to whoever lacks information on the presence and the hazard of asbestos minerals.

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