## ASBESTOS: A REVIEW WITH SPECIAL EMPHASIS ON NATURAL CARPATHIAN-DINARIC OCCURRENCES

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#### A technological material with drawbacks

Asbestos used to be an industrial term for fibrous silicate minerals with a large number of industrial applications, including insulation (heat, electricity, noise, etc.) and friction materials (brake linings), engineered materials (fibre-reinforced composites like asbestos cement) and textiles (fire-resistant clothing) among others. The first use of these minerals dates back to the Stone Age, probably as earthenware reinforcing additive, followed by applications like lamp wicks, cremation clothes and other textiles. Since that time, asbestos has been in use continuously, with large scale mining and applications blooming in the first half of the 20<sup>th</sup> century.

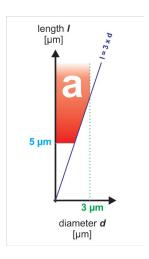
Dusty environment has often accompanied the mining, processing and occasionally also the end-use of asbestos. Data on the deleterious health effects of asbestos dust, in the first place related to the inhalation of asbestos fibres (the main associated diseases are asbestosis, lung cancer and mesothelioma), accumulated gradually. Consequently, workplace asbestos dust permissible exposures got gradually limited, and asbestosbearing products have been first limited, later prohibited in most industrialised countries. Asbestos removal from the built (man-made) environment has become a major issue, removal, waste treatment and safe deposition requiring large expenditure from the industrialised societies. Large sums are spent on compensations for asbestos-related diseases, too. While asbestos is being removed from the man-made environment in the developed countries, it is still widely applied and built into the man-made environment in the developing and undeveloped countries, due to its cheapness and good technological performance. In these latter countries, safe working conditions are often lacking, too. Whatever the final fate of these minerals, it is clear that asbestos plays an important role also in the 21<sup>st</sup> century.

### Current legislation in Europe and Hungary

Based on the long and broad-range experience of mankind with asbestos, one would surely think that asbestos is a clear term. From the human health-concerned, legal point of view (Directive 83/477/EEC, repealed by 148/2009/EC), fibres of the serpentine mineral chrysotile and the amphiboles "crocidolite", grunerite ("amosite"), actinolite, anthophyllite and tremolite are to be called asbestos, if they are longer than 5  $\mu m$ , thinner than 3  $\mu m$  and their length : diameter (aspect) ratio is larger than 3 : 1 (WHO, 1997; Fig. 1). Simple as it sounds, it includes a lot of ambiguities and confu-

sions, both on the mineralogical and the morphological side

The only allowed activities related to asbestos are treatment and disposal of products resulting from demolition and asbestos removal (148/2009/EC; Hungarian legislation: 4/2011. (I. 14.) VM order), mining and processing is prohibited in Europe. Workplace exposure limit for asbestos fibre concentration in air is set at 100 fibre/dm³, as an 8-hour time-weighted average (TWA). If workers are exposed to higher concentrations, they shall be issued with suitable respiratory and other personal protective equipment. In Hungary, additional permissible exposure limits are defined, too (12/2006. (III. 23.) EüM order): 10 fibre/dm³, as control after asbestos removal; 1 fibre/dm³, as general background.



**Fig. 1.** Morphological definition of asbestos fibre, white "a" on red background being the international symbol of asbestos.

Asbestos concentration in air should be determined by phase contrast microscopy (PCM, 148/2009/EC), measurement and fibre counting guidelines according to WHO (1997). Hungarian legislation also includes control analysis by scanning electron microscopy (4/2011. (I. 14.) VM order; not yet in daily practice).

Currently, all the declared asbestos minerals are regarded as Type I carcinogens by the WHO International Agency for Research on Cancer (IARC, 2012), irrespective of the fact that chrysotile is far less harmful than the fibrous amphiboles. Luckily enough, around 90% of asbestos use involved chrysotile, and the rest is mainly crocidolite and amosite.

# Gaps between current legislation and current knowledge on asbestos

In spite of the large expenditure related to the "asbestos issue", legislation is decades behind the current knowledge on these minerals.

The mineralogical criterion is poorly defined. The six "declared" asbestos minerals are chrysotile (white asbestos; CAS# 12001-29-5) from the serpentine group, and five members of the amphibole group, namely, riebeckite (common name crocidolite or blue asbestos; CAS# 12001-28-4), grunerite (common name amosite or brown asbestos; CAS# 12172-73-5), anthophyllite (CAS# 77536-67-5), tremolite (CAS# 77536-68-6) and actinolite (CAS# 77536-66-4). These minerals are identified in most laws by their CAS registry numbers (CAS#), a US chemical database identifier with practically no structural data and only approximate chemical composition. The recently used CAS registries were created in 1984, and are based on the industrially applied fibrous silicates. Since then, amphibole nomenclature has been largely restructured (LEAKE et al., 1997, 2003). As a consequence of the discrepancy, the Bolivian "blue asbestos", used in industrial applications, is classified as magnesioriebeckite (RRUFF database) by the current amphibole nomenclature, offering a potential escape route in legal cases. Legislation is also behind the scientific knowledge in terms of minerals that were "accidentally used" as minor components of industrial raw materials, and have similar health effects to the "classic" asbestos fibres. These include the fibrous variety of the amphibole fluoroedenite in the hydrothermally altered tuffaceous rocks of Biancavilla (Sicily, Italy), and the fibrous forms of the amphiboles richterite and winchite (mixed under the vermiculite of Libby, Montana, USA). Recently, health concerns have also been raised about fibrous antigorite (CARDILE et al., 2007).

The morphological definition of an asbestos fibre seems straight forward, though amphiboles complicate fibre counting, as amphibole cleavage fragments overlap with the fibre size range. These fragments can thus contribute to the apparent fibre concentration in air, yet having a rather inert health impact, risk can be overestimated. Amphibole cleavage fragments usually derive from natural sources, not from anthropogenic materials.

## Asbestos in the natural environment: a growing concern

Asbestos fibres form part of our natural environment, too, and both natural and disturbed outcrops (e.g., road-cuts, open-pit asbestos mines) may pose health risks to the inhabitants. Asbestos fibres are different from most risk agents: they do not carry chemical risk (no soluble toxic element content, no acidic dissolution), risk is purely associated with the fibres becoming airborne and inhalable, and to a lesser extent, contaminating waters and becoming ingestible.

In Europe, these occurrences are mainly related to serpentinised ultramafic-mafic rocks of ophiolitic origin. As these occurrences are not engineered, anthropogenic fibre sources, with usually well-known (easy to identify) asbestos type(s), they need special attention and a clear environmental mineralogical approach. To assess the real health risks related to natural outcrops, the routine phase contrast microscopy fibre counting method may not be sufficient, especially as a number of minerals exist in acicular to fibrous form. Both morphological and chemical (structural) information is needed to identify the airborne fibres, best performed with the combination of scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

In this work, the first results will be presented on disturbed outcrops of the Carpathian-Dinaric region.

The first example is a disturbed natural outcrop (Fig. 2), the east-west trending ridge of the Parâng Mountains, Southern Carpathians, Romania, cut by the north-south trending road 67C (Transalpina). The few 100 meters long roadcut exposes tectonically deformed serpentinite blocks that contain pale green, splintery to fibrous antigorite (weathering to thin laths fulfilling the size criteria of asbestos fibre, Fig. 3) and vein filling, silky white, slip-fibre tremolite (Fig. 1). The young (2–3 years old) roadcut is not consolidated, weathering goes on, bunches of tremolite up to 10 cm length can be found along the road. The soil (regolith) is occasionally a fibrous mass of antigorite and a subordinate amount of tremolite, and both minerals produce airborne particles. The surroundings are not inhabited, road construction / maintenance workers, tourists and local shepherds may be exposed to the fibrous dust on the open, often windy road. The first air analysis yielded 17 fibre/dm<sup>3</sup> (tremolite counted only), 35 fibre/dm<sup>3</sup> (tremolite and antigorite counted), suggesting that covering of the most weathering rock surfaces may be useful. Further information on the locality is given by TOPA et al. (2012).

Of special interest are the former asbestos mines, some of which, right in the Carpathian-Dinaric region, are still awaiting rehabilitation (e.g., Dobšiná, Slovakia; Korlaće and Stragari, Serbia). Here, uncovered serpentinite rock surface, unprocessed serpentinite debris, "rock flour" (crushed and ground, processed serpentinite with residual asbestos content) and process dust may be the source of asbestos fibres. Most of the unprocessed debris and processed material are deposited as waste dumps in the mine surroundings. Processing (crushing and grinding) of the serpentinite enhances the possibility of fibrous dust formation. Fibre dissemination by means of erosion and water needs to be tested, too. The first environmental mineralogical studies on these localities are presented by GROZDICS et al. (2012, this volume - Dobšiná, Slovakia) and HARGI-TAI et al. (2012, this volume - Korlaće and Stragari, Serbia).

In the European Union, examples exist for almost complete asbestos mine rehabilitation (*e.g.*, MABE, Kozani Prefecture, Northern Greece), too, offering a good opportunity to compare the environmental impact of rehabilitated and non-rehabilitated mines.

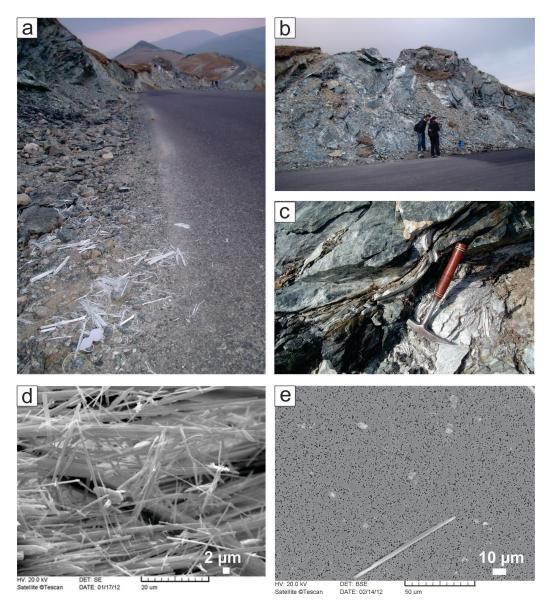


Fig. 2. a: Eastwards oriented photo of the Parâng pass with white tremolite asbestos bunches at the roadside. b: Road cut with white tremolite veins in the greenish serpentinite. c: Slip-fibre tremolite. d: Tremolite bunch, with most long fibres fulfilling the size criteria of an asbestos fibre (SE image). e: Tremolite asbestos fibre on the air sampling gold filter (BSE image). Work of TOPA et al. (2012).

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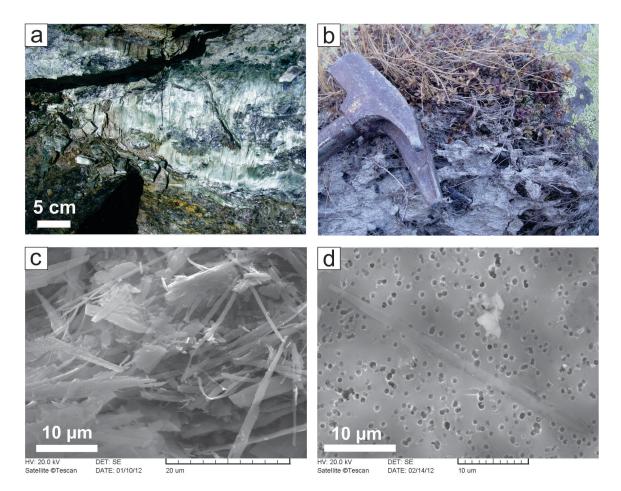


Fig. 3. a: Silky green antigorite at the Parâng pass. b: Fibrous regolith (primitive soil) form the surroundings of the road. c: Antigorite laths from a soil sample, most long laths on the picture fulfilling the size criteria of a fibre (SE image). d: Antigorite lath (fibre size) on the air sampling gold filter (SE image). Work of TOPA et al. (2012).