PRESENCE OF ASBESTIFORM MINERALS IN VERMICULITE. PROVINCE OF CORDOBA, ARGENTINA

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Abstract: *Presence of asbestos in a vermiculite mine was identified in Argentina. Vermiculite has the property of expanding itself nearly 20 times its original size when heated. This process, called exfoliation, releases asbestos fibers from the vermiculite ore into the air, where they can be inhaled by people who work in the mines or live in bordering zones. Inhalation of asbestos fibers suspended in air can result in lung diseases such as asbestosis, mesothelioma and lung cancer.*

Introduction

Vermiculite is a naturally occurring sheet silicate mineral; its chemical formula is $(Mg,Fe^{2+},Al)_3(Si,Al)_4O_{10}(OH)_2.4H_2O$, and it is usually formed by the hydrothermal alteration of mica minerals such as biotite and phlogopite [1, 2].

All vermiculite ores contain a range of other minerals that were formed along with the vermiculite in the rock [3]. There may be major components such as feldspars, pyroxenes, amphiboles, carbonates, and quartz, as well as minor components such as phosphates, iron oxides, titanium oxides and zircon [4].

Asbestos is a group of highly fibrous minerals with separable, long, thin fibers often arranged in parallel in columns or in matted masses [5]. Separated asbestos fibers are generally strong and flexible enough to be spun and woven, they are heat resistant and chemically inert [6]. OSHA (Occupational Safety and Health Administration) and EPA (Environmental Protection Agency) recognize six asbestos minerals: the serpentine mineral, chrysotile; and five asbestiform amphibole minerals, actinolite, tremolite, anthophyllite, amosite (also known as asbestiform cummingtonite-grunerite), and crocidolite (also known as asbestiform riebeckite) [7, 8, 9].

Vermiculite ores from some sites were found to contain asbestos minerals but they are not intrinsic to vermiculite and only a few ore bodies have been found to contain more than tiny trace amounts. Nevertheless serious public concern was generated since the occurrence of tremolite asbestos in vermiculite deposits such as those in Libby Montana, in the United States was known and they were closed some years ago [10]. It was the most important case of contaminated vermiculite mines with asbestos and one of the greatest environmental disasters in the history of that country. The vermiculite ore from the mine was heated to produce a commercial product used widely as insulation and as a soil amendment. As with other forms of asbestos, chronic exposure to airborne tremolite asbestos is expected to increase risks of lung cancer, mesothelioma, and non-malignant lung and pleural disorders.

Vermiculite has the property of expanding itself nearly 20 times its original size when heated, because of the water loss. This process is called exfoliation, and the resulting lightweight material is chemically inert, fire-resistant, and odorless [11].

The exfoliation process and the weakening of the structure releases asbestos fibers from the vermiculite ore into the air, where they can be inhaled by people who work in the mines or live in bordering zones. Inhalation of asbestos fibers suspended in the air can result in lung diseases such as asbestosis, mesothelioma and lung cancer [12].

In Argentina [13, 14, 15] among others, have studied vermiculite deposits, but no asbestos presence has been reported.

The object of this work is to evaluate the asbestos contained in a vermiculite mine "Penachos Blancos", in the province of Córdoba, Argentina.

Geological setting

The studied minerals were collected from Penachos Blancos mine (32ş17'54.9"S, 64ş39'12.8"W) located in Department of Calamuchita at south of Cerro Pelado dam in the province of Córdoba, Argentina (Figure 1).

The area of study is composed of high-grade metamorphic rocks that belong to the Atos Pampa-Cerro Pelado anatectic complex [15]. It is formed of cordieritic diatexites and stromatites within which amphibolites and serpentinized harzburgites and piroxenites occur.

The studies carried out on these mineralized bodies are scarce. However, [16] in which the serpentinites as industrial rocks are analyzed can be mentioned.

In the area there are three bodies of serpentinites (Inés, Penachos Blancos and Inés II mines) aligned with NNW strike. The Penachos Blancos body is lens-shaped, 350 m long and 150 m maximum width, with N340° strike. It is covered by amphibolites and it has been intruded by pegmatites, which produces a reaction halo rich in biotite in the contact with serpentinite. These areas are those which, by a later alteration, have produced vermiculite that is recovered in the mine. This pattern of vermiculite formation is very similar to the one proposed by [17].

Methods

To identify the sampled minerals, an Olympus SZ-Pt trinocular stereomicroscope, an Olympus B2-UMA trinocular petrographic microscope, both equipped with a built-in SONY videocamera with a digital capture system, a JEOL JSM 35 CP scanning electron microscope, equipped with an EDAX probe, DX4 with an ultrathin window with a range of analysis from Z = 5 (B) to Z = 92 (U), and a X Rigaku D-Max III - C X-ray diffractometer with Cu Kα radiation and a graphite monochromator operated at 35 kV and 15 mA were used.

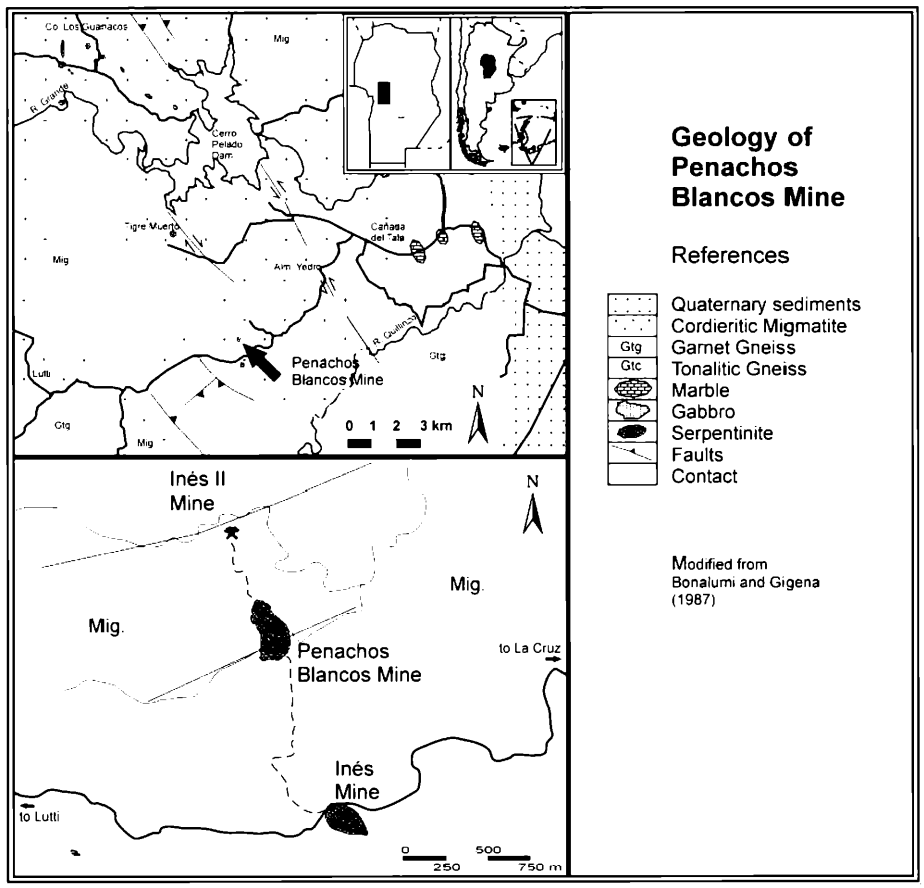

Figure 1. Geologic map of the "Penachos Blancos" mine, province of Córdoba, Argentina

Results

X-ray diffraction

The total sample was analyzed by XRD, and a micaceous mineral associated with scarce quartz and amphiboles were identified. To concentrate the amphiboles, the sample was ground up to passing N° 400 mesh; it was put in acetone to eliminate the lighter material. Part of the settled material was spread on a glass sample holder and it was irradiated from 3 to 60ş (2θ Cu Kα). In figure 2 the main reflections in 3.11, 8.37 and 3.36 Ĺ comparable to the ICDD 41-1366 card [18] are recognized, confirming the presence of a mineral of tremolite-actinolite series.

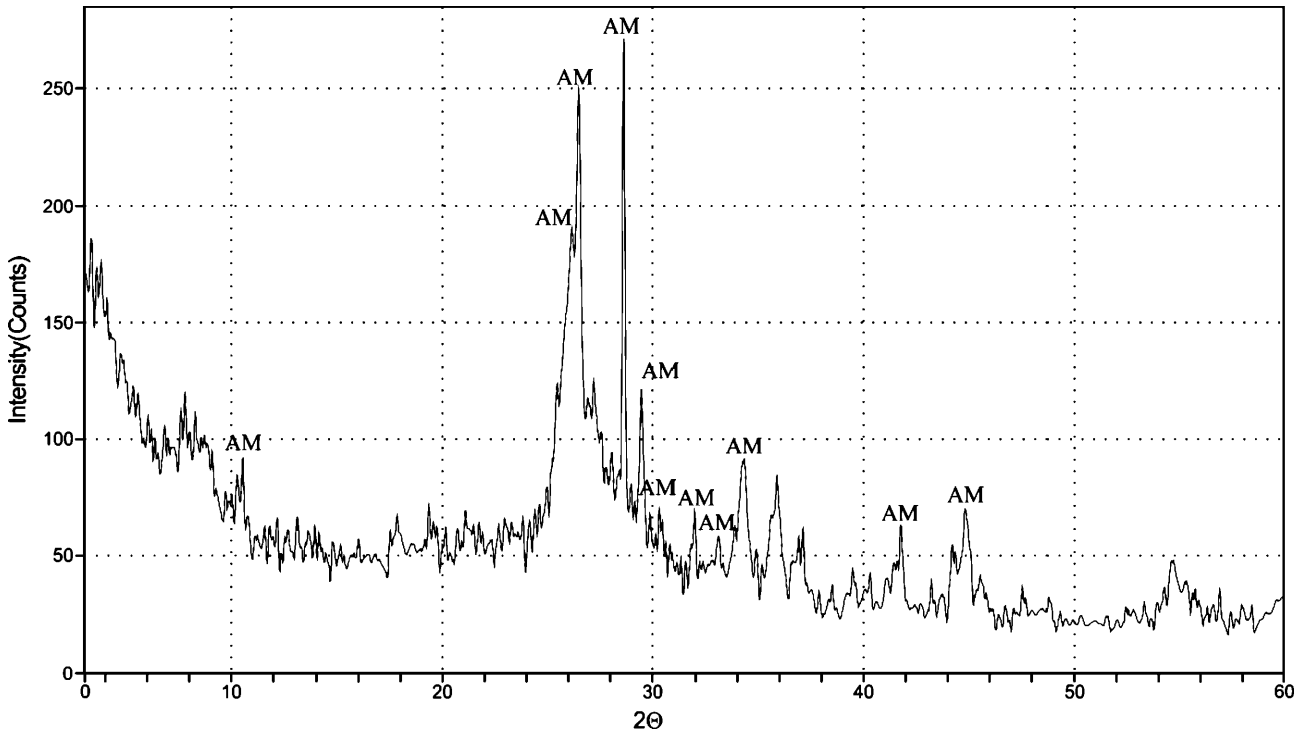

Figure 2. X-ray diffraction diagram of asbestiform minerals (AM).

Mineralogical characteristics

The material analyzed in thin section is formed by big brown crystals, with strong pleochroism and parallel extinction. The optical characteristics correspond to a mineral of the mica group. Because of its expansive properties when it was heated it was determined as vermiculite. The intercrystalline spaces are filled with anhedral quartz. Amphiboles (tremolite – actinolite series) are associated with them. The fibres size ranges between 6 μm to 30 μm in length and 0.8 to 3.5 μm in width. They are acicular and brittle and the habit of some crystal aggregates shows the characteristics of asbestos. In some zones, iron oxides have precipitated as consequence of the mica alteration. The opaque mineral is hematite and those with birefringence were considered as iron hydroxides.

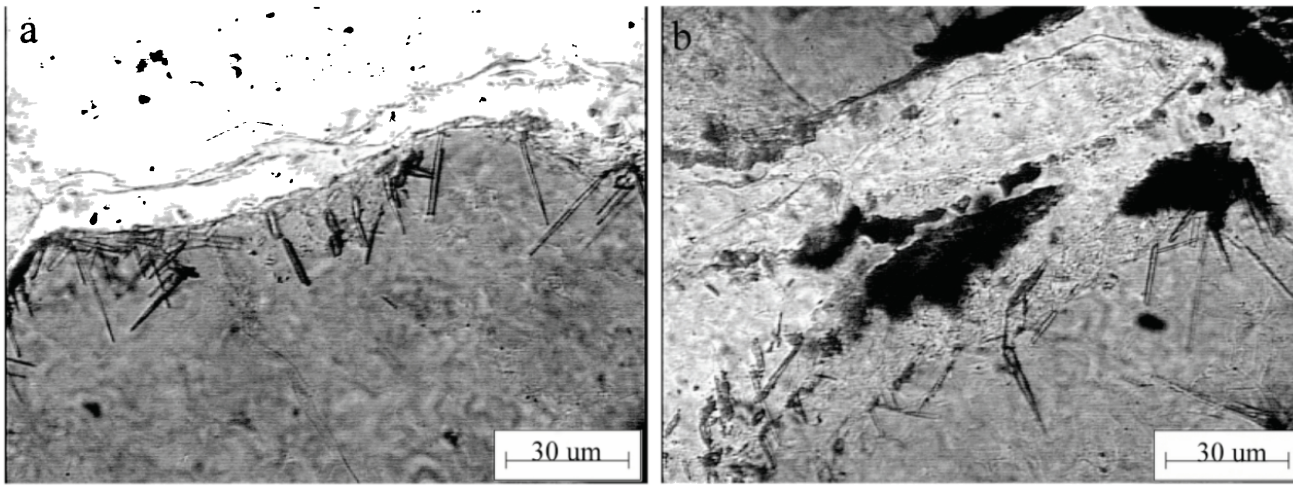

Figure 3. a: Ampholites fibers in vermiculite. b: Fibers and iron oxides in vermiculites

Scanning electron microscopy - EDS

Figure 4 illustrates the "pseudo fibrous" habit of amphiboles in a mass of vermiculite. Fibers appear as cleavage fragments, do not show splayed ends but the mineral habit looks like fibers with a length 5 μm and a length: width ratio ≥3:1.

The EDS analysis identified Si, Al, O, Mg, Fe and K (Fig. 4).

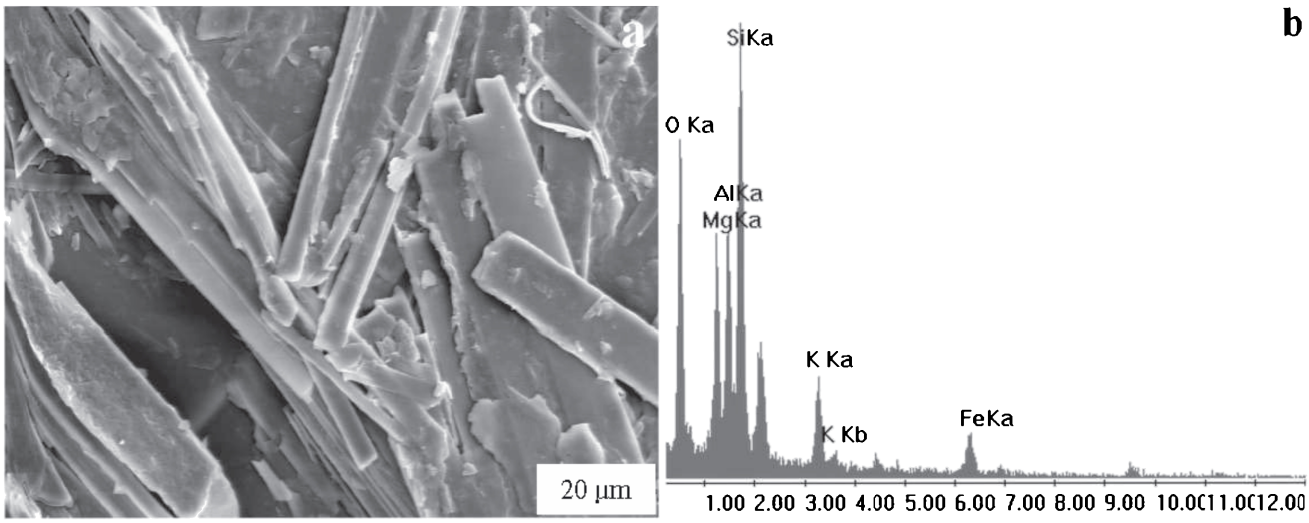

Figure 4. a: Habit of amphiboles. b: EDS analysis.

Discussion

There are controversies regarding the damage produced by asbestos-amphiboles related to the distinction between asbestiform habit and cleavage fragments.

When amphiboles are broken they form a wide range of particle shapes, many of which will be elongate, diamond cross-section rods which are then described as amphibole cleavage fragment fibers. A proportion of these cleavage fragments will meet the size criteria for a regulatory fiber within the asbestos regulations of the United States or the United Kingdom. They could also be counted as fibers in any count of airborne fibers even though they are not asbestos [19].

In 1992 OSHA concluded that there was insufficient evidence that nonasbestiform forms of tremolite, actinolite, and anthophyllite will produce adverse health effects of the same type and severity as those produced by chronic exposure to amphibole asbestos [8], [9]. Nevertheless, some authors warn that repeated exposure to excessive amount of insoluble dusts of any type can cause adverse health effects including interstitial pulmonary fibrosis [20], [8]. According to [21], most of the Libby particles display characteristics that are "intermediate between cleavage fragments and long flexible fibers."

The amphibole fibers included in the vermiculite of the Penachos Blancos mine display asbestiform habit and in some cases cleavage fragment habit. This was determined by its optical properties. A variation in the size of amphiboles fibres between 6 µm and 30µm in length was observed. Fiber dimension is widely considered to be the most important determinant of fiber pathogenicity in terms of cancer development [22]. More recent evidence supports the premise that asbestos fibers of all lengths, not simply long fibers, induce pathological responses [23].

Conclusions

1. Asbestos minerals have been identified in a vermiculite mine, in Department of Calamuchita, Province of Córdoba, Argentina.
2. The analytical methods allowed determining that the asbestiformes minerals are amphiboles from tremolite – actinolite series.
3. Fibers with asbestiform habits and cleavage fragments were recognised.
4. Due to the negative social and environmental impact that causes the presence asbestiformes minerals in active vermiculite mines, it is necessary to continue with the studies to confirm such impacts and their importance.

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References

1. *Harben P.W., Bates R.L.*, 1990. Industrial Minerals Geology and World deposits. Metal Bulletin Plc, London.

2. *Brindley G.W., Brown G.*, 1980. Crystal Structure of clay minerals and their X-ray identification; 3rd ed. Mineralogical Society Monograph No 5. Min. Society, London.

3. *Addison J., Davies L.S.T.,* 1990. Analysis of amphibole asbestos in chrysotile and other minerals. Ann.Occ.hyg.; 34: 159-175.

4. *Atkinson G.R., Rose D., Thomas K., Jones D., Chatfield E.J., Going J.E.*, 1982. Collection, analysis and characterization of vermiculite samples for fiber content and asbestos contamination. Midwest Research Institute, Final Report on EPA Prime Contract No 68-01-5915, US Environmental Protection Agency, Washington.

5. *Zoltai, T.* 1979. Asbestiform and acicular mineral fragments. NY Ac. Sc. 330: 621-643.

6. *Wylie A.G, Bailey K.F, Kelse J.W, et al.*, 1993. The importance of width in asbestos fiber carcinogenicity and its implications for public policy. Am Ind Hyg Assoc J 54(5):239-252.

7. *ATSDR.* 2001a. Toxicological profile for asbestos. U.S. Dep. of Health and Human Serv., Public Health Service, Agency for Toxic Substances and Disease Registry. Atlanta, GA.

8. *OSHA.* 1992. U.S. Department of Labor, Occupational Safety and Health Administration. Federal Register 57:7877-7878, 24310-24331, 49657-49661.

9. *Vu V.* 1993. Regulatory approaches to reduce human health risks associated with exposures to mineral fibers. In: Guthrie G, Mossman B, MSA Rev. in Mineralogy Vol 28: 545-554.

10. *Addison J.,* 1994. Vermiculite is not asbestos. There are no real causes for concern about health risks from vermiculite: a review of the mineralogy of vermiculite and its fundamental differences to asbestos explains why. Addison-Lynch, Edinburgh.

11. *Badawy N.A.& El-Bayaa A.A. & Abd AlKhalik E.*, 2010. Vermiculite as an exchanger for copper (II) and Cr(III) ions, kinetic studies. Ionics (2010) 16:733–739.

12. *Battista R., Speltini C., Choren H., Sota J., Carrizo E.,* 2006. Reciclado de residuos conteniendo asbestos. Transformación de fibras de asbestos por sinterizado en matriz cerámica. Reciclado de residuos de construcción y demolición (RCD) y de residuos de procesos (RP). PROCQMA-Univ. Tecnológica Nacional, Mendoza. ISBN 950-42-0056-7

13. *Angelelli, V., Schalamuk, I. y Fernández, R.*, 1980, Los yacimientos de minerales no metalíferos y rocas de aplicación de la región Centro-Cuyo. Secretaría de Estado de Minería. Anales XIX. 261 pp. Buenos Aires.

14. *Fernández Gianotti, J.*, 1977. Geología de la faja de rocas ultrabásicas de la ladera oriental de la Sierra de los Comechingones, Prov. de Córdoba. Tesis Doctoral, UBA.

15. *Bonalumi, A. y Gigena, A.* 1987. Relación entre las metamorfitas de alto grado y las rocas básicas y ultrabásicas, Prov. de Córdoba. Rev. Asoc. Geol. Argentina, XLII (1-2):73-81.

16. *Sfragulla, J., Bonalumi, A., Briolini, N. y Cabrera, J.*, 2009. Prospección de rocas ultramáficas de Córdoba, orientada a su aplicación industrial. Actas del IX Congreso Argentino de Geología Económica: 287-292, Catamarca.

17. *Simandl, G.J.; Birkett, T. and Paradis, S.*, 1999. Vermiculite; in Selected British Columbia Mineral Deposit Profiles, Volume 3, Industrial Minerals, G.J. Simandl, Z.D. Hora and D.V. Lefebure, Editors, British Columbia Ministry of Energy and Mines.

18. International centre for diffraction data (ICDD) 1986. Mineral Powder Diffraction File Data book: 228-229, Swarthmore, Pennsylvania, U.S.A.

19. *Langer, A., Nolan, R. and Addison, J.*, 1991, Distinguishing between amphibole asbestos fibers and elongate cleavage fragments of their non-asbestiform analogues, in Brown, R.C. and others, eds., Mechanisms in fiber carcinogenesis, New York, Plenum Press, p. 253-267.

20. *ACGIH.* 1996. Particulates (insoluble) Not Otherwise Classified. In: Documentation of the threshold limits values and biological exposure indices. Supplement. American Conference of Governmental Industrial Hygienists. Cincinnati, OH.

21. *Meeker G.P., Brownfield I.K., Clark R.N., et al.* 2001. The chemical composition and physical properties of amphibole from Libby, Montana: a progress report. Asbestos Health Effects Conference. Sponsored by U.S. Environmental Protection Agency. San Francisco, CA.

22. *Oberdorster G.* 1994. Macrophage-associated responses to chrysotile. Ann Occup Hyg 38(4):601-615.

23. *Dodson R.F., O'Sullivan M., Corn C.J., et al.* 1997. Analysis of asbestos fiber burden in lung tissue from mesothelioma patients. Ultrastruct Pathol 21:321-336.