J. W. Wolter

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Fiber Contamination of Vermiculites: A Potential Occupational and Environmental Health Hazard[1]

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Vermiculite ores from Montana, Virginia, and South Africa have been analyzed for the presence of amphibole contamination. Fibrous actinolite was found in unexpanded Montana vermiculite ore at a maximum concentration of 2.0%. The fibers persisted in the expanded ore at a maximum concentration of 0.6%. Actinolite was also found in the Virginia vermiculite ore but at a lower concentration and mostly as cleavage fragments with low length-to-width ratios. South African ore contained rare anthophyllite fibers also with low length-to-width ratios. Vermiculite ores have the potential for amphibole contamination and can represent potential health hazards without proper occupational and environmental control measures. © 1986 Academic Press, Inc.

INTRODUCTION

A recent study of an industrial plant utilizing vermiculite as an inert carrier for various chemical agents identified measurable airborne levels of the amphibole tremolite. There was a significant relationship between cumulative airborne fiber exposure and pleural changes in exposed workers as identified by chest radiographs (1). Tremolite has previously been identified in some vermiculite ores (2–4). To identify potential biological hazards of vermiculite ores, the ores should be mineralogically characterized and the type and amount of amphibole and serpentine contamination estimated. Unexpanded and expanded vermiculite ore samples from Montana, Virginia, and South Africa sources were analyzed using polarized light microscopy, x-ray diffraction, scanning electron microscopy, and analytical scanning-transmission electron microscopy. The results of these mineralogic analyses are described in this article.

Vermiculite is a hydrated, laminar, aluminum–iron–magnesium silicate mineral first named and described in 1824 by Thomas H. Webb from a deposit near Worchester, Massachusetts. The first significant domestic vermiculite deposit was found near Libby, Montana, in 1916, with commercial production beginning in 1921. Subsequent domestic production has come from Pennsylvania, North Carolina, Colorado, Georgia, Texas, and Wyoming. Current domestic production is from Libby, Montana; Enoree, South Carolina; and Louisa County, Virginia. The major source of vermiculite outside the United States is from mining operations

[1] This work is supported in part by the Veterans Administration.
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at Palabora, northeastern Transvaal, Republic of South Africa. The United States and the Republic of South Africa meet 90% of the world demand for vermiculite (5–7).

The crystal structure of vermiculite consists of layers of silicon–oxygen tetrahedra arranged in pairs, with apex oxygens pointing in opposite directions. Each pair of tetrahedral sheets shares a sheet of octahedra occupied by Fe and Mg (8). Substitution of Al for Si in the tetrahedra produces a negative charge, which is balanced by cations occurring between the three-layer units. The diagnostic physical properties of vermiculite are (1) the presence of water molecules along with exchangeable cations in the interlayer sites; (2) spontaneous rehydration following dehydration at temperatures below 300°C; (3) acceptance of a single plane of ethylene glycol molecules which produces a characteristic x-ray diffraction peak; and (4) individual layers collapse to a "talc-like" structure with heating to temperatures greater than 600°C.

The name vermiculite is derived from vermicular, meaning "to produce worms." Vermiculite has the unique property of expanding with the application of flash heat between 400 and 1100°C. This property is dependent on conversion of some of the water of hydration to steam, which forces apart the "talc-like" laminar plates at right angle to the cleavage planes to form an accordion-like or "worm-like" configuration. The expanded or exfoliated form is as much as 12 times the bulk of the unexpanded ore (5–7).

Expanded vermiculite is lightweight, noncombustible, and chemically inert, with a high surface area and ion exchange capacity. These properties make the mineral useful as thermal insulation, as lightweight agregates in building material such as cement, as inert carriers for pesticides and herbicides, as absorptive material used in the water purification and chemical industries, and as soil conditioners. The ore is transported in the unexpanded form and exfoliated at over 47 regional expanding plants located in 30 states (5–7).

MATERIALS AND METHODS

Samples. The unexpanded and expanded Libby vermiculite ores (grade Nos. 2 and 3) were obtained in 1981 from a Salt Lake City expander facility exclusively utilizing Libby, Montana, ore. The Virginia and South Africa ores (grade No. 4) were obtained in 1981 from separate rail hopper cars and expander furnaces at a plant utilizing vermiculite as an inert carrier for chemicals. All samples were kept in separate containers prior to analysis.

Light microscopy. Vermiculite samples were examined with a standard polarizing microscope using index oils. Minerals present were identified using their distinctive optical properties. The relative abundance of blocky amphibole fragments in each sample was determined using a binocular microscope to separate large amphibole fragments which were then weighed to determine weight percentage of the amphiboles. Light microscopy identifies only the massive amphibole fragments in the ore. Additional analytical techniques are needed to examine for the existence of submicroscopic respirable fibers which may be intimately admixed physically with the unexpanded and expanded vermiculite sheets.

X-Ray diffraction. X-Ray diffraction analysis was used to determine minerals

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TABLE I
AMPHIBOLE CONTENT OF VERMICULITE SAMPLES

Sample	Percentage amphibole	Method
Libby No. 2		
Unexpanded	2.0	Optical
Expanded	0.6	Optical
Libby No. 3		
Unexpanded	0.08	Optical
Expanded	0.6	Optical
South Africa No. 4		
Unexpanded	0.4	X-Ray diffraction
Expanded	0.0	Optical, x-ray diffraction
Virginia No. 4		
Unexpanded	1.3	X-Ray diffraction
Expanded	1.3	X-Ray diffraction

present and estimate abundance of vermiculite. Vermiculite samples were gently ground in an agate mortar under water. A slurry of the ground material was smeared on a standard petrographic glass slide and allowed to air-dry. X-Ray diffraction patterns were obtained of each sample following exposure to ethylene glycol vapor at 60°C for 24 hr. Amphibole fragments separated from the vermicu-



FIG. 1. This is a typical secondary electron image of an unexpanded Libby No. 2 pellet showing the fine plate structures at the cross-sectional level. No fibers can be seen at this magnification.

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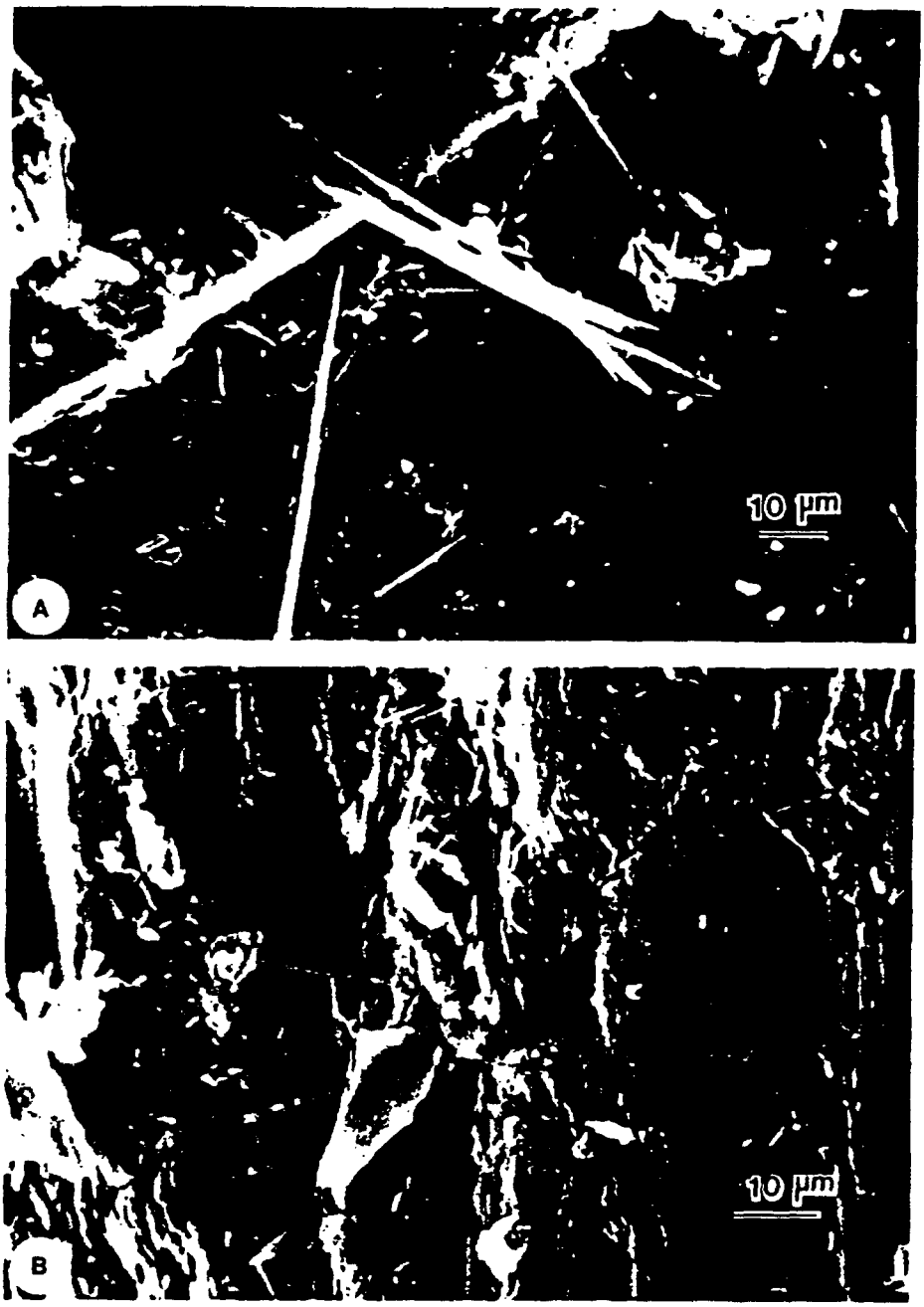


FIG. 2. This shows the higher magnification of the secondary electron image of unexpanded Libby No. 2 ore. (A) Fibers on the surface. (B) Fibers at the edge of the ore.

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lite were also examined by x-ray diffraction. Amphibole fragments were ground in an agate mortar and sprinkled on a vaseline-coated, petrographic slide for x-ray analyses. All x-ray diffraction analyses were performed using a Phillips x-ray diffractometer, copper target x-ray tube, graphite crystal monochrometer, and 1°, 2 theta-per-minute scanning speed.

Scanning electron microscopy. The unexpanded and expanded forms of vermiculite were mounted on carbon planchettes and coated with carbon using a Denton vacuum evaporator (Denton Vacuum, Cherry Hill Industrial Center, Cherry Hill, N.J.). The carbon planchettes were mounted on the aluminum stubbs and placed in a JEOL scanning electron microscope JSM-35U (JEOL USA Inc., Peabody, Mass.) equipped with a Kevex energy dispersive x-ray spectrometer Model 7000 (Kevex Corp., Foster City, Calif.) and interfaced with an MINC LSI11/23 computer (Digital Equipment Corp., Marborough, Mass.). The working resolution of the scanning electron microscope was capable of identifying fibers as small as 0.01 μm in diameter. The samples were viewed using secondary electron imaging mode at various magnifications to search for fibers both in unexpanded and expanded forms. The samples containing fibers were used to measure the fiber sizes manually on the photographs.

Analytical scanning-transmission electron microscopy. One-gram samples of unexpanded and expanded vermiculite were weighed and each was separately

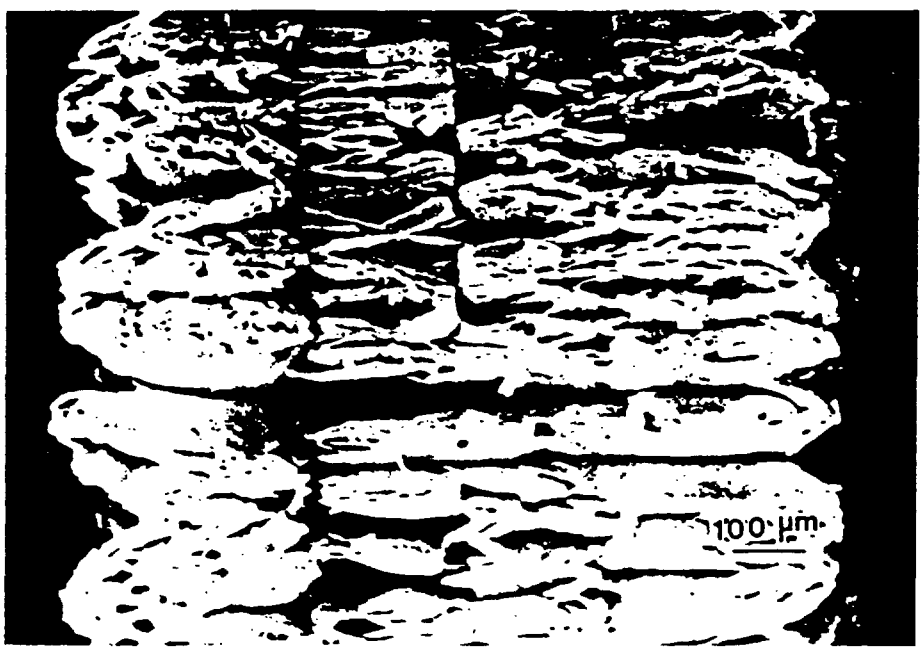


FIG. 3. Expanded Libby No. 2 vermiculite shown with secondary electron image. Note the typical accordion-expanded plates.

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suspended in a volume of distilled water and sonicated for 10 sec. The supernatant was centrifuged at 3000 rpm (2000*g*). The supernatant was decanted and the pellet was resuspended in 100 μl of deionized water. Then, 5 μl of the suspension was placed on a carbon-coated Formvar grid and placed in a JEOL scaning-transmission electron microscope (JEOL USA Inc.), Model JEM 100-CX, equipped with a Kevex energy-dispersive x-ray spectrometer Model 8000. The purpose of this procedure was to isolate and identify the fibers. The fibers were photographed and analyzed with the energy-dispersive x-ray spectrometer in conjunction with selected area electron diffraction. Five to ten fibers from each expanded and unexpanded sample were randomly selected and each fiber was analyzed for 100 sec. The acquired analytical spectra, following background subtraction, were analyzed. The atomic percentages (not weight percentage) of the elements in the fiber were tabulated, and each fiber was labeled according to accepted mineralogical nomenclature (9). Since most of the fibers were calcic amphiboles (containing calcium), the Mg/(Mg + Fe) ratio was used to distinguish among the different calcic amphibole fibers. Tremolite and actinolite were indistinguishable in crystalline structure by x-ray diffraction and are only distinguishable based on the virtual absence of iron in tremolite and the presence of iron in actinolite as documented by energy-dispersive x-ray analysis.

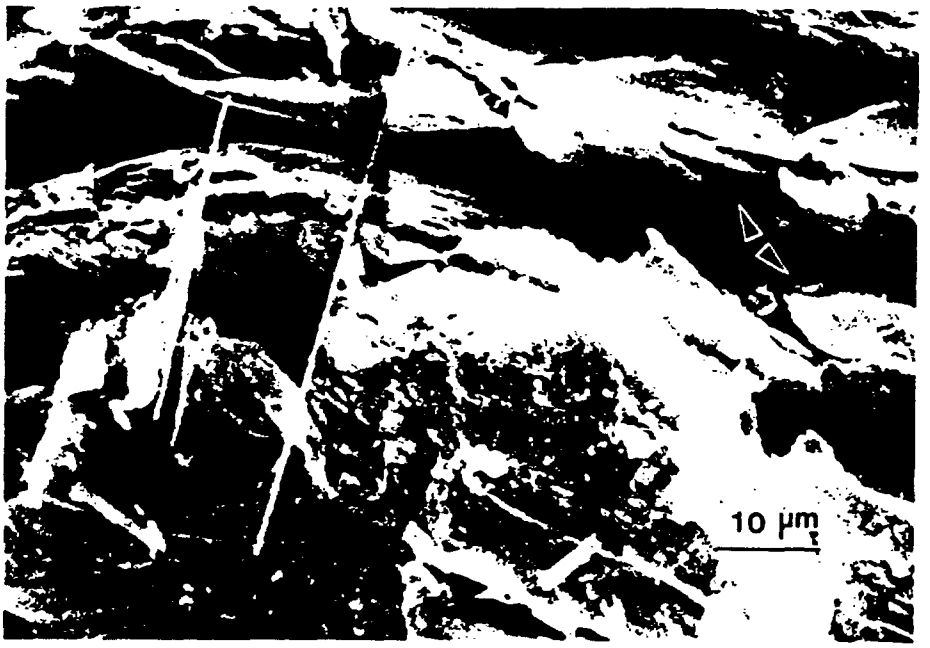


FIG. 4. Higher magnification of the expanded Libby No. 2 vermiculite showing the accordion plates (arrows) as well as several amphibole fibers.

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RESULTS

Light Microscopy

Visible fragments of amphibole were present in both unexpanded and expanded Libby vermiculite, in unexpanded and expanded Virginia vermiculite, and in unexpanded South Africa vermiculite. The percentage of bulk weight of amphibole was calculated by manually separating the amphibole fragments from the unexpanded Libby No. 2 vermiculite and the unexpanded and expanded Libby No. 3 vermiculite. The bulk weight of amphibole in the remaining samples was obtained by x-ray diffraction. The greatest amount of amphibole was in the unexpanded Libby No. 2 vermiculite at 2%. South Africa unexpanded ore contained 0.4% amphibole and Virginia unexpanded ore 1.3% amphibole (Table 1).

Characterization by X-Ray Diffraction

Libby No. 2. The unexpanded vermiculite sample consisted of a mixture of biotite mica, vermiculite, and a regular interstratification of biotite and vermiculite layers. In addition, the Libby No. 2 sample contained substantial quantities (2%) of fibrous amphiboles, which have been identified as mostly actinolite with some anthophyllite. The expanded Libby No. 2 showed typical accordion-like expansion structures and the same x-ray diffraction characteristics as the unex-



FIG. 5. This is a secondary electron image of expanded Virginia vermiculite. Note the presence of a rare fiber at the edge of the expanded plates.

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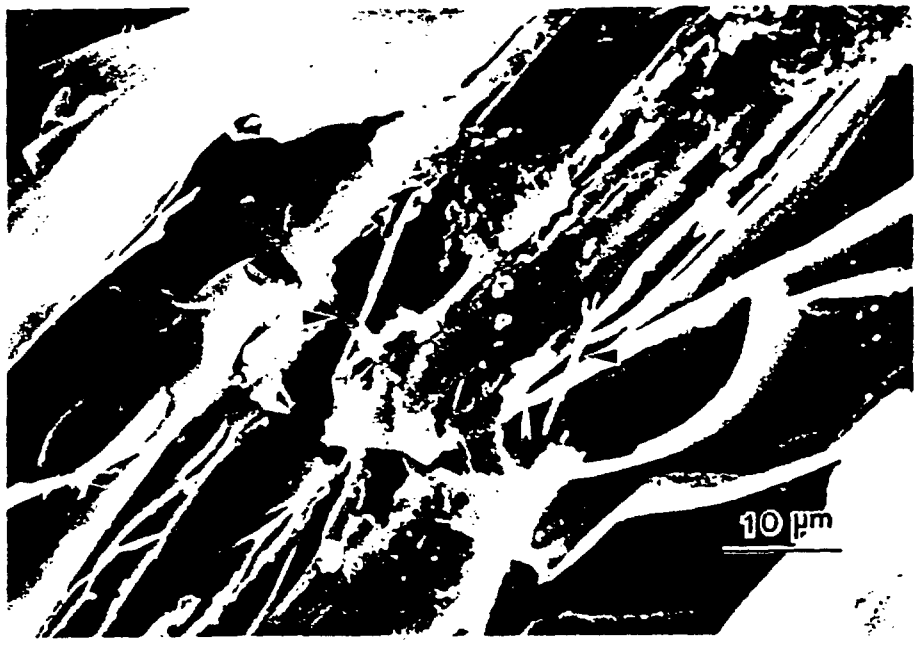


FIG. 6. Secondary electron image of expanded South Africa vermiculite showing the plates as well as two short, fibrous structures (arrows).

panded sample. Solvation with ethylene glycol produced the expected single glycol layer in the vermiculite layers.

Libby No. 3. The unexpanded vermiculite sample consisted of a mixture of vermiculite and interstratified vermiculite–biotite. Unlike the No. 2 sample, Libby No. 3 contained only a trace of discrete biotite. The fibrous amphibole minerals were also present in Libby No. 3. Expanded ore showed a substantial fraction of the material that did not spontaneously rehydrate indicating that the maximum temperature for spontaneous rehydration (300°C) was exceeded.

Virginia. The unexpanded Virginia sample consisted of vermiculite and interstratified biotite–vermiculite. Traces of fibrous amphibole were also present. None of the vermiculite layers from the expanded sample spontaneously rehydrated.

South Africa. The unexpanded vermiculite sample consisted of a mixture of vermiculite and interstratified biotite–vermiculite. The expanded sample contains vermiculite and interstratified biotite–vermiculite in which the majority spontaneously rehydrated. Fibrous amphibole was detected by x-ray diffraction at 0.4% in the unexpanded ore but none was found in the expanded ore.

Scanning Electron Microscopy

Libby No. 2. The unexpanded sample showed characteristic mica-like plates at low magnifications (Fig. 1). At higher magnifications, there were a large number

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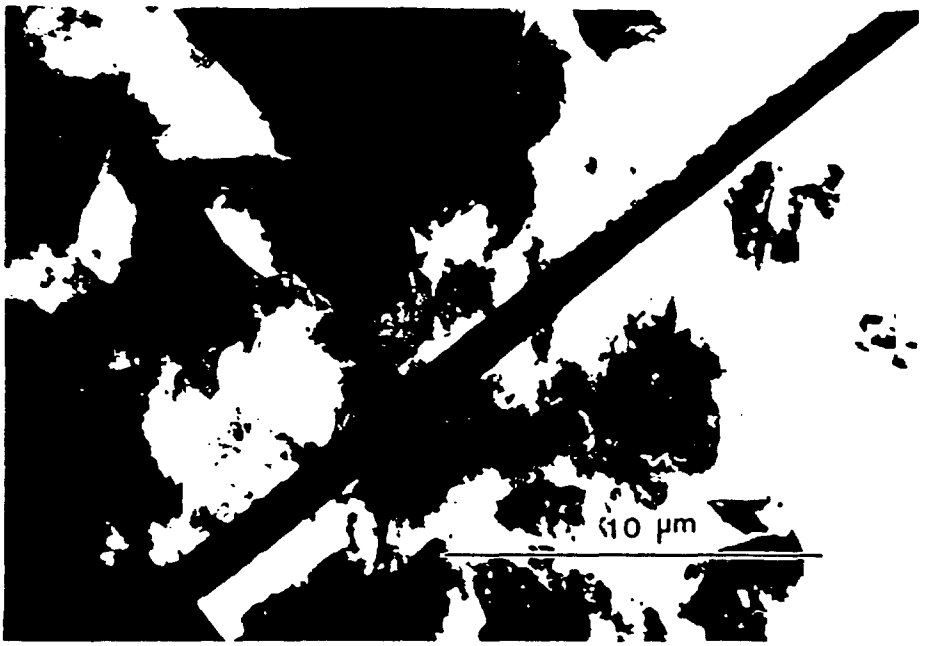


FIG. 7. A fiber mixed with the plate-like structure, identified by transmission electron microscope in Libby No. 2 vermiculite sample. Spots on the fiber away from the plate-like structures were used to analyze the elemental content of the fiber.

of fibers located both on the surface (Fig. 2A) and at the edge (Fig. 2B). Acicular and prismatic cleavage fragments were also present. The size of the fibers was variable, measuring up to 40 μm in length and from 0.2 to 5 μm in diameter. The expanded vermiculite showed characteristic accordion-shaped periodicity (Fig. 3). At higher magnification, similar amphibole fibers were identified throughout the specimen, particularly at the edge of the plates (Fig. 4).

Libby No. 3. The unexpanded ore was similar to that observed in the previous specimen. The higher magnification of the ore revealed similar amphibole fibers to those observed in the previous specimen, with similar shapes and sizes. The expanded form also showed similar periodicity to the Libby No. 2 sample, as well as amphibole fibers, particularly at the edge of the plates.

Virginia. The unexpanded vermiculite showed morphology similar to the Libby ores. Infrequent short, fibrous structures were most likely cleavage fragments present either on the surface or at the edges. The number of fibrous fragments were extremely low in comparison to the Libby vermiculite. Extensive examination of the expanded form revealed rare fibrous structures, as the one noted in Fig. 5.

South Africa. The unexpanded ore showed morphology similar to the other ores, with the same mica-plate appearance. The major difference between this sample and the previous one was the near absence of fibers. The expanded South

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TABLE 2
RANDOM FIBER IDENTIFICATION IN THE VERMICULITE SAMPLES USING ATOMIC Mg/(Mg + Fe)[a] RATIO

	Tremolite[b]	Actinolite[b]	Ferro-actinolite[b]	Anthophyllite[c]	Rolled vermiculite
Libby No. 2					
Unexpanded	—	10/10	—	—	—
Expanded	—	10/10	—	—	—
Libby No. 3					
Unexpanded	1/10	9/10	—	—	—
Expanded	—	9/10	1/10	—	—
South Africa					
Unexpanded	—	2/8	—	4/8	2/8
Expanded	—	—	—	3/5	—
Virginia					
Unexpanded	—	4/5	1/5	—	—
Expanded	—	1/5	—	—	4/5

[a] The Mg/(Mg + Fe) ratio for tremolite, actinolites, ferro-actinolite were 0.9–1.0, 0.5–0.9, and 0.0–0.5, respectively. Anthophyllite fibers were noncalcic and rolled vermiculites contained aluminum.
[b] Calcic fibers (contains calcium).
[c] Noncalcic fibers.

Africa sample at the higher magnification showed rare, short fibrous structures (Fig. 6).

Analytical Scanning-Transmission Electron Microscopy

The suspension samples from all unexpanded and expanded specimens examined under transmission electron microscopy revealed the presence of frequent fibers with Libby Nos. 2 and 3 ores. The samples from Virginia and South Africa, however, revealed infrequent fibers on the grids. A fiber examined with the transmission electron microscope is represented in Fig. 7. Selected area electron diffraction confirmed that the majority of these fibers were crystalline amphibole. Energy-dispersive x-ray analysis of these fibers revealed magnesium, silicon, calcium, and iron, predominantly, except for the fibrous structures in the South Africa sample. The fibers were differentiated, based on the Mg/(Mg + Fe) ratios, according to the established criteria, and tabulated in Table 2 (9). The criteria for such identification are given in the footnotes of Table 2.

The energy-dispersive x-ray analysis of ten different spots on five vermiculite fragments in unexpanded and expanded forms has revealed similar concentration of magnesium, aluminum, silicon, and iron, which constitutes over 80% of the total weight (Fig. 8). In addition, there were potassium, calcium, and titanium, with traces of phosphorus, sulfur, and chromium.

DISCUSSION

Vermiculite from Libby, Montana, contains the amphibole actinolite as a contaminant mineral. The percentage of concentration per bulk weight in raw ver-

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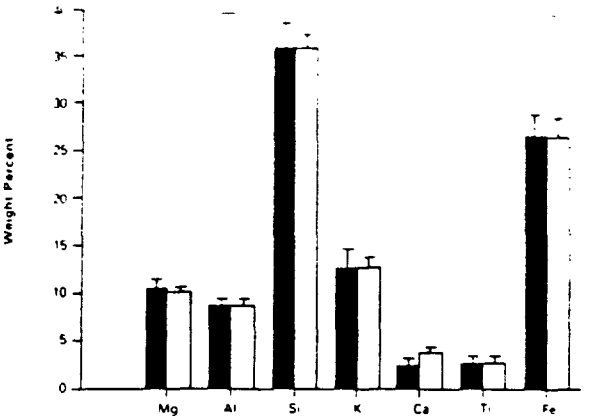


FIG. 8. Weight percentage concentration of the elements of Libby No. 3 unexpanded (raw, ■) and expanded (□) vermiculites. A similar result was obtained with the other three vermiculite ores. Bars indicate SE per group. Elemental composition by energy-dispersive X-ray analysis.

miculite ore in this analysis is equal to or less than 2%. The actinolite is fibrous, with high aspect ratios (>10:1 length to width). The fibrous actinolite persists in the expanded vermiculite ore. The presence of fibrous actinolite in the raw and expanded forms represents a potential health hazard to humans unless proper environmental and respiratory protection is utilized. Fibrous tremolite, which differs from actinolite only in iron content, has been demonstrated to cause pulmonary abnormalities commonly associated with commercial asbestos exposure (10).

Virginia vermiculite also contains actinolite as a contaminant mineral. The actinolite is of a variety that forms mostly cleavage fragments with low aspect ratios. Few fibers were identified in the expanded form. The health implications of actinolite as cleavage fragments with short aspect ratios is not well defined. Animal studies have demonstrated that various types of fibers in excess of 8 μm in length and equal to or less than 1.5 μm in diameter have high potential of producing pleural sarcomas (11).

South Africa vermiculite ore in the unexpanded form is essentially fiber free. The rare fibers identified were mostly anthophyllite with low aspect ratios. Vermiculite can roll up on itself, resulting in a scroll configuration. The scrolls are tubular in nature and can form bundles with an appearance similar to chrysotile (12). No chrysotile fibers were identified in any of the vermiculite ores. Chrysotile fibers have previously been reported to be present in the Libby, Montana, ore (4).

The mineralogic dividing line between actinolite and tremolite is based solely on iron content, is arbitrary, and may have no biological significance. Tremolite is used when the atomic proportion of Mg/(Mg + Fe) is greater than 0.90, indicating the near absence of iron. Actinolite refers to a ratio of 0.50 to 0.90, and ferro-actinolite refers to ratios of 0 to 0.50 (9). Morphologic characterization using polarized light microscopy cannot differentiate tremolite from actinolite without supplemental chemical identification utilizing energy-dispersive x-ray analyses.

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Previous studies reporting tremolite within the Libby, Montana, ore did not report the utilization of chemical analyses to establish the Mg/(Mg + Fe) ratio of the amphibole fibers (1,2,4), or did not differentiate between tremolite and actinolite according to current nomenclature of amphiboles (9). Bowes *et al.* (3) did identify tremolite within Libby, Montana, ore by energy-dispersive x-ray analyses. The slight differences, in comparison to this study, most likely represent the geologic variability of the Mg/(Mg + Fe) ratios of the amphibole mineral found in the Libby, Montana, vermiculite deposits.

In conclusion, some vermiculite ore has the potential for containing the amphibole actinolite either in fibrous form or as cleavage fragments. Proper mineralogic analysis of these ores prior to utilization will help identify if a potential health hazard exists because of fiber contamination and will allow for proper occupational and environmental control measures.

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Expanded	0.6	Optical
South Africa No. 4		
Unexpanded	0.4	X-Ray diffraction
Expanded	0.0	Optical, x-ray diffraction
Virginia No. 4		
Unexpanded	1.3	X-Ray diffraction
Expanded	1.3	X-Ray diffraction

present and estimate abundance of vermiculite. Vermiculite samples were gently ground in an agate mortar under water. A slurry of the ground material was smeared on a standard petrographic glass slide and allowed to air-dry. X-Ray diffraction patterns were obtained of each sample following exposure to ethylene glycol vapor at 60°C for 24 hr. Amphibole fragments separated from the vermicu-



FIG. 1. This is a typical secondary electron image of an unexpanded Libby No. 2 pellet showing the fine plate structures at the cross-sectional level. No fibers can be seen at this magnification.

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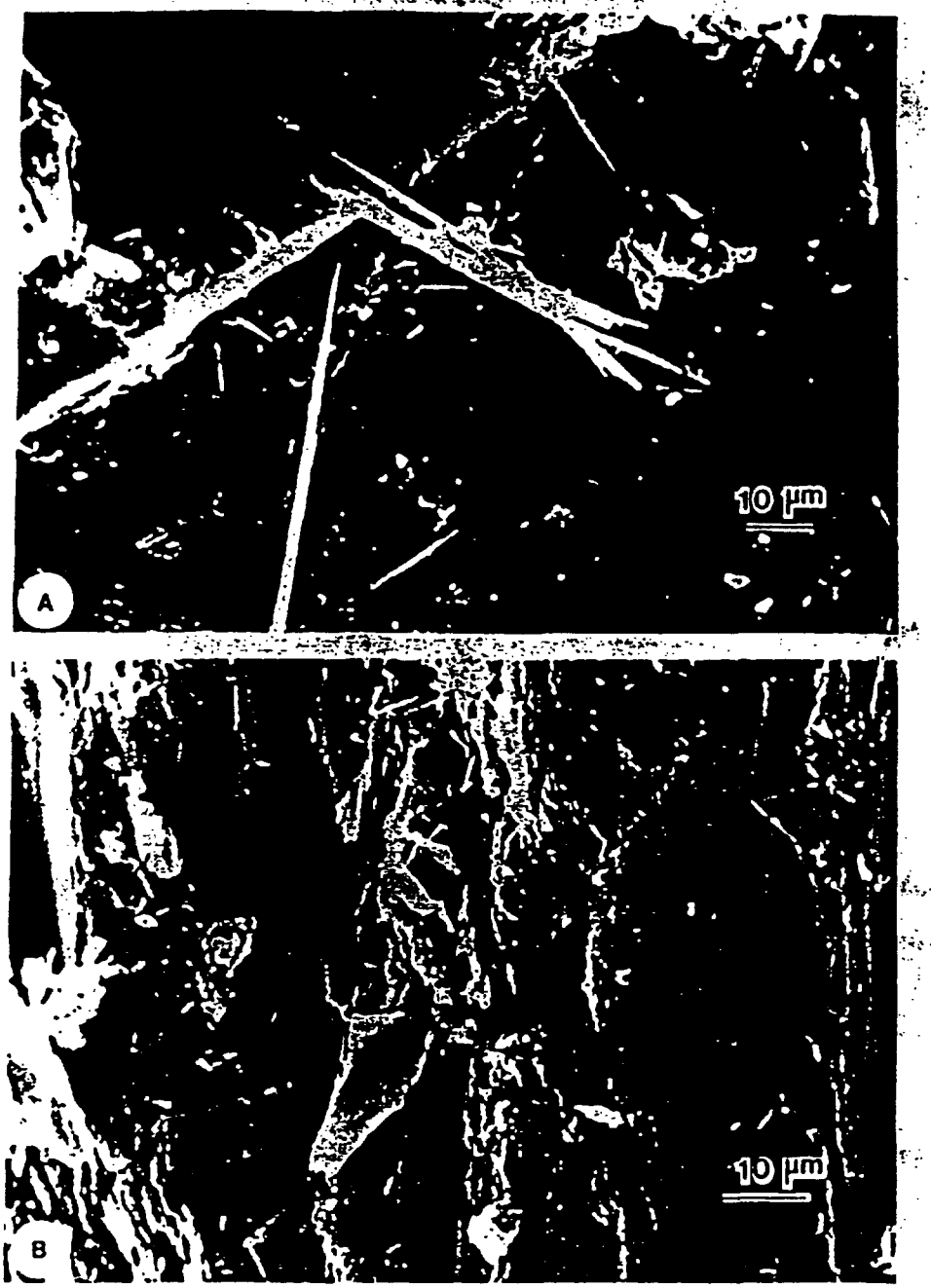


FIG. 2. This shows the higher magnification of the secondary electron image of unexpanded Libby No. 2 ore. (A) Fibers on the surface. (B) Fibers at the edge of the ore.

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lite were also examined by x-ray diffraction. Amphibole fragments were ground in an agate mortar and sprinkled on a vaseline-coated, petrographic slide for x-ray analyses. All x-ray diffraction analyses were performed using a Phillips x-ray diffractometer, copper target x-ray tube, graphite crystal monochrometer, and 1°, 2 theta-per-minute scanning speed.

Scanning electron microscopy. The unexpanded and expanded forms of vermiculite were mounted on carbon planchettes and coated with carbon using a Denton vacuum evaporator (Denton Vacuum, Cherry Hill Industrial Center, Cherry Hill, N.J.). The carbon planchettes were mounted on the aluminum stubbs and placed in a JEOL scanning electron microscope JSM-35U (JEOL USA Inc., Peabody, Mass.) equipped with a Kevex energy dispersive x-ray spectrometer Model 7000 (Kevex Corp., Foster City, Calif.) and interfaced with an MINC LSI11/23 computer (Digital Equipment Corp., Marborough, Mass.). The working resolution of the scanning electron microscope was capable of identifying fibers as small as 0.01 μm in diameter. The samples were viewed using secondary electron imaging mode at various magnifications to search for fibers both in unexpanded and expanded forms. The samples containing fibers were used to measure the fiber sizes manually on the photographs.

Analytical scanning-transmission electron microscopy. One-gram samples of unexpanded and expanded vermiculite were weighed and each was separately

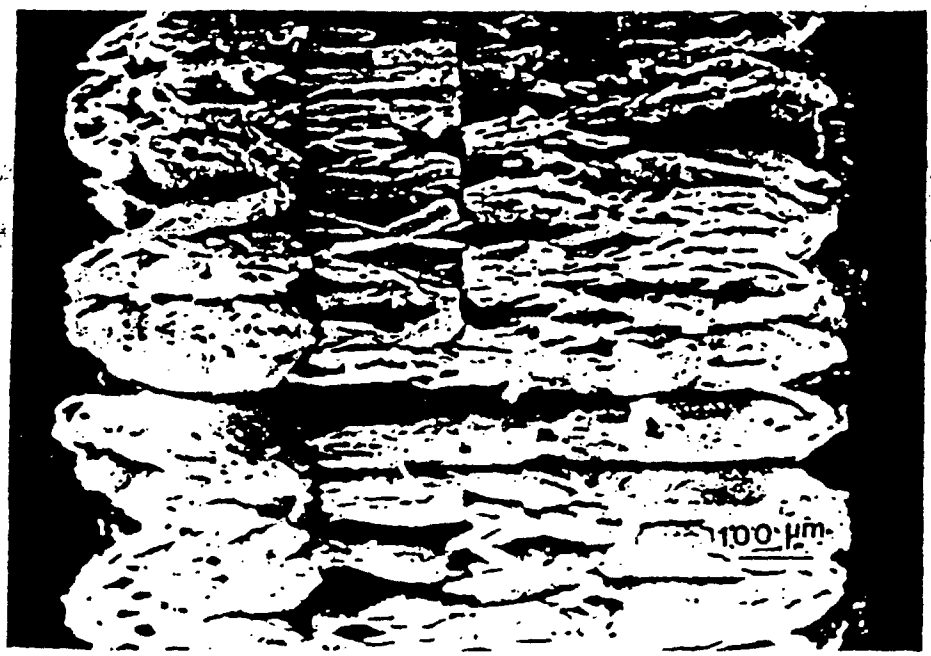


FIG. 3. Expanded Libby No. 2 vermiculite shown with secondary electron image. Note the typical accordion-expanded plates.

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suspended in a volume of distilled water and sonicated for 10 sec. The supernatant was centrifuged at 3000 rpm (2000*g*). The supernatant was decanted and the pellet was resuspended in 100 μl of deionized water. Then, 5 μl of the suspension was placed on a carbon-coated Formvar grid and placed in a JEOL scaning-transmission electron microscope (JEOL USA Inc.), Model JEM 100-CX, equipped with a Kevex energy-dispersive x-ray spectrometer Model 8000. The purpose of this procedure was to isolate and identify the fibers. The fibers were photographed and analyzed with the energy-dispersive x-ray spectrometer in conjunction with selected area electron diffraction. Five to ten fibers from each expanded and unexpanded sample were randomly selected and each fiber was analyzed for 100 sec. The acquired analytical spectra, following background subtraction, were analyzed. The atomic percentages (not weight percentage) of the elements in the fiber were tabulated, and each fiber was labeled according to accepted mineralogical nomenclature (9). Since most of the fibers were calcic amphiboles (containing calcium), the Mg/(Mg + Fe) ratio was used to distinguish among the different calcic amphibole fibers. Tremolite and actinolite were indistinguishable in crystalline structure by x-ray diffraction and are only distinguishable based on the virtual absence of iron in tremolite and the presence of iron in actinolite as documented by energy-dispersive x-ray analysis.

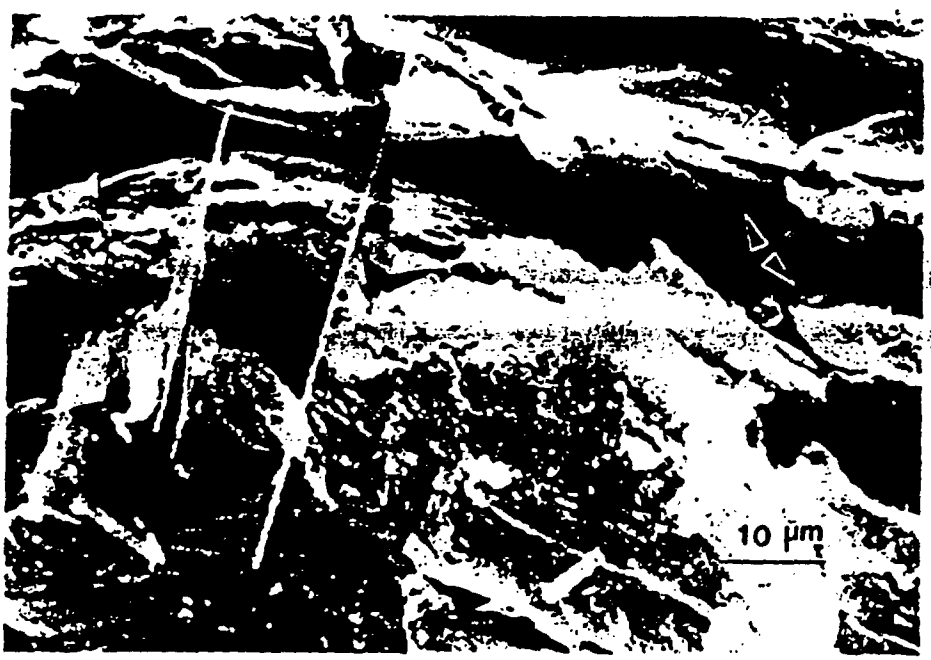


FIG. 4. Higher magnification of the expanded Libby No. 2 vermiculite showing the accordion plates (arrows) as well as several amphibole fibers.

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RESULTS

Light Microscopy

Visible fragments of amphibole were present in both unexpanded and expanded Libby vermiculite, in unexpanded and expanded Virginia vermiculite, and in unexpanded South Africa vermiculite. The percentage of bulk weight of amphibole was calculated by manually separating the amphibole fragments from the unexpanded Libby No. 2 vermiculite and the unexpanded and expanded Libby No. 3 vermiculite. The bulk weight of amphibole in the remaining samples was obtained by x-ray diffraction. The greatest amount of amphibole was in the unexpanded Libby No. 2 vermiculite at 2%. South Africa unexpanded ore contained 0.4% amphibole and Virginia unexpanded ore 1.3% amphibole (Table 1).

Characterization by X-Ray Diffraction

Libby No. 2. The unexpanded vermiculite sample consisted of a mixture of biotite mica, vermiculite, and a regular interstratification of biotite and vermiculite layers. In addition, the Libby No. 2 sample contained substantial quantities (2%) of fibrous amphiboles, which have been identified as mostly actinolite with some anthophyllite. The expanded Libby No. 2 showed typical accordion-like expansion structures and the same x-ray diffraction characteristics as the unex-



FIG. 5. This is a secondary electron image of expanded Virginia vermiculite. Note the presence of a rare fiber at the edge of the expanded plates.

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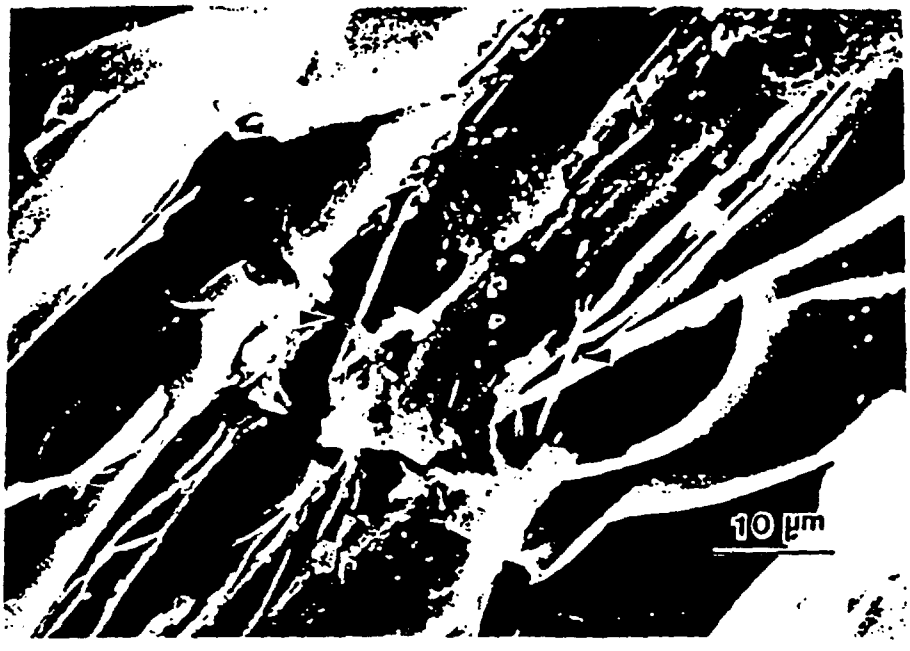


FIG. 6. Secondary electron image of expanded South Africa vermiculite showing the plates as well as two short, fibrous structures (arrows).

panded sample. Solvation with ethylene glycol produced the expected single glycol layer in the vermiculite layers.

Libby No. 3. The unexpanded vermiculite sample consisted of a mixture of vermiculite and interstratified vermiculite–biotite. Unlike the No. 2 sample, Libby No. 3 contained only a trace of discrete biotite. The fibrous amphibole minerals were also present in Libby No. 3. Expanded ore showed a substantial fraction of the material that did not spontaneously rehydrate indicating that the maximum temperature for spontaneous rehydration (300°C) was exceeded.

Virginia. The unexpanded Virginia sample consisted of vermiculite and interstratified biotite–vermiculite. Traces of fibrous amphibole were also present. None of the vermiculite layers from the expanded sample spontaneously rehydrated.

South Africa. The unexpanded vermiculite sample consisted of a mixture of vermiculite and interstratified biotite–vermiculite. The expanded sample contains vermiculite and interstratified biotite–vermiculite in which the majority spontaneously rehydrated. Fibrous amphibole was detected by x-ray diffraction at 0.4% in the unexpanded ore but none was found in the expanded ore.

Scanning Electron Microscopy

Libby No. 2. The unexpanded sample showed characteristic mica-like plates at low magnifications (Fig. 1). At higher magnifications, there were a large number

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FIG. 7. A fiber mixed with the plate-like structure, identified by transmission electron microscope in Libby No. 2 vermiculite sample. Spots on the fiber away from the plate-like structures were used to analyze the elemental content of the fiber.

of fibers located both on the surface (Fig. 2A) and at the edge (Fig. 2B). Acicular and prismatic cleavage fragments were also present. The size of the fibers was variable, measuring up to 40 μm in length and from 0.2 to 5 μm in diameter. The expanded vermiculite showed characteristic accordion-shaped periodicity (Fig. 3). At higher magnification, similar amphibole fibers were identified throughout the specimen, particularly at the edge of the plates (Fig. 4).

Libby No. 3. The unexpanded ore was similar to that observed in the previous specimen. The higher magnification of the ore revealed similar amphibole fibers to those observed in the previous specimen, with similar shapes and sizes. The expanded form also showed similar periodicity to the Libby No. 2 sample, as well as amphibole fibers, particularly at the edge of the plates.

Virginia. The unexpanded vermiculite showed morphology similar to the Libby ores. Infrequent short, fibrous structures were most likely cleavage fragments present either on the surface or at the edges. The number of fibrous fragments were extremely low in comparison to the Libby vermiculite. Extensive examination of the expanded form revealed rare fibrous structures, as the one noted in Fig. 5.

South Africa. The unexpanded ore showed morphology similar to the other ores, with the same mica-plate appearance. The major difference between this sample and the previous one was the near absence of fibers. The expanded South

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TABLE 2
RANDOM FIBER IDENTIFICATION IN THE VERMICULITE SAMPLES USING ATOMIC Mg/(Mg + Fe)[a] RATIO

	Tremolite[b]	Actinolite[b]	Ferro-actinolite[b]	Anthophyllite[c]	Rolled vermiculite
Libby No. 2					
Unexpanded	—	10/10	—	—	—
Expanded	—	10/10	—	—	—
Libby No. 3					
Unexpanded	1/10	9/10	—	—	—
Expanded	—	9/10	1/10	—	—
South Africa					
Unexpanded	—	2/8	—	4/8	2/8
Expanded	—	—	—	3/5	—
Virginia					
Unexpanded	—	4/5	1/5	—	—
Expanded	—	1/5	—	—	4/5

[a] The Mg/(Mg + Fe) ratio for tremolite, actinolites, ferro-actinolite were 0.9–1.0, 0.5–0.9, and 0.0–0.5, respectively. Anthophyllite fibers were noncalcic and rolled vermiculites contained aluminum.
[b] Calcic fibers (contains calcium).
[c] Noncalcic fibers.

Africa sample at the higher magnification showed rare, short fibrous structures (Fig. 6).

Analytical Scanning-Transmission Electron Microscopy

The suspension samples from all unexpanded and expanded specimens examined under transmission electron microscopy revealed the presence of frequent fibers with Libby Nos. 2 and 3 ores. The samples from Virginia and South Africa, however, revealed infrequent fibers on the grids. A fiber examined with the transmission electron microscope is represented in Fig. 7. Selected area electron diffraction confirmed that the majority of these fibers were crystalline amphibole. Energy-dispersive x-ray analysis of these fibers revealed magnesium, silicon, calcium, and iron, predominantly, except for the fibrous structures in the South Africa sample. The fibers were differentiated, based on the Mg/(Mg + Fe) ratios, according to the established criteria, and tabulated in Table 2 (9). The criteria for such identification are given in the footnotes of Table 2.

The energy-dispersive x-ray analysis of ten different spots on five vermiculite fragments in unexpanded and expanded forms has revealed similar concentration of magnesium, aluminum, silicon, and iron, which constitutes over 80% of the total weight (Fig. 8). In addition, there were potassium, calcium, and titanium, with traces of phosphorus, sulfur, and chromium.

DISCUSSION

Vermiculite from Libby, Montana, contains the amphibole actinolite as a contaminant mineral. The percentage of concentration per bulk weight in raw ver-

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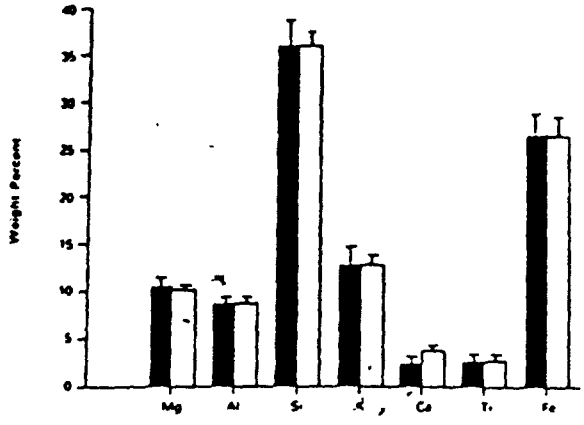


FIG. 8. Weight percentage concentration of the elements of Libby No. 3 unexpanded (raw, ■) and expanded (□) vermiculites. A similar result was obtained with the other three vermiculite ores. Bars indicate SE per group. Elemental composition by energy-dispersive X-ray analysis.

miculite ore in this analysis is equal to or less than 2%. The actinolite is fibrous, with high aspect ratios (>10:1 length to width). The fibrous actinolite persists in the expanded vermiculite ore. The presence of fibrous actinolite in the raw and expanded forms represents a potential health hazard to humans unless proper environmental and respiratory protection is utilized. Fibrous tremolite, which differs from actinolite only in iron content, has been demonstrated to cause pulmonary abnormalities commonly associated with commercial asbestos exposure (10).

Virginia vermiculite also contains actinolite as a contaminant mineral. The actinolite is of a variety that forms mostly cleavage fragments with low aspect ratios. Few fibers were identified in the expanded form. The health implications of actinolite as cleavage fragments with short aspect ratios is not well defined. Animal studies have demonstrated that various types of fibers in excess of 8 μm in length and equal to or less than 1.5 μm in diameter have high potential of producing pleural sarcomas (11).

South Africa vermiculite ore in the unexpanded form is essentially fiber free. The rare fibers identified were mostly anthophyllite with low aspect ratios. Vermiculite can roll up on itself, resulting in a scroll configuration. The scrolls are tubular in nature and can form bundles with an appearance similar to chrysotile (12). No chrysotile fibers were identified in any of the vermiculite ores. Chrysotile fibers have previously been reported to be present in the Libby, Montana, ore (4).

The mineralogic dividing line between actinolite and tremolite is based solely on iron content, is arbitrary, and may have no biological significance. Tremolite is used when the atomic proportion of Mg/(Mg + Fe) is greater than 0.90, indicating the near absence of iron. Actinolite refers to a ratio of 0.50 to 0.90, and ferro-actinolite refers to ratios of 0 to 0.50 (9). Morphologic characterization using polarized light microscopy cannot differentiate tremolite from actinolite without supplemental chemical identification utilizing energy-dispersive x-ray analyses.

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Previous studies reporting tremolite within the Libby, Montana, ore did not report the utilization of chemical analyses to establish the Mg/(Mg + Fe) ratio of the amphibole fibers (1,2,4), or did not differentiate between tremolite and actinolite according to current nomenclature of amphiboles (9). Bowes *et al.* (3) did identify tremolite within Libby, Montana, ore by energy-dispersive x-ray analyses. The slight differences, in comparison to this study, most likely represent the geologic variability of the Mg/(Mg + Fe) ratios of the amphibole mineral found in the Libby, Montana, vermiculite deposits.

In conclusion, some vermiculite ore has the potential for containing the amphibole actinolite either in fibrous form or as cleavage fragments. Proper mineralogic analysis of these ores prior to utilization will help identify if a potential health hazard exists because of fiber contamination and will allow for proper occupational and environmental control measures.

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