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SERPENTIN MINERALS IN SOME GEOCHEMICAL SAMPLES FROM THE BORDER CROSS BLACE (REPUBLIC OF MACEDONIA)

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ABSTRACT: The results from the examination of the presence of serpentine minerals in some geochemical media (air and soil) from the border cross Blace are presented in this paper. The presence of the serpentine mineral of chrysotile type in samples of air and soil is unambiguously shown.

Keywords: asbestos; air; soil; Blace; investigations

INTRODUCTION

Until recently serpentines minerals were considered very attractive for research because they are the last group of minerals, components of rocks, with incompletely elucidated structural polytypes as well as not thoroughly defined thermodynamic conditions of formation. The serpentine minerals are divided into chrysotiles, lisardites and antigorites, and in the last few years another group of so called polygonal serpentinites is established (Kunze, 1958; Zussman et al, 1975; Uehara & Shirozu, 1985).

The chrysotile (Midgley, 1952; Melini, 1982) group is considered as the most important having in mind that chrysotile (usually called white asbestos) is the most abundant serpentine mineral. In terminology asbestos is referred to natural silicate minerals with fiber forms and crystalline structure. Besides the serpentine group, asbestos includes: the **amphiboles** group which contains **amosite** (brown or gray asbestos), **crocidolite** (gray asbestos), **tremolite, actinolite** and **anthophyllite**. There are a lot of minerals with fiber forms, which are not considered as asbestos because of their other characteristics.

The asbestos minerals have many commercially important characteristics such as hardness, elasticity, thermal and chemical resistance.

Putting asbestos in the group of minerals harmful for the human health greatly intensified the interest for research in this field of mineralogy. When materials containing asbestos are damaged or destroyed, they can release fibers in the air, which can be inhaled and then show their effects. The main negative effects for the human health due to exposure to asbestos in the air are well known: asbestosis, lung cancer and **mesothelioma.** In spite of many data about these diseases, the mechanism of the development of the disease caused by asbestos is still not elucidated.

The aim of this work is examination of the serpentine minerals-asbestos in samples of air and soil from the lokality of Blace.

METHODOLOGY OF COLLECTING THE SAMPLES

Soil

The soil samples were collected from area of 2 m^2. First, the upper layer was cleaned from leaves, grass, roots, bigger stones, and then samples were taken with a combined probe (6 times). The collected soil was dried at 240 °C for 24 hours and after that milled and sowed with a 200 mesh sieve.

Air

The air samples were taken with a high volume sample collector type EBERLINE with flow rate of 40 l/min and filter Sofiltra-France, Schneider-Poleman blue (d = 4.5 cm) with 75 % efficiency of retaining of aerosols. The principle of sampling is to keep all the fractions of flying particles with various sizes on the filter. This way all total suspended particles (TSP) are filtrated.

EXPERIMENTAL

The collected samples were treated using special methodology. For the soil sample the procedure includes sample preparation by grinding, sowing and concentration, and then optical methods for treatment. The pretreated samples were then analyzed using X-ray diffraction method, infrared spectroscopy, differential thermal methods and scanning electron microscopy.

As for the air samples, the filters were examined using optical methods and infrared spectroscopy, as well.

RESULTS

The treatment of the soil samples was carried out in two phases. In the first phase, all the materials (mineral forms) with crystallographic characteristics similar to those of the minerals of the serpentine group, i.e. asbestos, were separated from the sample. The minerals content of the soil sample was approximately established in this phase, too. Quartz, clay minerals, carbonates, mica and pyroxenes were identified in the sample together with a great quantity of organic residues, waste materials and some forms of snails.

In the second phase, after a detailed optical treatment of the sample *two* mineral types with similar optical and crystallographic forms to the serpentine group, i.e. to chrysotile asbestos, were isolated.

General characteristics of the ***first*** mineral having longer fibers are the following: white color, form of fiber aggregates lengthened and ending with many little fibers. These forms split into even smaller fiber aggregates when subjected to small pressure (Fig. 1 and Fig. 2). This isolate was very difficult for preparing a good object for microscopic study, which nevertheless indicated that it is a chrysotile type of mineral. Its abundance in the analyzed soil sample was relatively high (0.2 mg/200 g soil sample).

Fig. 1. Microscopic aggregates of serpentine mineral chrysotile (Mob. 20 X H +)

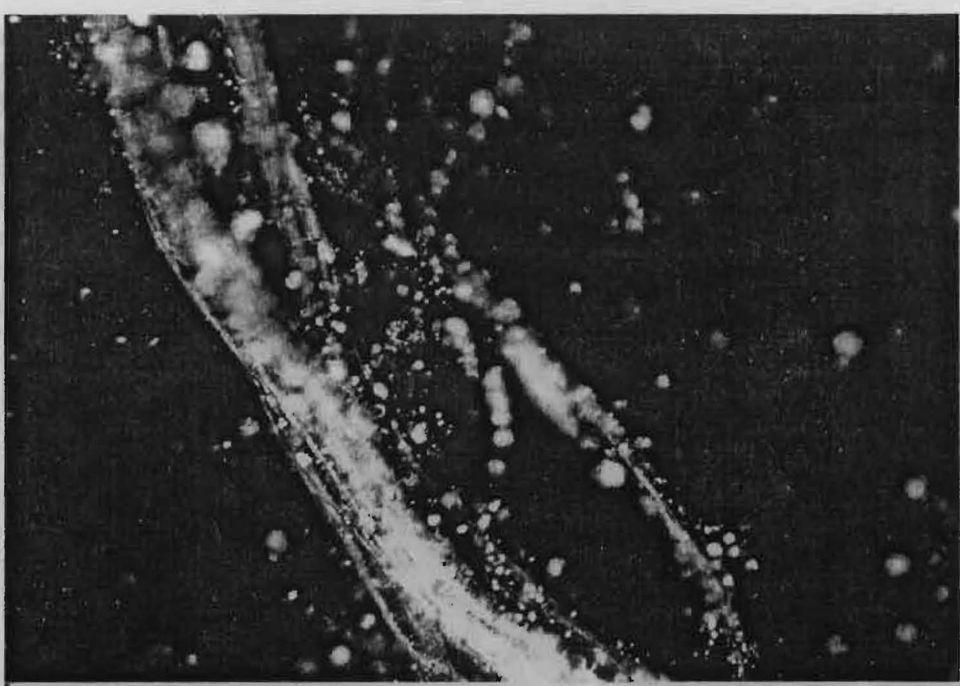

Fig. 2. Microscopic aggregates of serpentine mineral chrysotile (Mob. 20 X H +)

The prepared material was then subjected to further analysis using four different methods: infrared spectroscopy, differential thermal analysis, X-ray diffraction and scanning electron microscopy.

The results from the X-ray diffraction were not as expected, which can be explained by presence of semicrystal and fractionally amorphous forms in the sample. An X-ray diffraction's result suggests that this mineral form has been in the soil for a long time, which caused degradation of the primary structure (this research continues).

The Fourier Transformed Infrared (FTIR) spectra of this first isolate were also recorded, which were then compared with the ones of some asbestos samples and of some materials with confirmed presence of asbestos (Fig. 3). Here, it should be mentioned that the sample isolate was not very pure, but had some other components attached to the fibers. In its infrared spectrum, according to the structural data for asbestos (Farmer, V. C.) with free and hydrogen bonded OH groups, in the OH stretching region, sharp bands above 3600 cm^{-1} and a broad one at around 3400 cm^{-1} appear. In the region under 1000 cm^{-1}, bands which can be attributed to vibrations of the SiO_4 groups are found. Having this in mind, we can identify this sample as a silicate material. The close similarity of its spectrum with the ones of the asbestos materials implies that it is an asbestos material, as well.

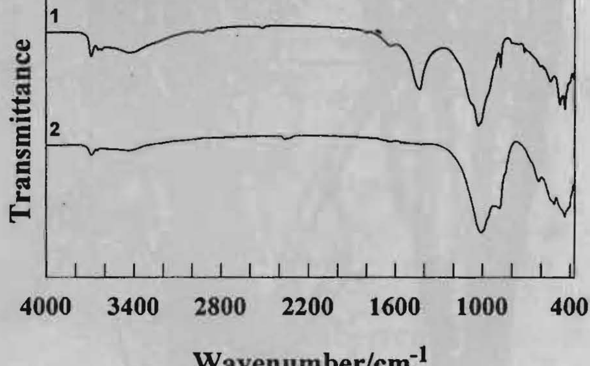

Fig. 3. The FTIR spectra of serpentine minerals in soil (1) and asbestos (2)

The *second* isolated mineral was characterized by white color and shorter fibers, which are separated into smaller ones under pressure. Microscopic examination showed that this mineral was more crystalline and not subjected to transformations, as was the first one. The abundance of this mineral was very low, which made impossible its quantification as well as X-ray diffraction analysis. The microscopic photographs of this chrysotile are shown in Fig. 4 and Fig. 5.

Fig. 4. Microscopic aggregates of serpentine mineral chrysotile (Mob. 20 X H +)

Fig. 5. Microscopic aggregates of serpentine mineral chrysotile (Mob. 20 X H +)

As already mentioned, four filters with air samples were collected. They were optically treated and then all the minerals with characteristics of serpentine minerals, asbestos type, were carefully isolated. The further optical treatment of the isolated material clearly indicated a serpentine mineral of the chrysotile type (Fig. 6). If we compare the quantity of the analyzed material with the time of collection and the volume of air passed through the filters, it is evident that the quantity of these minerals in air can be neglected. The remainder on the filters was burned and this residue was exanimate by X-ray diffraction, which indicated the presence of quartz and degraded carbonates. Infrared spectrum of the collected minerals was recorded as well (Fig. 7-1). This spectrum is almost identical with the one of the soil sample (Fig. 7-2) which confirms that the material isolated from the soil and from the air is practically the same.

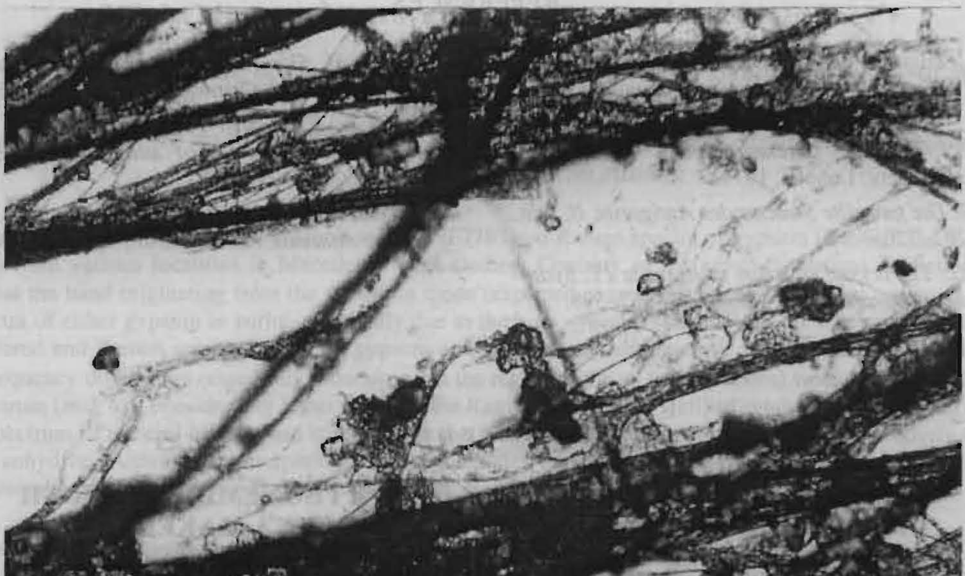

Fig. 6. Microscopic aggregates of serpentine mineral chrysotile (Mob. 20 X H +)

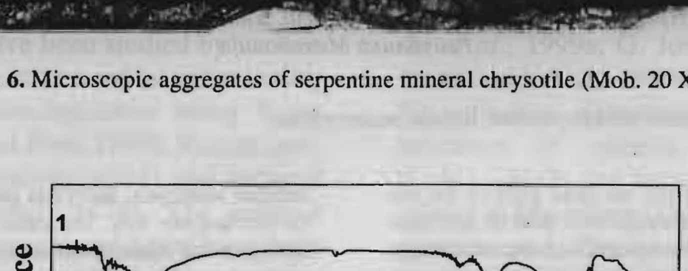

Fig. 7. The FTIR spectra of serpentine minerals in air (1) and soil (2)

CONCLUSION

Complex mineralogical examination was performed on soil and air samples for identification of serpentine minerals, particularly asbestos. The presence of serpentine minerals of the chrysotile type in both media was detected in very low concentration. Only one of the minerals was found in significant quantities in the soil samples. Its optical characteristics and infrared spectra suggested that it is a serpentine mineral, but the X-ray diffraction results did not support this assumption. This disagreement can be explained by transformations during the prolonged stay of the mineral in the soil. Further analyses of this mineral are in progress and will be reported soon.

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Резиме

СЕРПЕНТИНСКИ МИНЕРАЛИ ВО НЕКОИ ГЕОХЕМИСКИ ПРОБИ ОД ГРАНИЧНОТО МЕСТО БЛАЦЕ (РЕПУБЛИКА МАКЕДОНИЈА)

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Клучни зборови: азбест; воздух; почва; Блаце; испитувања

Како генерален заклучок од оваа работа би можело да се каже дека во материјалите кои се доставени за анализа е утврдено присуство на серпентински минерали од типот на хризотил, и тоа во двете средини, со забелешка дека концетрацијата е многу мала. Само во почвата е утврдена поголема количина на еден минерал, чии оптички особености и инфрацрвените спектри укажуваат дека станува збор за серпентински минерал, меѓутоа рендгенската дифракција не го потврдува тоа. Во оваа фаза сметаме дека тој е продукт на трансформација на серпентинските минерали како последица на неговото подолготрајно присуство во почвата. Додатните истражувања на овој минерал (минералот со подолги влакна, кој е опишан во извештајот) се во тек и тие резултати дополнително ќе бидат објавени.