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MRI REPORT

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COLLECTION, ANALYSIS AND CHARACTERIZATION OF VERMICULITE SAMPLES FOR FIBER CONTENT AND ASBESTOS CONTAMINATION

TASK 32
FINAL REPORT

September 27, 1982

EPA Prime Contract No. 68-01-5915
MRI Project No. 4901-A32

Prepared for

U.S. Environmental Protection Agency
Office of Pesticides and Toxic Substances
Field Studies Branch
401 M Street, S.W.
Washington, D.C. 20460

Attn: Dr. Frederick Kutz, Project Officer
Mr. Thomas Dixon, Task Manager

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by

Gaylord R. Atkinson
Donna Rose
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MIDWEST RESEARCH INSTITUTE 425 VOLKER BOULEVARD, KANSAS CITY, MISSOURI 64110 • 816 753-7600

PREFACE

This final report presents the results obtained on MRI Project No. 4901-A, Task 32, "Collection, Analysis and Characterization of Vermiculite Samples for Fiber Content and Asbestos Contamination." The task was undertaken for the Environmental Protection Agency under EPA Contract No. 68-01-5915 with Midwest Research Institute. Sample collection was conducted by MRI, Mr. Kenneth Thomas, sampling crew chief. The analytical portion of this task was conducted through subcontracts with Ontario Research Foundation, Dr. E. J. Chatfield, Project Manager, and IIT Research Institute, Mr. David Jones, Project Manager. This report was prepared by Mr. Gaylord R. Atkinson, MRI Task Leader, with assistance from Mr. Thomas, Dr. Chatfield, Mr. Jones, and Ms. Donna Rose (MRI).

MIDWEST RESEARCH INSTITUTE

John E. Going
Program Manager

Approved:

James L. Spigarelli, Director
Analytical Chemistry Department

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George Yamate IITRI Chicago

subcontract # 61-4900-15

home- 312-478-7670

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ABBREVIATIONS, DEFINITIONS, AND SPECIFICATIONS

The following are special terms or specifications that are used in this report.

1. Vermiculite - A naturally occurring hydrated laminar mineral silicate. Due to layers of water of hydration between the laminae, the vermiculite exfoliates or expands when heated.

2. Beneficiation - The process of obtaining vermiculite particles from the ore.

3. Vermiculite grades - W. R. Grace, the largest U.S. vermiculite producer, separates the beneficiated vermiculite into five size grades. Grade 1 is the largest; Grade 5 the smallest. Company grade specifications were not obtained, but the following size data were determined by examination of the five grades from Libby, Montana. The data are presented as an indication of differences among the grades.

Grade No.	Approximate maximum dimension (mm)	Approximate number of particles/g	Approximate weight/ average particle
1	5-10	23	42 mg
2	3-5	130	7.4 mg
3	1-3	1,700	0.58 mg
4	0.5-1	11,000	91 µg
5	0.2-0.5	130,000	7.6 µg

4. Asbestos - A general term for a number of naturally occurring fibrous mineral silicates. Asbestos falls into two major classes, the serpentines and amphiboles. Chrysotile is the generally encountered serpentine. The various amphiboles are not easily identified using the electron microscope, and the entire group is generally reported as "amphiboles" from the EM analysis. (With greater effort the chemical composition can be determined with the microprobe.)

The major fibers identified by optical microscopy in this study were amphiboles of the tremolite/actinolite series. Tremolite and actinolite differ by the ratio of iron and magnesium in the molecule, which results in a range of refractive indices. The series is comprised of a continuous variation with an arbitrary division between the two. The composition of tremolite ranges from $Ca_2Mg_5SiO_{22}(OH)_2$ to $Ca_2Mg_4FeSi_8O_{22}(OH)_2$ and that of actinolite ranges from $Ca_2Mg_4FeSi_8O_{22}(OH)_2$ to $Ca_2MgFe_4Si_8O_{22}(OH)_2$. Any composition within this series is often reported simply as "tremolite/actinolite."

EM - Electron microscpy

TEM - Transmission electron microscopy

SAED - Selected area electron diffraction

JCPDS - Joint Committee on Powder Diffraction Standards

MRI - Midwest Research Institute, the prime contractor.

IITRI - IIT Research Institute
10 W. 35th Street
Chicago, Illinois 60616

ORF - Ontario Research Foundation
Sheridan Park Research Community
Mississauga, Ontario, Canada L5K 1B3

SECTION 1

INTRODUCTION

In December 1978, the vermiculite industry submitted information to the EPA regarding health problems experienced by employees who were processing asbestos-contaminated vermiculite. The original submission indicated that bloody pleural effusions had been detected in 4 of 350 employees; symptomatology and clinical findings in the employees were similar to those found in individuals with asbestos-related diseases. Subsequent follow-up studies by the Occupational Safety and Health Administration (OSHA) revealed an even higher prevalence of health problems among the employees.

Vermiculite, mined in the United States since 1929, is a hydrated magnesium-iron-aluminum silicate and is often contaminated with asbestiform minerals. After mining, vermiculite is processed to remove impurities; however, some impurities, including asbestos, may remain in processed vermiculite.

Although vermiculite may contain fibrous materials, the health effects from vermiculite itself are unknown. A priority review of asbestos-contaminated vermiculite, completed by the Office of Testing and Evaluation in June 1980, suggested that the asbestos in vermiculite may be responsible for the reported adverse health effects, and it concluded that certain information gaps needed to be filled before an in-depth risk assessment on vermiculite could be initiated.

The available information on the composition of commercial vermiculite indicated that asbestos contamination of vermiculite does occur but that the degree and kind of contamination might be difficult to assess and might vary with the source of the vermiculite. Therefore, the objective of this task was to sample and analyze vermiculite to determine the contaminants, particularly the amount of asbestiform minerals present. The study was to provide information to be used in the assessment of the risk to the population exposed to asbestiform minerals from vermiculite at each of the various stages of its commercial distribution.

The original task objective was divided into two phases. The first phase was to conduct an in-depth analysis of fibers present in, and associated with, vermiculite ore concentrates and beneficiated vermiculite from the major vermiculite mines in the United States and beneficiated vermiculite from the ports of entry. Both bulk and air samples were to be collected and analyzed. The second phase was to have been a similar analysis of bulk and air samples from a representative number of exfoliation plants in the United States. Because of a shift of priorities within EPA, the scope of the task was reduced. The task was limited to the collection of air and bulk samples from three U.S.

mines (W. R. Grace in Libby, Montana; W. R. Grace in Enoree, South Carolina; and Patterson in Enoree, South Carolina). The air samples were analyzed only by phase contrast microscopy, and the originally planned electron microscopic analysis was omitted.

With the reduction of effort, a set of the bulk samples that was considered to be representative of each mine was selected as "priority" samples for immediate analysis. This set included the head feed for the ore processing mill and, where size grades were produced, the smallest and mid-size grades. This set, representing seven samples, was analyzed by various techniques including electron microscopy for fiber content, with emphasis on asbestiform minerals. The analysis was done by two independent laboratories. It was considered possible that fibers could be bound between the vermiculite plates and that fibers could be released with exfoliation. Therefore, analyses were conducted both on the samples as received and after laboratory exfoliation. Laboratory exfoliation differs from commercial exfoliation in that under the conditions of commercial exfoliation much of the fines and heavies are removed from the vermiculite. The laboratory exfoliation is done under conditions that produce no sample fractionation. Thus, much of the asbestos would be removed from the vermiculite during commercial exfoliation, but none would be removed during laboratory exfoliation.

The analyses of these samples were in various stages of completion when the decision was made to reduce the scope of the task. Analytical results are available for most of this set, but for some samples the complete set of results from both laboratories was not obtained.

This report includes material compiled from reports submitted by Ontario Research Foundation and IIT Research Institute. The remainder of this report presents the summary, experimental methods, sampling, sample handling, analytical results, and appendix. Three additional volumes of appendices contain the detailed analytical results.

SECTION 2

SUMMARY

In December 1978, the vermiculite industry submitted information to EPA regarding the health problems experienced by employees who were processing asbestos-contaminated vermiculite. A priority review of asbestos-contaminated vermiculite, completed by the Office of Testing and Evaluation in June 1980, suggested that asbestos in vermiculite may be responsible for the reported adverse health effects, and it concluded that certain information gaps needed to be filled before an in-depth risk assessment of vermiculite could be initiated.

The objective of this task was to develop the protocol and to conduct sampling and analysis to determine the composition of vermiculite with emphasis on the content of asbestiform minerals.

The original scope of the study included two phases. The first phase was for the collection and analysis of air and bulk samples associated with vermiculite ore and beneficiated vermiculite from the four major U.S. mines and ports of entry. The second phase was for a similar effort for a representative number of exfoliation plants.

Due to priority shifts within EPA, the second phase was not undertaken and the scope of the first phase was reduced. Three mines and benefication plants were sampled and the samples analyzed, but the scope of the analysis was reduced from the original protocol. The air sample analysis was limited to phase contrast optical microscopy for a selected set of the samples, and the electron microscopic analysis of the air samples was not performed.

The bulk samples were analyzed by optical microscopy and x-ray diffractions (XRD) for the density separated fractions and by transmission electron microscopy (TEM) for the iospropanol suspended fractions of nonexfoliated vermiculite and the water suspended fractions of exfoliated vermiculite. The results of the optical microscopy and XRD analyses are summarized in Table 1.

The bulk sample TEM analyses were conducted in a semirandom sequence, but with the sequence ordered for the two analytical laboratories so that each of a set of priority samples would be analyzed by at least one of the laboratories early in the program.

When the program scope was reduced, a set of seven priority samples was selected to best represent the two largest mine operations. However, the sample for TEM analysis undergoes many steps of preparation for analysis, and when the program scope was reduced, several low priority samples had been prepared for analysis. Authorization was later obtained for the completion of

TABLE 1. SUMMARY OF OPTICAL MICROSCOPY/XRD ANALYSIS RESULTS

Sample[a]	Fibrous phases: Estimated mass, %	Fibrous phases: Mineral types	Nonfibrous amphiboles: Estimated mass, %	Nonfibrous amphiboles: Mineral types
Libby Grace				
Grade 1, 270-I	4-6	Trem-actin	1-3	Trem-actin
Grade 2, 276-I	4-7	Trem-actin	3-5	Trem-actin
Grade 3, 259-I	2-4	Trem-actin	< 1	Trem-actin
Grade 4, 282-I	0.3-1	Trem-actin	1-3	Trem-actin
Grade 5, 264-I	2-4	Trem-actin	2-5	Trem-actin
Grade 5 (1-day), 267-I	2-5	Trem-actin	4-8	Trem-actin } 9%
			< 1	Anthophyllite }
Head feed, 291-I	21-26	Trem-actin	6-9	Trem-actin
Extract, 294-I	1-4	Trem-actin	1-3	Trem-actin
Baghouse mill, 297-I	8-12	Trem-actin	2-6	Trem-actin
Screen plant, 288-I	2-5	Trem-actin	1-4	Trem-actin
S.C. Grace				
Grade 3, 430-I	< 1[b]	Mixed Anthophyllite Trem-actin	2-4	Trem-actin
			< 1	Anthophyllite
Grade 4, 433-I	< 1[b]	Mixed Anthophyllite Trem-actin	1-3	Anthophyllite
			1-4	Trem-actin
Grade 5, 427-I	< 1[b]	Mixed Anthophyllite Trem-actin	4-6 } 10%	Anthophyllite
			2-4 }	Trem-actin
Mill feed (+100 mesh), 436-I	< 1	Mixed Anthophyllite Trem-actin	1-3 } 12%	Anthophyllite
			6-9 }	Trem-actin
Grade 3, expanded, 439-I	< 1[b]	Mixed Anthophyllite Trem-actin	< 1	Anthophyllite
			< 1	Trem-actin
Grade 4, expanded, 442-I	< 1[b]	Mixed Anthophyllite Trem-actin	< 1	Anthophyllite
			0.5-1	Trem-actin
S.C. Patterson				
Ungraded, 573-I	< 1	Mixed Trem-actin Anthophyllite	4-8 } 20%	Anthophyllite
			8-12 }	Trem-actin

a With the exception of Sample No. 267-I, all results are for composite samples.

b Fiber bundles were mixed phase materials--both anthophyllite and tremolite-actinolite were present.

analyses of samples nearly completed. The analysis data are complete from both laboratories for the seven priority samples, but the data may or may not be complete for the others.

A difference in the interpretation of the analytical protocol resulted in a variation in the counting procedure. The requirement to count 100 fibers was interpreted by ORF to mean 100 asbestiform fibers, while IITRI counted 100 particles, defined as fibers by their aspect ratio of equal or greater than 3. To check the significance of this counting variation, two samples with different fiber characteristics (the grade 5 samples from Libby, Montana, and Enoree, South Carolina) were selected for each laboratory to repeat the analysis using the alternate procedure. Table 2 is a summary of the TEM analysis of the selected samples and includes the number and parts per million of fibers as determined by the two laboratories.

The results suggest that there are more asbestiform fibers associated with the smaller size grades of vermiculite than with the larger grades. Both dust samples collected at Libby were found to have a very high amphibole content and indicate that considerable asbestos is removed from the vermiculite during beneficiation. The South Carolina vermiculite appears to contain substantially less asbestiform fibers than does that from Libby, Montana.

Table 3 is a summary of the phase contrast results of the air samples. Only one of the analyzed air samples exceeded 2.0 fibers/cc. However, the rainy weather conditions at the time of sampling for all three locations might have resulted in lower than normal fiber counts.

Given the expected variability of the method, IITRI and ORF results appear to be in general agreement.

TABLE 2. SUMMARY OF ELECTRON MICROSCOPY ANALYSIS

Sample[a]	Priority[b] sample	Analysis,[c] exfoliated		Asbestiform fibers, all lengths			
				Amphibole		Chrysotile	
		no	yes	Fibers/g x 10^6	Mass (ppm)	Fibers/g x 10^6	Mass (ppm)
Libby Grace							
Grade 1							
270-I			X	31.6	78	0.9	3.5×10^{-3}
Grade 2							
276-I			X	23.4	48.5	0	0
Grade 3	P						
259-I		X		38.9	210	0.9	0.01
259-0		X		25	59	< 2.1	-
259-I			X	42.0	250	0.4	6.1×10^{-3}
259-0			X	59	240	< 1	-
Grade 4							
282-0		X		1	1		
282-I			X	65	460	0	0
282-0			X	1.8	17	< 0.4	-
Grade 5	P						
264-I		X		118	840	-	-
264-0		X		100	600	< 1.4	-
264-I(0)		X		127	1,200	-	-
264-0(I)		X		98	570	-	-
264-I			X	142	2,600	-	-
264-0			X	160	1,800	< 1.6	-
264-I(0)			X	119	350	-	-
264-0(I)			X	110	2,600	< 1.6	-
Head feed	P						
291-I		X		62.5	670	1.4	0.13
291-0		X		130	690	1.2	< 1
291-I			X	73.8	590	-	-
Extractor							
294-I			X	55.0	420	0.7	3.4×10^{-3}
Mill dust							
297-0		X		100	4,600	-	-
297-I			X	777	35,000	-	-
Screening dust							
288-0		X		300	3,000	< 1.6	-
288-I			X	1,800	41,000	-	-

(continued)

TABLE 2 (continued)

Sample[a]	Priority[b] sample	Analysis,[c] exfoliated: no	exfoliated: yes	Asbestiform fibers, all lengths: Amphibole Fibers/g x 10^6	Amphibole Mass (ppm)	Chrysotile Fibers/g x 10^6	Chrysotile Mass (ppm)
S.C. Grace							
Grade 3	P						
430-I		X		1.0	0.55	0.1	5×10^{-4}
430-0		X		2.7	< 1	< 0.3	-
430-I			X	3.1	3.7	-	-
430-0			X	2.4	1	< 0.5	-
Grade 4							
433-I		X		1.6	6.5	-	-
433-0		X		2.7	35	< 0.3	-
433-I			X	3.1	1.4	-	-
433-0			X	2.7	2	< 0.3	-
Grade 5	P						
427-I		X		0.6	1.5	-	-
427-0		X		17	37	2.6	-
427-I(0)		X		3.0	4.8	0.07	1×10^{-4}
427-0(I)		X		31	130	2.6	< 1
427-I			X	3.5	4.1	-	-
427-0			X	2.9	120	< 0.3	-
427-I(0)			X	3.2	7.3	-	-
427-0(I)			X	2.4	9	0.9	< 1
Head feed	P						
436-I		X		0.3	0.49	-	-
436-0		X		12	22	0.3	< 1
436-I			X	1.3	0.81	-	-
Grade 3 exfoliated							
439-I				11.7	-	-	-
S.C. Patterson beneficiated							
Ungraded	P						
573-I		X		0.03	3.7×10^{-4}	0.03	1.4×10^{-4}
573-0		X		1.7	27	< 0.3	-
573-I			X	0.5	3	0.2	5.3×10^{-3}
573-0			X	1.1	4	< 0.3	-

a The "I" and "0" following the sample number indicates the analyzing laboratory, IITRI and ORF, respectively. The "(I)" and "(0)" indicates the counting procedure, e.g., 264-I(0) are the results from IITRI using the ORF procedure.

b Seven samples were designated as priority samples for complete analysis at the time the program was reduced in scope.

c Analysis was conducted on the samples as received and following laboratory exfoliation, which unlike commercial exfolintion, does not cause sample fractionation.

TABLE 3. RESULTS OF THE PHASE CONTRAST ANALYSIS OF AIR SAMPLES COLLECTED AT THREE VERMICULITE SITES

Sample		Sample vol. (ℓ)	Fibers/cc ORF	Fibers/cc IITRI
Libby, Grace				
106	Field blank[a]	-	< 0.02	0.04
133	Field blank[a]	-	0.03	0.05
131	Front loader	303	0.02	0.04
148	Pit haul driver	297	< 0.01	0.01
138	Mine analyst	294	1.5	1.9
141	Bottom operator	276	1.2	0.4
130	No. 2 operator	285	3.1	9.7
139	Dozer operator	270	0.02	0.2
101	Shuttle truck	385	0.1	0.2
104	Screening plant, DW	390	0.08	0.5
111	Screening plant, DW	368	0.1	0.02
108	Trailer court	169	0.03	ND[b]
136	No. 5 substation	111	0.03	0.02
South Carolina, Grace				
312	Field blank[a]	-	< 0.02	0.04
346	Field blank[a]	-	< 0.02	0.02
340	Mill monitor	340	0.03	0.03
321	Mill lab technician	478	0.07	0.2
301	Dragline operator	240	< 0.01	ND[b]
347	No. 4 bagger	314	0.06	0.1
330	No. 3 bagger	285	0.1	0.05
328	Mill (ENE) downwind	287	0.05	0.04
335	Mill (N) crosswind	80	0.04	ND[b]
307	Mine (N) crosswind	291	< 0.01	0.02
323	Mine (E) downwind	154	0.01	0.02
338	Mine (W) upwind	264	0.03	0.01
310	Truck driver	257	< 0.01	0.3
300	Screening plant floor	354	0.06	0.14
South Carolina, Patterson				
505	Field blank[a]	-	< 0.02	< 0.01
533	Field blank[a]	-	< 0.02	0.02
508	Payload operator	255	< 0.01	0.04
520	Plant foreman	252	0.01	0.3
542	Bagger/forklift	249	< 0.01	0.1
513	(NE) downwind	188	< 0.01	ND[b]
506	Control off-site	274	< 0.01	ND[b]
515	(SE) crosswind	299	0.01	0.01
528	(SW) upwind	147	0.02	ND[b]

a Values for blanks were calculated assuming a 100-liter sample.

b ND: No fibers detected (100 grids).

SECTION 3

EXPERIMENTAL PROTOCOL

A study protocol was prepared for the task and reviewed by EPA and the subcontractors before sampling and analyses were undertaken. Appropriate modifications were made following additional reviews. The protocol "Task 32 - Study Protocol for the Collection and Analysis of Vermiculite and Related Samples for the Evaluation of Fiber Content with Emphasis on Asbestiform Fibers" appears in this volume as Appendix A. A detailed analytical procedure for bulk samples prepared by IITRI appears as Appendix B.

During the program some modifications from the study protocol were found to be necessary or desirable, and minor changes were made. This section discusses the general protocol briefly, with major emphasis on areas where modifications were made.

SAMPLE COLLECTION

No major changes were made in the sampling protocol. The following items are noted:

1. W. R. Grace representatives would not allow MRI personnel into any of the processing facilities. All samples, both bulk and air, from within the processing facilities were collected by EPA personnel.

2. Ore processing at Libby, Montana, involved a wet beneficiation process, while both facilities in South Carolina used dry beneficiation processes. The differences in processes resulted in different types of waste materials.

3. W. R. Grace has automatic sampling equipment at various places in their processing for their QA program. Portions of these samples were obtained that represented 7 to 10 days of operation before our sampling. One day of automatic sample collection was observed by the sampling crew EPA representative.

SAMPLE HANDLING

Bulk Samples

The bulk samples were packed in double sealed bags in the field and shipped by air freight to MRI. The increment samples were riffle divided, and approximately equal portions of each increment of the same sample type were combined, mixed, and riffle divided to obtain replicate composite samples for analysis.

Air Samples

The air sample filters were retained in the filter cartridges during transport to MRI. The plugged cartridges were placed in a special container to maintain the filters in a horizontal position with the collecting surface up and hand-carried back to MRI. At MRI the filters were cut into three equal portions and each portion individually taped to the bottom surface of a 49 x 9 mm Millipore® plastic petrie dish. A set of one-third of each air sample filter was hand-carried to the two laboratories for analysis.

SAMPLE ANALYSIS

Bulk Sample Analysis

Since no microscopy technique is capable of measurement over the whole size range of fragments present in vermculite samples, it is of extreme importance, prior to selection of the analysis procedure, to understand precisely how the analytical results are to be applied.

The basic choice in the analysis of vermiculite was either to completely pulverize the material and reduce the particle sizes into a range suitable for a single analytical technique, or to retain the original size distribution and measure relevant parameters on the material as normally used. Using the latter approach, numerical fiber counts per unit mass of original material are meaningful and assist interpretation on the basis of current medical opinion that fiber numbers are the important exposure criterion.

If the material is completely crushed, there are a number of disadvantages:

1. The fiber size distribution is not preserved, and any numerical fiber count is meaningless except that fiber volume can be considered as an indication of the mass percentage of fiber in the original sample material.

2. Even the mass value thus obtained is not representative of that in the final product, since at exfoliation much of the massive material is separated and discarded.

3. Simple X-ray diffraction (XRD) measurements of the amphibole or serpentine content of such a pulverized sample is of inadequate sensitivity (about 1% for amphiboles and possible 5% for serpentine). Moreover, XRD is incapable of distinguishing the fibrous varieties from other amphiboles or serpentine.

4. The crystallography of the fibers may be altered (Spurny et al., 1979).[1]

The procedure of Chatfield and Lewis (1980)[2] was designed to retain the size distribution of the material as it is normally used, and to allow very sensitive measurement of asbestos fiber concentrations down to detection limits in the parts per million (ppm) region.

Essentially, their procedure was:

1. To suspend the beneficiated vermiculite in water and sample, for transmission electron microscope (TEM) analysis, only the range of particle sizes which would include all respirable fibers.

2. To simulate on a laboratory scale the industrial exfoliation procedure, and to examine by TEM the fraction which does not float on water. The floating fraction would in fact be the final product. If fibers have been found in the earlier analyses, the floating fraction could also be examined to determine its fiber content.

3. To examine typical vermiculite flakes for the presence of intercalated fibers which may be released on exfoliation.

If there are no very large fibers present, the assumption can be made that any fibrous component has been sampled representatively from the aqueous suspension, and the results can be interpreted as total fiber concentrations by weight. Where large amounts of asbestos fibers are present throughout the whole size spectrum, the procedure introduces a size cut-off above which no particles are included in the analysis. Under these conditions the concentration by weight must be interpreted carefully, although concentrations by number will be almost unaffected. It is important when using this method that the size cut-off established does not restrict the representative sampling of the largest fibers considered to be respirable. Timbrell (1965)[3] has determined that the free falling speed of high aspect ratio fibers is proportional to the square of the diameter and only increases slowly with length. The largest compact particles normally found in lungs are about 10 micrometers (μm) in diameter (unit density), which as a first approximation was found to be equivalent to a fiber of about 3.5 μm in diameter, whatever its length may be. Hence, the size cut-off in the analytical method should exceed a unit density equivalent spherical diameter of 10 μm, which corresponds to a sphere of 5.6 μm diameter if the density is assumed to be 3.2 g/cm^3. The falling velocity of a sphere is obtained from the Stokes' relationship:

$$V = \frac{g \cdot d^2 \ (\rho s - \rho L)}{18\eta}$$

where V = terminal velocity
g = acceleration due to gravity
d = diameter of the sphere
ρs = density of the sphere
ρL = density of the liquid
η = coefficient of viscosity of the liquid

For a sphere of 5.6 μm diameter and density of 3.2 g/cm^3 the terminal velocity in water is calculated to be 0.0037 cm/sec, or 270 sec/cm. Under the agitation conditions in the ultrasonic bath, it is unlikely that particles of this low falling velocity will deposit during the period when representative samples of the dispersion are withdrawn for analysis. Accordingly, it can be stated that the method yields a fiber count which includes all fibers considered to be respirable.

The analytical procedure described above does not yield an actual total fiber content by weight where very large fibers are present, and it is for this reason that the initial step of a low magnification optical examination was incorporated. In this way such samples can be detected before effort is expended on TEM fiber counts which may be irrelevant. However, the TEM procedure must still be used if determination of the respirable fiber concentration is required.

Both analytical laboratories contributed to the preparation of the adopted protocol and both laboratories followed the protocol. However, there were variations in emphasis and interpretation of the protocol by the two laboratories, and these differences were not recognized until some of the results were obtained. While to a degree the variations in procedures prevent the direct comparison of results, the slightly different approaches complement each other and give a better overall understanding of the samples than would either single approach.

The significant differences were as follows:

1. ORF examined the bulk samples by optical microscopy for the presence and qualitative identification of asbestiform fibers. IITRI performed more complete qualitative and semiquantitative analysis of the bulk sample using density fractional separation, followed by component identification by optical microscopy and X-ray.

2. The following appeared in the protocol for the TEM analysis: "Make fiber count - determine chrysotile or amphiboles. Count 100 fibers or 10 grids of 200-mesh screen. Determine the limits of detection and count more grids if necessary." ORF interpreted this statement to mean count 100 chrysotile or amphibole fibers; IITRI interpreted the statement to mean count 100 particle units with an aspect ratio of equal to or greater than 3. To determine the effect of the difference of counting procedure between the two laboratories, two samples were selected for cross comparison. For these two samples each laboratory examined the sample by the other's procedure as well as their own. The two samples were selected to represent a high and low concentration of asbestiform fibers (Grade 5 from Libby and Grade 5 from South Carolina Grace).

Air Sample Analysis

Due to a change in the scope of the task, the analysis of the air sample filters by TEM was not undertaken. The optical phase contrast analysis was conducted according to the protocol.

SECTION 4

SAMPLING

Sampling trips were made to the Grace mine and processing facilities near Libby, Montana, during October 21-26, 1980, and to both the Grace and Patterson mines and processing facilities near Enoree, South Carolina, during November 3-6, 1980. Both air samples and bulk samples were collected at each location. Air sampling was of two types, personal and stationary. For the personal samples, nine Dupont Model 4000 samplers were used. The flow rates were calibrated before and after sampling. Stationary air sampling was conducted using battery-powered stationary samplers designed by MRI. These samplers have proven to be effective in previous air sampling projects.[4,5,6] Wind conditions during sampling were recorded using a Wang meteorological station. Brief descriptions of sampling conditions and a list of samples collected follow.

W. R. GRACE MINE, LIBBY, MONTANA

Mr. Fred Eaton of W. R. Grace, Cambridge, Massachusetts, was the company representative for the coordination of sampling. Mr. Jim Salois of MSHA, Helena, Montana, was present at the request of Ms. Diana M. Kraft, MSHA, Arlington, Virginia. Mr. Salois was familiar with the Libby facilities, and his presence and suggestions were very helpful.

At the request of Mr. Eaton, duplicate concurrent personnel air samples were taken, one for this task and one for Grace. Thus each subject was fitted with two samplers. Mr. Eaton also requested that all personal air sampler pumps used for this task be recalibrated at the Libby facility even though they had been calibrated just before shipment from MRI. The nine pumps used were determined to have flow rates ranging between 2.03 and 2.19 liters/min. The flow rates for the stationary samplers were measured at the time the samplers were set up, periodically during sampling, and at the end of sampling. The specific flow rates, calibration data, and related information appear in Appendix C of this report.

Sampling was scheduled and conducted on Thursday, October 23, 1980. For several days prior to sampling the weather had been rainy, and sampling was started in heavy fog with essentially no wind in the mine area. There was no evidence of dust in the mine, from either the mining operation or along the truck routes. The weather cleared shortly after noon. The wind direction and speed were recorded during the sampling day.

The objective was to take a short (2-hr) sample, followed by a longer (6-hr) sample that would complete the work shift. The actual times varied somewhat from the intended times, but the actual times and volumes for each sample were recorded (Appendix D).

Grace has a routine bulk sampling procedure as part of their product quality control program. At our request they had taken and retained bulk samples of the five grades of product plus related head feed, tailings, and dusts for 7 to 10 days before air sampling. The samples taken on October 23 were comparable to the earlier samples, but their collection was observed and verified by Tom Dixon of EPA.* The air samples collected at Libby, along with the approximate sampling duration, are given in Table 4. Figures 1 and 2 show the wind conditions and site positions for the stationary air samplers. The bulk samples collected at Libby are given in Table 5.

W. R. GRACE MINE AND PROCESSING MILL, ENOREE, SOUTH CAROLINA

Mr. Fred Eaton, who was the company representative at Libby, Montana, was also the company representative at Enoree. Ore from two mines (Lanford and Foster) are hauled to the processing mill at a third location. During the sampling period only the Foster mine was in operation. The Foster mine is located near the southwest corner of the junction of County Road 50 and Interstate 26 in Spartanburg County. The mill is located on Highway U.S. 221 about 1 mile south of the junction with Highway 92, in Laurens County. The initial schedule was to sample at the mine on Tuesday, November 6, 1980, and at the mill on Wednesday. However, because of rain during Tuesday morning, the mine was closed and the schedule was reversed. A light rain fell Tuesday morning; the remainder of the sampling period was clear and cool.

The air samples collected at the Grace Enoree operations are given in Table 6 and the bulk samples are given in Table 7. The wind conditions and air sampling site positions are shown in Figures 3 and 4 for the mill and in Figures 5 and 6 for the mine.

PATTERSON VERMICULITE COMPANY, ENOREE, SOUTH CAROLINA

The Patterson mine and exfoliation/bagging operations are located approximately 7 miles northeast of the W. R. Grace mill. No mining was underway on the day of sampling, November 6, 1980, so sampling was only conducted around the processing plant. Patterson does not size their product and produces a single size grade. The air samples collected at the Patterson plant are listed in Table 8 and the bulk samples in Table 9. The wind conditions and air sampling site positions are shown in Figures 7 and 8.

* MRI employees were excluded from all mill operations.

TABLE 4. AIR SAMPLES COLLECTED AT THE GRACE MINE AND MILL, LIBBY, MONTANA

Sample description	Filter No.	Approx. time (hr)	Analysis assignment[a] PC	EM	Hold
Pesonnel samplers					
Front loader	131	2	X		
Front loader	135	5			X
Pit driver	148	2	X		
Pit driver	126	5			X
Mine analyst	138	2	X		
Mine analyst	129	5		X	
Mill operator, bottom	141	2	X		
Mill operator, bottom	146	5			X
Mill operator No. 2	130	2	X		
Mill operator No. 2	125	5			X
Bulldozer operator	139	2	X		
Bulldozer operator	128	5			X
Shuttle truck driver	101	2	X		
Shuttle truck driver	121	7		X	
Stationary samplers[b]					
Station 7 screening plant D.W.	104	2	X		
Station 7 screening plant D.W.	111	2	X		
Station 7 screening plant D.W.	112	6		X	
Station 7 screening plant D.W.	120	6		X	
Station 6 screening plant U.W.	116	2			X
Station 6 screening plant U.W.	124	6			X
Station 2 perimeter D.W.	109	2			X
Station 2 perimeter D.W.	113	2			X
Station 2 perimeter D.W.	145	6			X
Station 2 perimeter D.W.	147	6			X
Station 4 perimeter C.W.	103	2			X
Station 4 perimeter C.W.	149	2			X
Station 5 lower meadow	119	2			X
Station 5 lower meadow	115	6			X
Station 9 trailer court	108	2	X		
Station 9 trailer court	102	6		X	
Station 8 car loading	123	2			X
Station 8 car loading	122	3			X
Station 3 "22" level dump	107	2			X
Station 3 "22" level dump	134	6			X
Station 1 substation No. 5	136	2	X		
Station 1 substation No. 5	132	6		X	
Field blanks	114			X	
	137			X	
	106		X		
	133		X		
	110				X

a PC - phase contrast optical microscopy, EM - electron microscopy, Hold - sample retained without analysis.

b Station numbers indicated in Figure 2.

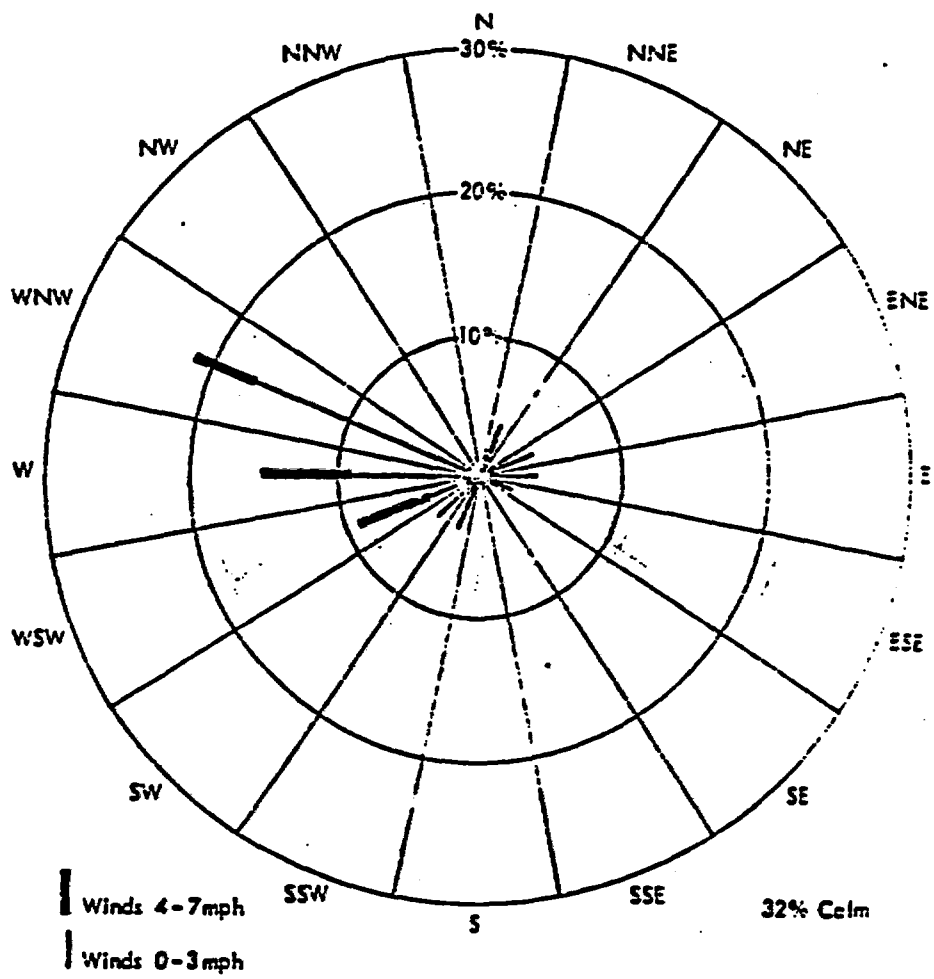

Figure 1. Wind rose pattern showing the direction and intensity of the wind during the air sampling period at the Grace, Libby, Montana, facility.

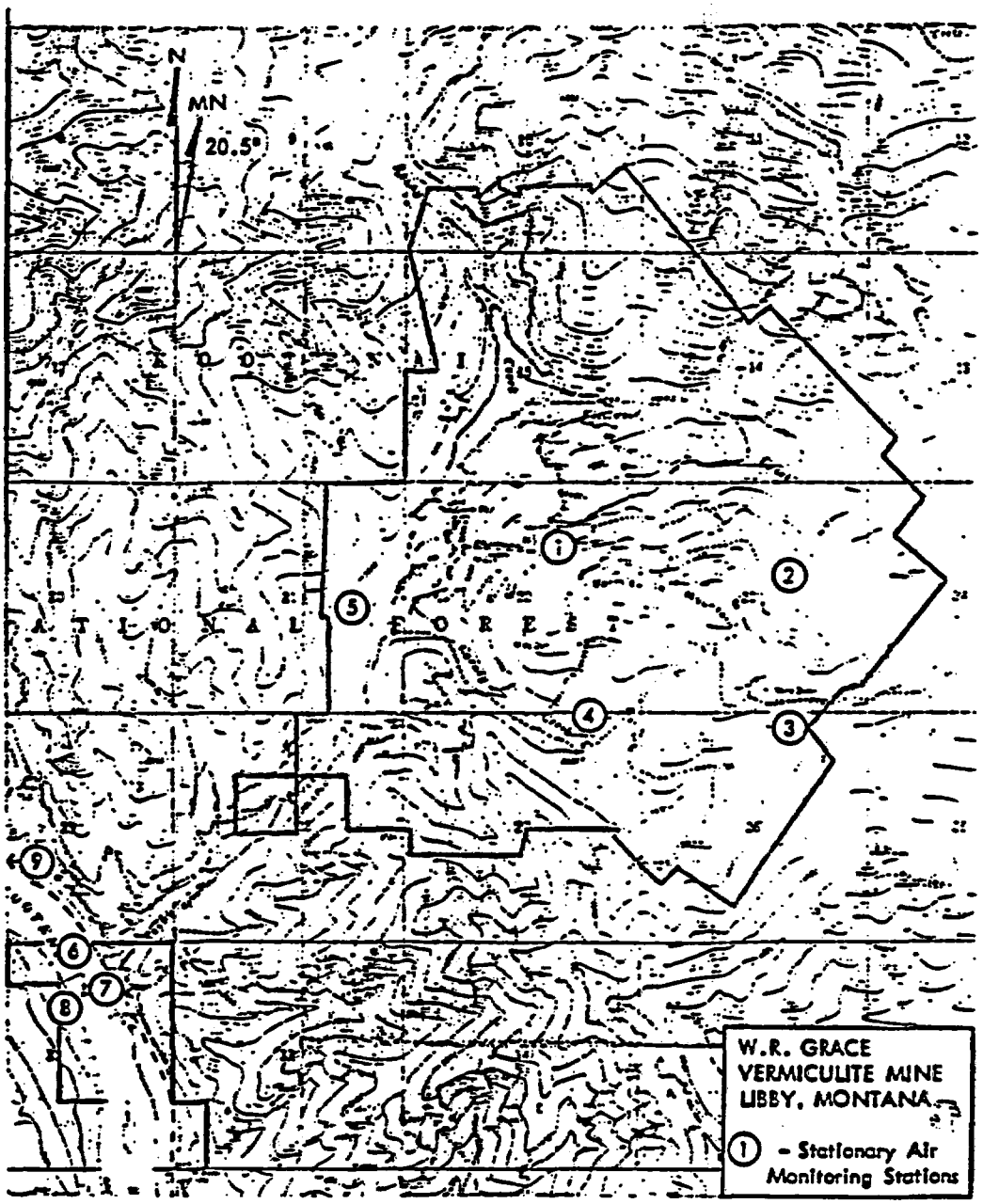

Figure 2. Map of the Grace, Libby, Montana, facility showing the stationary air sampling locations.

TABLE 5. BULK SAMPLES COLLECTED AT THE GRACE MINE AND MILL, LIBBY, MONTANA

Sample description	No. of samples
Beneficiated Grade 1 vermiculite	11[a]
Beneficiated Grade 2 vermiculite	11[a]
Beneficiated Grade 3 vermiculite	11[a]
Beneficiated Grade 4 vermiculite	11[a]
Beneficiated Grade 5 vermiculite	11[a]
Dust from screening plant	8[b]
Dust from dryer	9[c]
Head feed	9[c]
Under 90 mesh	9[c]
Coarse tails	9[c]
Extractor	9[c]

a Days collected for 11-day samples: October 7, 8, 9, 10, 13, 14, 15, 16, 17, 21, 23, 1980.

b Screening plant dusts collected: October 8, 9, 10, 13, 14, 15, 17, 23, 1980.

c Collected October 8, 9, 10, 13, 14, 15, 16, 17, 23, 1980.

TABLE 6. AIR SAMPLES COLLECTED AT GRACE, ENOREE, SOUTH CAROLINA

Sample description	Filter No.	Approx. time (hr)	Analysis assignment[a] PC	EM	Hold
Mine personnel samples					
Truck driver 1	315	2			X
Truck driver 1	324	2			X
Truck driver 2	310	2	X		
Truck driver 2	320	5		X	
Dragline operator 6	301	2	X		
Dragline operator 6	306	6		X	
Mine stationary samples[b]					
Crosswind N. station 1	351	5			X
Crosswind N. station 1	318	4			X
Crosswind S. station 3	307	2	X		
Crosswind S. station 3	353	5			X
Upwind W. station 4	316	4			X
Upwind W. station 4	338	2	X		
Downwind E. station 2	323	2	X		
Downwind E. station 2	352	6			X
1 mile offsite station 5	334	2			X
1 mile offsite station 5	350	5			X
Along haul route	331	2			X
Along haul route	354	5			X
Mill personnel samples					
Forklift operator	305	2			X
Forklift operator	339	4		X	
Bagger	314	2			X
Bagger	322	4			X
Bagger	330	2	X		
Bagger	349	4		X	
Bagger	347	3	X		
Bagger	337	4			X
Mill monitor	336	3		X	
Mill monitor	340	3	X		
Mill laboratory technician	308	3		X	
Mill laboratory technician	321	4	X		
Mill stationary samples[b]					
Mill office	304	7			X
Screening floor	300	2	X		
Screening floor	332	3		X	
Screening floor	341	1			X
Crosswind N. station 1	345	2			X
Crosswind N. station 1	343	5			X

(continued)

TABLE 6 (continued)

Sample description	Filter No.	Approx. time (hr)	Analysis assignment[a] PC	EM	Hold
Mill stationary samples (continued)					
Crosswind N. station 1	328	2	X		
Crosswind N. station 1	313	5			X
Crosswind S. station 3	342	5			X
Crosswind S. station 3	326	2	(void)		
Upwind W. station 4	344			X	
Upwind W. station 4	309	5			X
Downwind E. station 2	335	2	X		
Downwind E. station 2	302	5			X
Offsite control	329	7			X
Field blanks	312		X		
	346		X		
	319			X	
	348			X	
	327				X

a PC - phase contrast optical microscopy, EM - electron microscopy, Hold - sample retained without analysis.

b Station numbers indicated in Figure 4.

TABLE 7. BULK SAMPLES COLLECTED AT THE PATTERSON OPERATIONS ENOREE, SOUTH CAROLINA

Sample description	No. of samples
Raw ore from stockpile	1
Raw ore prescreening hopper	1
Postscreen ore	3[a]
Dried ore	4[a]
Exfoliated final product	4[a]
Waste from screening	4[a]
Waste from exfoliater	4[a]

a Samples were collected at approximately 2-hr intervals.

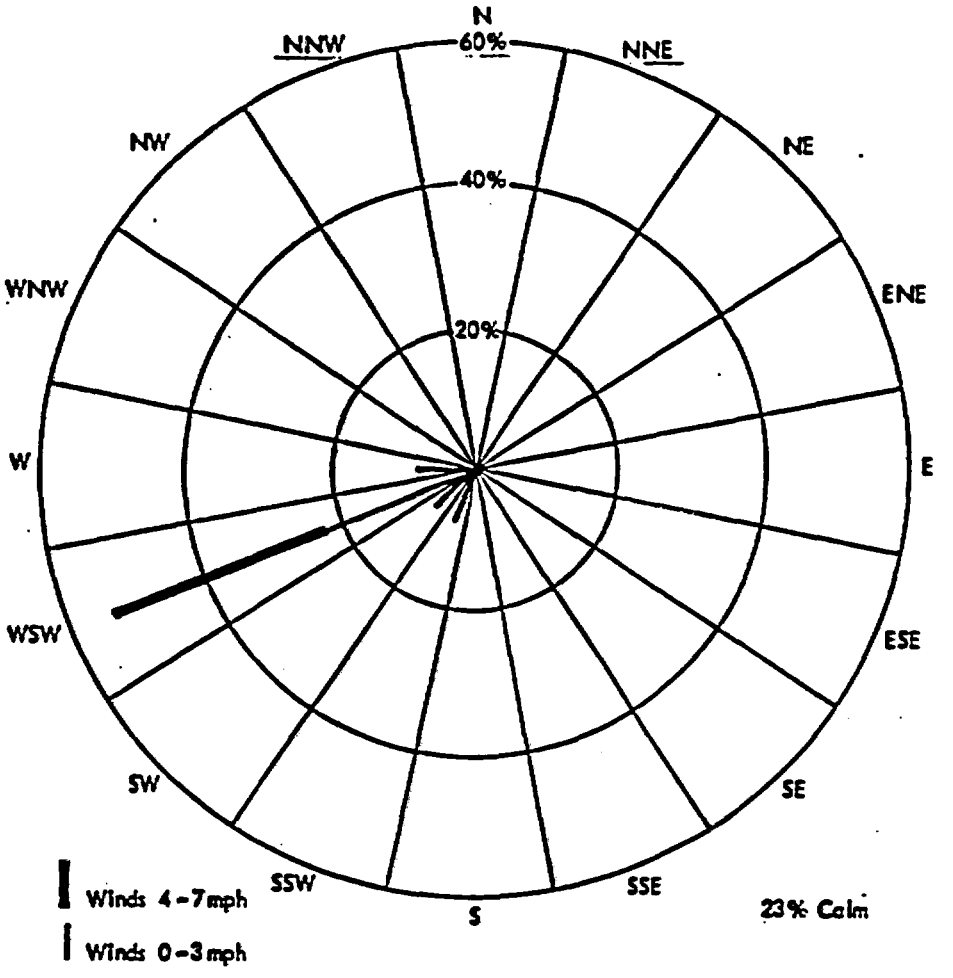

Figure 3. Wind rose pattern showing the direction and intensity of the wind during the air sampling period at the Grace, Enoree, South Carolina, mill.

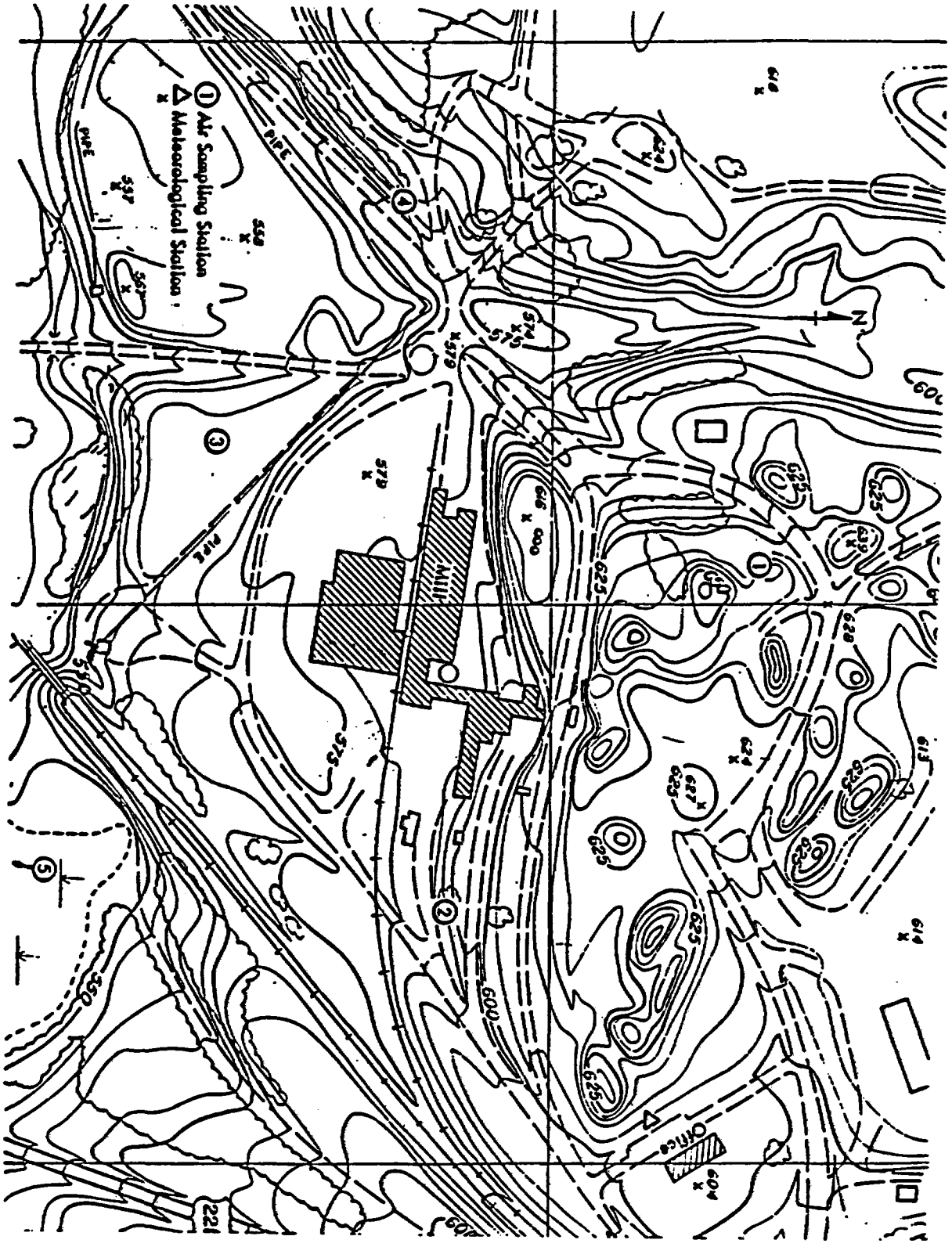

Figure 4. Map of the Grace, Enoree, South Carolina, mill area showing the stationary air sampling locations.

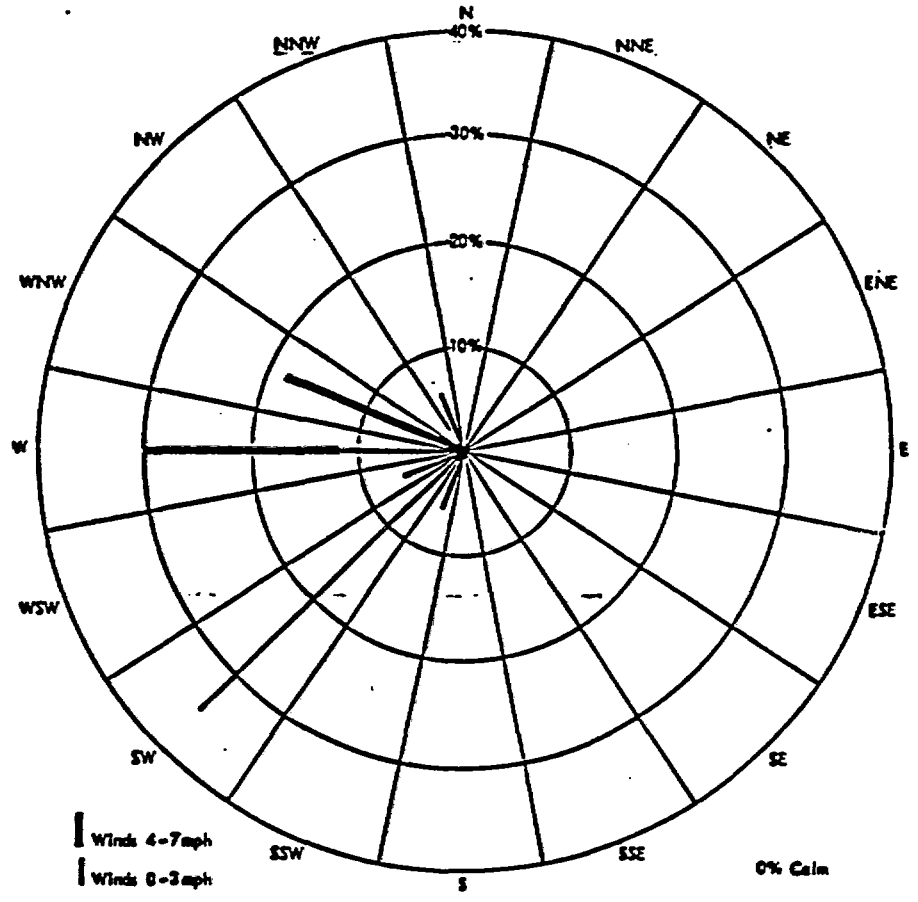

Figure 5. Wind rose pattern showing the direction and intensity of the wind during the air sampling period at the Grace, Enoree, South Carolina, mine.

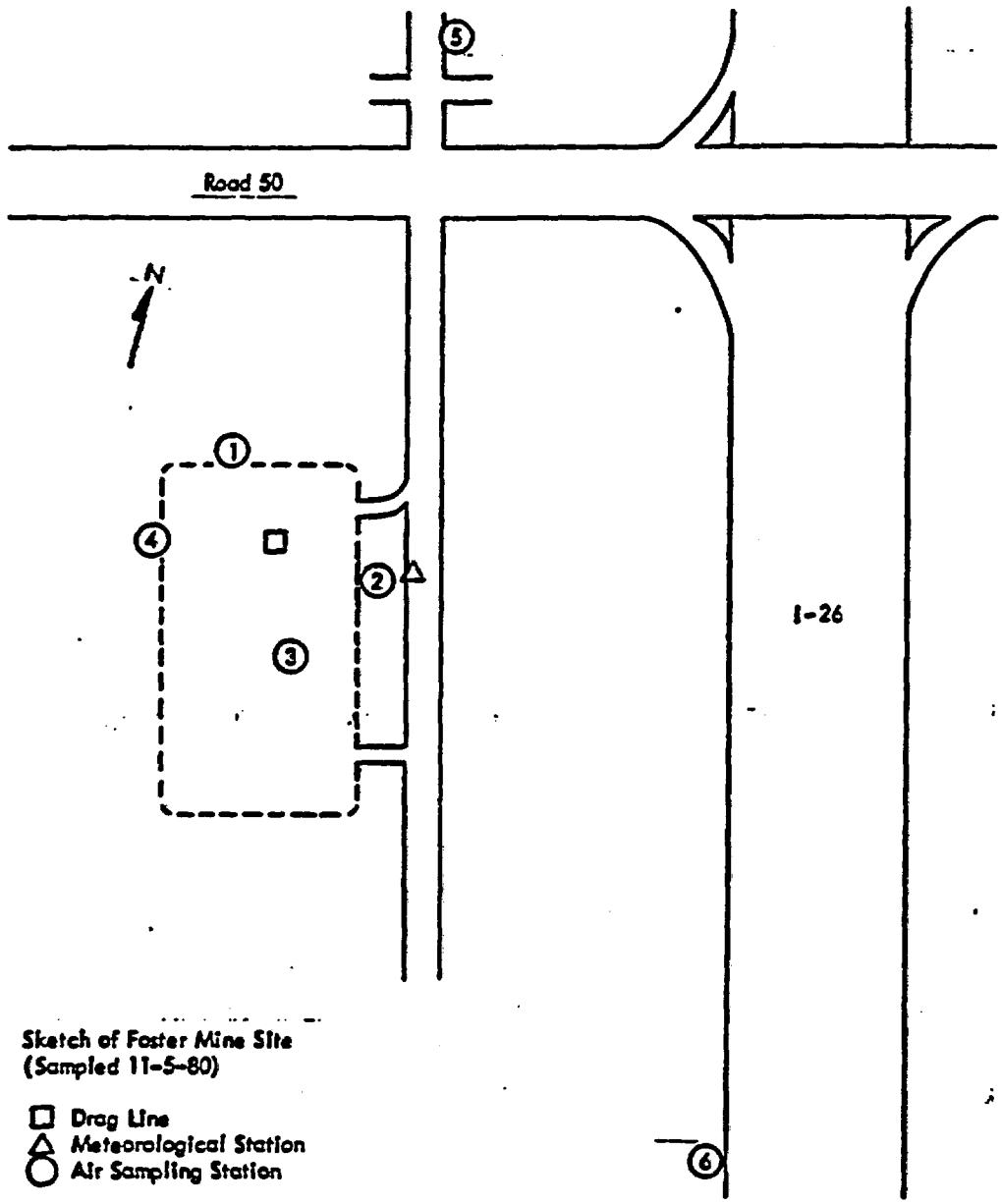

Figure 6. Map of the Grace, Enoree, South Carolina mine area showing the stationary air sampling locations.

TABLE 8. AIR SAMPLES COLLECTED AT PATTERSON, ENOREE, SOUTH CAROLINA

Sample description	Filter No.	Approx. time (hr)	Analysis assignment[a] PC	EM	Hold
Personnel samplers					
Bagger/forklift operator	542	2	X		
	504	3		X	
	517	3			X
Foreman	520	2	X		
	521	3		X	
	511	3			X
Payload operator	508	2	X		
	519	3		X	
	516	3			X
Stationary samplers[b]					
Crosswind S.E. station 2	515	3	X		
	502	6			X
Crosswind N.W. station 4	503	2			X
	518	6		X	
	531	2			X
	540	6			X
Upwind S.W. station 3	528	2	X		
	525	6		X	
Downwind N.E. station 1	513	2	X		
	523	6		X	
Remote, control	506	2	X		
	527	6			X
Field blanks	505		X		
	522			X	
	533		X		
	538			X	

a PC - phase contrast optical microscopy, EM - electron microscopy, Hold - sample retained without analysis.

b Station numbers indicated in Figure 4.

TABLE 9. BULK SAMPLES COLLECTED AT THE GRACE MINE AND MILL, ENOREE, SOUTH CAROLINA

Sample description	No. of samples
Beneficiated Grade 3 vermiculite	7[a]
Beneficiated grade 4 vermiculite	7[a]
Beneficiated grade 5 vermiculite	7[a]
Dryer composite	7[a]
Mill feed +100 mesh	7[a]
Mill feed -100 mesh	7[a]
Wet scrubber discharge composite	1[b]
Composite total tails, November 5	1
Lanford Mine composite, November 5	1
Foster Mine Composite, November 5	1
Exfoliated Grade 4 "stabilized"	1[c]
Exfoliated Grade 4 plain	1[c]
Exfoliated masonry insulation Grade 3 "coated"	1[c]
Exfoliated Grade 3 plain	1

a Days collected for 7-day samples: October 27, 28, 29, 30, 31, November 1, 1980.

b Composite collection for October 28, 29, 30, 1980.

c The exfoliated samples were sampled at the Kearney Expansion plant.

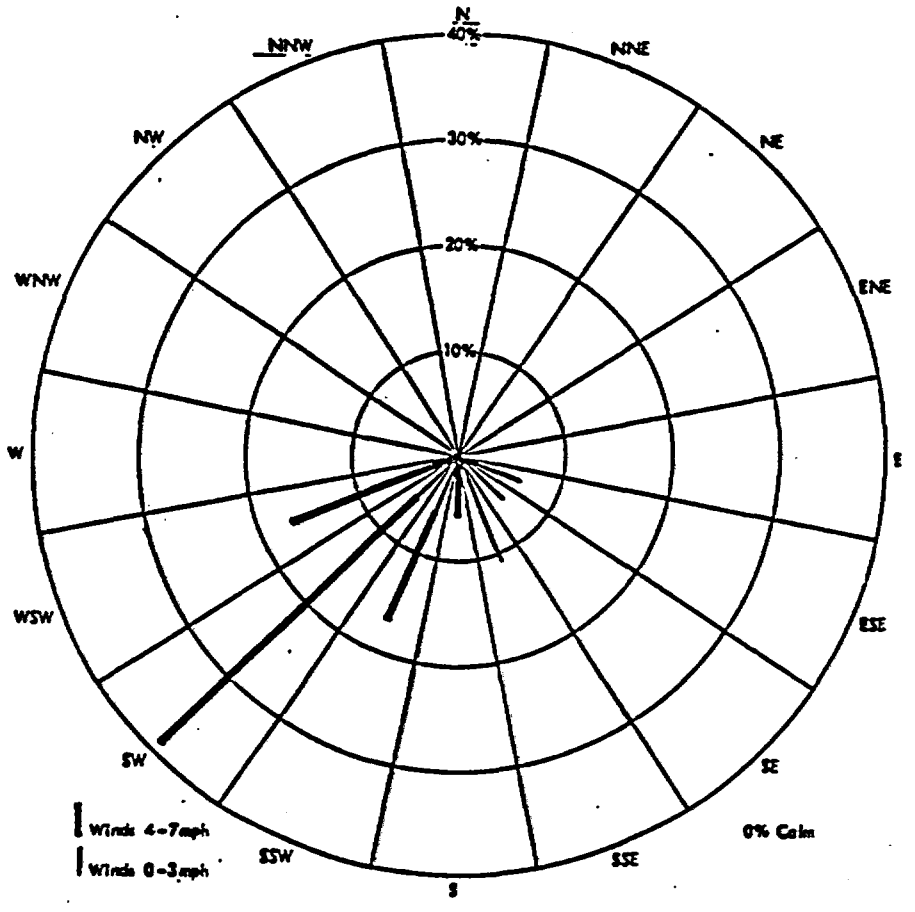

Figure 7. Wind rose pattern showing the wind direction and intensity of the wind during the air sampling period at the Patterson, Enoree, South Carolina, facility.

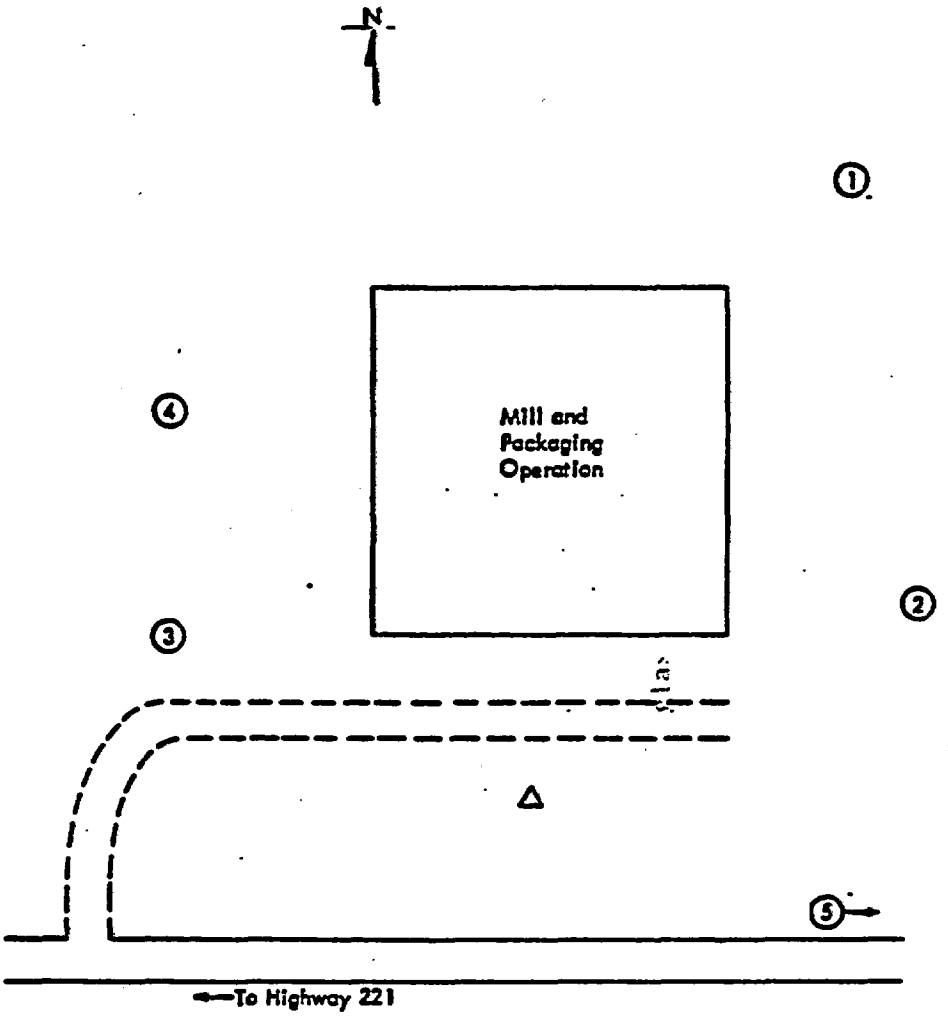

Figure 8. Map of the Patterson, Enoree, South Carolina, facility showing the stationary air sampling locations.

SECTION 5

SAMPLE HANDLING

All of the bulk samples were shipped air freight to MRI from the sampling sites. The air samples were hand-carried and maintained in a horizontal, sample-up position.

BULK SAMPLES

Most of the bulk samples were collected as increment samples representing a span of time. Composite samples were prepared for this analysis. To prepare the composite samples, each increment sample was riffled to obtain a representative fraction of the increment. Approximately equal weight fractions of each of the increments were combined to make a composite sample. The composite sample was then mixed and riffled to produce four equal samples. One of the fourths was set aside and retained as a control. One of the fourths was again riffled to produce two fractions, each one-eighth of the original sample. These two fractions were combined with the other two fourths to result in the composite division into 1/4, 3/8, and 3/8 of the original composite. The "1/4" fraction was retained at MRI, one "3/8" fracton was sent to IITRI, and the other "3/8" fraction was sent to ORF for analysis.

A list of the bulk samples and the increment weights used to prepare the composites are given in Appendix D.

AIR SAMPLES

The air sample filters were retained in the filter cartridges during transport to MRI. The top retainer portion of the cartridge was then removed and a cutting template positioned over the filter to allow the filter to be cut into three equal portions. The template held the filter around the circumference of the filter but did not contact the sampling portion of the filter. Each portion was then removed from the sampling cartridge and taped to the bottom surface of a 49 x 9 mm Millipore® plastic petrie dish. A set of one-third of each air sample filter was hand-carried to IITRI in Chicago, Illinois, and to ORF in Mississauga, Ontario.

SECTION 6

ANALYTICAL RESULTS

The analytical results of this program consist of findings from (a) the optical and x-ray diffraction (XRD) data and (b) electron microscopy data for the bulk samples and from the phase contrast optical microscopy data for the air samples. The detailed XRD and EM data are contained in three volumes of appendices. Specific data in the appendices are referenced for each sample in this section.

The data obtained for the bulk samples by IITRI from the density separated fractions provided a good overview of the composition and complexity of the samples. These data, including weight percent of three density fractions, and a listing of identified mineral phases in the various samples are presented in summary at the beginning of this section. This is followed by the complete results obtained for individual samples.

In the IITRI examination the samples are separated into three fractions based on density. The fractions are:

1. Density greater than 2.97 g/cc, sinks in 1,1,2,2-tetrabromoethane (TBE).

2. Density less than 2.97 and greater than 2.76, floats on TBE, sinks in TBE/isopropanol mixture with density of 2.76 g/cc.

3. Density less than 2.76, floats on 2.76 g/cc liquid.

Table 10 is a list of selected related minerals and their densities (specific gravity). From these values it can be seen that the vermiculite would be separated from most of the other materials, and that the materials more dense than vermiculite would be separated into two fractions. The weight percent of materials in each density fraction of samples is given in Table 11.

The mineral phases identified in each sample fraction analyzed by XRD are listed in Table 12. A key is provided with this table which groups the minerals according to types, and lists chemical formulas and JCPDS file card numbers for the patterns which were used to identify the mineral species. The raw data obtained in the analyses appear in Appendix I.

TABLE 10. SPECIFIC GRAVITIES OF SELECTED MINERALS

Mineral	Chemical formula	Specific gravity
Vermiculite	$(Mg,Ca)_{0.3}(Mg,Fe,Al)_{3.0}(Al,Si)_4O_{10}(OH)_4$	2.4
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	2.8 - 3.2
Chrysotile	$Mg_3Si_2O_5(OH)_4$	2.5 - 2.6
Serpentine	$Mg_3Si_2O_5(OH)_4$	2.3 - 2.6
Talc	$Mg_3Si_4O_{10}(OH)_2$	2.7 - 2.8
Anthophyllite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$	2.85- 3.2
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$	3.1 - 3.3
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	3.0 - 3.2
Ferroactinolite	$Ca_2Fe_5Si_8O_{22}(OH)_2$	3.2 - 3.3
Cummingtonite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$	3.1 - 3.3
Grunerite	$Fe_7Si_8O_{22}(OH)_2$	3.6
Diopside	$CaMgSi_2O_6$	3.2
Hornblende	$(Ca,Na)_{2.3}(Mg,Fe,Al)_5Si_6(Si,Al)_2O_{22}(OH)_2$	3.0 - 3.4
Quartz	SiO_2	2.65
Olivine	$(Mg,Fe)_2SiO_4$	3.27 - 4.37

TABLE 11. DENSITY-SEPARATED (AND HAND-PICKED) FRACTIONS PRODUCED

Sample[a]	Wt % hand-picked fibers	Wt % tetrabromoethane sinks	Wt % 2.76 sinks	Wt % 2.76 floats
Libby Grace				
Grade 1, 270-I	4.5	9.8	5.1	85.1
Grade 2, 276-I	4.5	12.2	5.6	82.2
Grade 3, 259-I	1.0	9.1	22.6	68.3
Grade 3, 259-I duplicate	-	8.7		
Grade 4, 282-I	0.3	10.9	14.1	75.0
Grade 5, 264-I	-	17.2	11.4	71.4
Grade 5 (1-day), 267-I	-	26.7	25.6	47.8
Head feed, 291-I	-	55.8	6.1	38.1
Extractor, 294-I	1.0	10.5	27.3	62.2
Baghouse mill, 297-I	-	2.7	17.6	79.8
Screen plant, 288-I	-	3.5	25.3	71.2
S.C. Grace				
Grade 4, 433-I	-	3.9	48.9	47.2
Grade 5, 427-I	-	10.9	4.6	84.4
Mill feed (+100 mesh), 436-I	-	26.3	23.6	50.1
Grade 3, expanded, 439-I	-	0.2	0.4	99.4
Grade 4, expanded, 442-I	-	~ 0.4	~ 0.4	~ 99.2
S.C. Patterson				
Ungraded, 473-I	-	18.1	13.9	68.0

a With the exception of Sample No. 267-I, all results are for composite samples.

TABLE 12. SUMMARY OF X-RAY DIFFRACTION ANALYSIS RESULTS

Sample[a]	Fraction-Phase	Mineral phases identified from XRD data (exluding vermiculite)
Libby Grace		
Grade 2, 276-I	TBE-SINK-fibers	Tremolite, talc
	TBE-SINK-milky, green	Tremolite, talc
	TBE-SINK-dk. green, glassy	Diopside, magnetite
	TBE-SINK-lt. green, glassy	Diopside, magnetite
Grade 3, 259-I	TBE-SINK-fibers	Tremolite
	TBE-SINK-total	Diopside, sphene, augite, fluorapatite
Grade 5, 264-I	TBE-SINK-fibers	Tremolite, diopside, sphene, talc, magnetite
	TBE-SINK-total	Diopside, tremolite, magnetite, fluorapatite, sphene, hematite, rhodonite
Grade 5 (1-day), 267-I	TBE-SINK-fibers	Tremolite, diopside, talc, sphene, augite, fluorapatite, quartz, magnetite
	TBE-SINK-total	Diopside, sphene, tremolite, augite, quartz, fluorapatite, magnetite, hematite
Head feed, 291-I	TBE-SINK-total	Diopside, tremolite, augite, fluorapatite, sphene, magnetite, hematite, quartz
	2.76 SINK-total	Biotite, tremolite, vermiculite-hydrobiotite, diopside, quartz, talc, fluorapatite, sphene, calcite, magnetite, hematite
	2.76 FLOAT-total	Tremolite, diopside, quartz, vermiculite-hydrobiotite, calcite, fluorapatite, talc, antigorite

(continued)

TABLE 12 (continued)

Sample[a]	Fraction-Phase	Mineral phases identified from XRD data (exluding vermiculite)
S.C. Grace		
Grade 3, 430-I	2.76 SINK-total	Sodium tremolite, hornblende, anthophyllite, talc, vermiculite-hydrobiotite, fluorapatite, sphene, calcite, quartz
	2.76 FLOAT-nonmicaceous	Quartz, microcline, albite, sodium tremolite, sphene, vermiculite-hydrobiotite
Grade 5, 427-I	TBE-SINK-fibers	Tremolite, anthophyllite, sodium hornblende, vermiculite-hydrobiotite, talc, sphene, fluorapatite, albite, magnetite
	TBE-SINK-total	Sodium hornblende, tremolite, anthophyllite, fluorapatite, sphene, vermiculite-hydrobiotite, magnetite
Mill feed, 436-I	TBE-SINK-fibers	Sodium tremolite, anthophyllite, talc, hornblende
	TBE-SINK-green, glassy	Hornblende, sodium tremolite, sphene
	TBE-SINK-green, milky	Sodium tremolite, hornblende, sphene, fluorapatite
	TBE-SINK-colorless, glassy	Fluorapatite, anthophyllite, sodium tremolite, hornblende
S.C. Patterson		
Ungraded, 571-I	TBE-SINK-total	Tremolite, iron anthophyllite, sodium hornblende, talc, fluorapatite, rutile, sphene, magnetite
	2.76 SINK-total	Talc, tremolite, anthophyllite, hornblende, quartz, rutile, fluorapatite, vermiculite-hydrobiotite

a With the exception of Sample No. 267-I, all results are for composite samples.

KEY TO TABLE 12

Mineral name	Chemical formula per JCPDS (file card number)	
Micaceous minerals		
Vermiculite	$(Mg_{2.37}Fe_{0.37}X_{0.26})(Al_{1.28}Si_{2.72})O_9(OH)_3 \cdot 4H_2O$	(16-613)
Biotite	$K(Fe,Mg)_3AlSi_3O_{10}(OH)_2$	(2-45)
Vermiculite-hydrobiotite	$K(Mg,Fe)_6(Si,Al)_8O_{20}(OH)_4 \cdot nH_2O$	(13-465)
Amphiboles		
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	(13-437)
Sodium tremolite	$Na_{0.25}(Ca_{1.75}Na_{0.25})Mg_5Si_8O_{22}(OH)_2$	(23-666)
Anthophyllite	$Mg_7Si_8O_{22}(OH)_2$	(16-401)
Iron anthophyllite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$	(9-455)
Hornblende	$Ca_2(Mg,Fe)_5(Si,Al)_8O_{22}(OH)_2$	(21-149)
Sodium hornblende	$(Ca,Na)_{2.26}(Mg,Fe,Al)_{5.15}(Si,Al)_8O_{22}(OH)_2$	(20-481)
Pyroxenes		
Diopside	$CaMg(SiO_3)_2$	(11-654)
Acmite-augite	$(Ca,Na)(Fe,Mn,Zn,Mg)(Si,Al)_2O_6$	(19-1)
Serpentine		
Antigorite	$Mg_3Si_2O_5(OH)_2$	(7-417)
Iron oxides		
Magnetite	Fe_3O_4	(19-629)
Hematite	α-Fe_2O_3	(13-534)
Others		
Talc	$Mg_3Si_4O_{10}(OH)_2$	(19-770)
Quartz	SiO_2	(5-490)
Microcline (feldspar)	$KAlSi_3O_8$	(19-932)
Albite (feldspar)	$NaAlSi_3O_8$	(10-393)
Calcite	$CaCO_3$	(5-586)
Fluorapatite	$Ca_5F(PO_4)_3$	(15-876)
Sphene (titanite)	$CaTiSiO_5$	(11-142)
Rutile	TiO_2	(21-1276)
Rhodonite	$MnSiO_3$	(13-138)

The XRD data generally confirmed the mineral identification made microscopically. The XRD data also confirmed the observation that partially altered mineral phases--particularly altered biotite-vermiculite phases--were present. Since vermiculite is generally formed as an alteration product of biotite mica, it was not surprising to find the intermediate phase, mixed layer vermiculite-hydrobiotite material in most samples.

The XRD analyses did provide some surprising results. The most interesting result was the abundance of vermiculite in the hand-picked fiber fraction of the Grade 5 composite from Grace's South Carolina mine (MRI Sample No. 427-I). Microscopical examination of the ground material submitted for XRD revealed that the vermiculite was intergrown with the amphibole fibers and also did in fact occur in a pseudomorphically fibrous crystal habit. Another rather interesting result of the XRD work was the identification of a sodium-bearing fibrous tremolite phase in the South Carolina samples.

Interpretation of the XRD data was hampered by the peak intensity alterations caused by crystal preferred orientations. Most of the mineral phases had crystal morphologies with at least one exaggerated crystallographic axis. Thus, in preparing samples for XRD as thin films by filtration onto silver membranes, the crystals tended to orient with the exaggerated crystal planes parallel to the filter surface--i.e., vermiculite plates and tremolite fibers landed on the filters lying flat, rather than on end. Even the pyroxenes, such as diopside, which generally do not show the prominent prismatic morphology because cleavage along the prism planes is not so perfect as it is in amphiboles, tended to orient themselves on the silver membrane and thus peak intensities in the XRD patterns did not correspond to published data. Quartz and feldspars were practically the only mineral species detected that did not exhibit preferred orientation effects in the XRD data.

The effects of crystal preferred orientations on diffraction peak intensities are very clearly demonstrated by the XRD data obtained for the phases analyzed of Sample No. 276-I (Libby, Grade 2). The phases analyzed were hand-picked and were relatively pure phase materials. Diffraction peak positions were consistent with the phases identified--tremolite and diopside--but relative peak intensities were not consistent with the published values. A careful review of the published crystal plane reflections corresponding to the peaks that demonstrated the greatest variation from published intensity values clearly indicated that the peak intensity variations were due to crystal orientation effects. That is, peaks showing higher relative intensities compared to published data corresponded to crystal planes that were preferentially placed in the x-ray path (e.g., the elongated axis of a prism or fiber) while absent peaks or peaks with low intensities compared to published data corresponded to crystal planes placed essentially out of view of the x-rays (e.g., the end-on-view of a prism or fiber).

Individual Sample Results

The results for individual samples follow. The order of presentation is (a) graded samples from Libby; (b) other Libby samples; (c) graded samples from South Carolina, Grace; (d) other samples from South Carolina, Grace; and (e) samples from South Carolina, Patterson.

Much of the detailed data and selected photographs are contained in appendices. The appendices appear in this volume and three supplementary volumes.*

The presentation for each sample include the sample type, code numbers assigned to the sample** and appendices page references, optical microscopy discription of the sample, and electron microscopy results.

The detailed optical microscopy examination results presented here are primarily those submitted by IITRI. The ORF optical microscopy examination provided qualitative information on the presence or absence of visible fibers and identification of those fibers observed. The ORF results were in agreement with the more detailed results presented here.

Sample 270, Libby, Montana, Grace, Grade 1, Composite

IITRI Code No. 129
Appendix references
Electron microscope I-84-87

Macroscopically, this sample was composed of 1- to 20-mm chunks of gold to green micaceous minerals, 1- to 15-mm bundles of white to pale green fibers, and 1- to 8-mm chunks of nonmicaceous, nonfibrous minerals. The nonmicaceous minerals ranged in color from deep green, to pale green, to white to colorless. Prismatic as well as conchoidally fractured chunks of nonmicaceous minerals were observed. Fibrous bundles were sufficiently large and numerous to allow hand-picking before the density separation was conducted.

The mineralogical composition of the sample, as determined by polarized light microscopy analyses of the density-separated and hand-picked fractions, is presented in Table 13. Tremolite-actinolite fibers were identified as significant sample components. No fibrous serpentine minerals were detected.

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* Photographs, this volume Appendix E, pp. E-2 to E-25.
IITRI EM, Appendix I, pp. I-1 to I-121.
IITRI XRD, Appendix I, pp. I-122 to I-160.
ORF EM, Appendix II (two volumes) pp. II-1 to II-203 and II-204 to II-420.

** Originally the three fractions of the sample composites were assigned unique ID numbers. For this report the designations were simplified so that portions of the same composite sample had the same ID number followed by a letter indicating the analyzing laboratory. Most of the computer generated data in appendices I and II relate to the original ID numbers.

TABLE 13. COMPOSITION OF SAMPLE 270-I

Mineral phase	Estimated mass concentration (%)
Tremolite-actinolite fibers	4-6
Tremolite-actinolite prisms	1-3
Sphene	1-2
Diopside	2-5
Augite	< 1
Hornblende	< 1
Magnetite, hematite	1-2
Calcite	1-3
Quartz	3-5
Biotite	1-2
Talc	< 1
Vermiculite	72-82
Other minerals	1-3

Tremolite-actinolite was identified as the primary fibrous phase present in the sample. Fiber color, refractive indices, and extinction angles were all consistent with a tremolite-actinolite amphibole. Both colorless (white, macroscopically) and green fiber bundles were evident; the green-colored fiber bundles were the more abundant.

The fibrous phase of this sample was not as well-formed as it was in the other bulk samples analyzed from Libby. That is, fiber bundles contained higher proportions of materials that would be more correctly classified as prismatic rather than fibrous, than did other samples from Libby. Particles that could readily be classified as fibers tended to be much shorter in this sample compared to other samples analyzed from Libby. An unusual morphological particle type was a significant component of the fibrous phase of this sample, and was noted as only a trace component of the tremolite-actinolite phase in other samples. The particle type was composed of lamellated tremolite-actinolite prisms, intergrown at angles as great as 60 degrees to each other. In other samples, particles composed of the lamellated prisms were composed of entirely parallel crystals. It would appear that the nonparallel intergrown prisms represent an intermediate metamorphic state, between prismatic and fibrous tremolite-actinolite.

Other mineral types such as diopside, hornblende, sphene, calcite, quartz, and even the vermiculite tended to mimic the nonparallel intergrown prism morphology of the tremolite-actinolite, rather than the truly fibrous morphology.

The degree of intergrowth of amphibole and pyroxene mineral phases with the vermiculite appeared to be greater in this sample compared to other Libby samples. That is, a higher proportion of the vermiculite plates in this sample contained other mineral phases sandwiched between layers, than other Libby

samples did. A higher proportion of the stacked vermiculite plates also appeared to be weathered in this sample compared to other samples. A summary of the EM results for this sample appears in Table 14.

TABLE 14. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE LIBBY, GRACE, GRADE 1

Sample	Fibers of all lengths: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fibers greater than 5.0 μm in length: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
276-1 Exfoliated	31.6	6.6-51.5		78	26	5.3			46	6	A
	73.6	2.54-12.3	0.9		64	5.3		0.9		6	T
	0.9			3.5×10^{-3}	1					0	C

[a] A = amphibole (RAIT); C = chrysotile; and T = total.

Sample 276, Libby, Montana, Grace, Grade 2, Composite

IITRI Code No. 128, ORF No.
Appendix references
Photographs E-14,15; XRD I-157-160
Electron microscope I-88-91

The sample was composed of 1- to 12-mm flakes of gold to deep green micaceous flakes. White to gray to green fiber bundles ranging in diameter from 1 to 5 mm and in lengths from 2 to 15 mm were relatively abundant. Other constituents observed macroscopically were glassy, light to dark green mineral chunks; milky, pale green chunks; and colorless to milky white chunks.

The abundance and large grain sizes of the fibrous bundles allowed for easy hand-separation of fibers for gravimetric determinations.

The mineralogical composition of the sample, as determined by polarized light microscopy analyses of the various hand-picked and density-separated fractions, is listed in Table 15. The hand-picked fibrous material was readily recognized as the tremolite-actinolite amphibole. No serpentine fibrous material was detected.

TABLE 15. COMPOSITION OF SAMPLE 276-I

Mineral phase	Estimated mass concentration (%)
Tremolite-actinolite fibers	4-7
Tremolite-actinolite prisms	3-5
Sphene	< 1
Diopside	4-7
Augite	1-2
Hornblende	< 1
Magnetite, hematite	1-2
Calcite	1-2
Quartz	3-5
Biotite	2-4
Talc	< 1
Vermiculite	66-72
Other minerals	1-4

Tremolite-actinolite was found to be the primary constituent of the fibrous phase of this sample. Although fiber bundles were up to 15 mm in length, no single fibers were found anywhere near this length. Rather, the fiber bundles were composed of short fibers intergrown at slight angles to each other. All fiber bundles contained both the truly fibrous material as well as the more bulky, lamellated prisms. Inclusions such as diopside, hornblende, and calcite within fiber bundles tended to adopt a fibrous morphology.

Optical properties of the tremolite-actinolite fibers again included inclined extinction angles and refractive indices slightly greater than the truly prismatic tremolite-actinolite fragments. Most of the fiber bundles exhibited a slightly greenish color when mounted in immersion oil. The fibers were also pleochroic.

The fiber bundles also probably contained some traces of anthophyllite; and talc was detected microscopically within several fiber bundles.

There was an unusual fibrous phase found in the 2.76 sink fraction that could not be identified. The fibers had refractive indices higher than the tremolite-actinolite fiber bundles and were a deep blue-green color. The strong coloration resulted in anomalous interference colors similar to those seen for glaucophane-riebeckite. This component was less than 0.1% of the total sample; therefore insufficient material was available for additional characterization studies. A summary of the EM results for this sample appears in Table 16.

TABLE 16. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE LIBBY, GRACE, GRADE 3

Sample	Fibers of all lengths: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fibers greater than 5.0 μm in length: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
259-I Exfoliated	22.6			48.5	53	6.8			38.8	20	A
	31.5		0.6		74	8.3		0.6		20	T
				0	0						C

a A = amphibole (SAED); C = chrysotile; and T = total.

Sample 259, Libby, Montana, Grace, Grade 3, Composite

IITRI Code No. 122, ORF No. 261
Appendix references
Photographs E-2-4, XRD I-123-125
Electron microscope I-14-25, II-20-43

Microscopically, the sample was composed of large (1 to 7 mm) gold to black micaceous flakes; dark green, glassy fragments; white to pale green flexible fiber bundles up to 8 mm in length; and at least three other colorless to pale green mineral phases.

The mineralogical composition of the sample, as determined in the PLM analysis of the three density-separated fractions, is listed in Table 17. Amphibole (tremolite-actinolite) asbestos fibers were found in rather significant concentrations. No serpentine minerals were detected, however.

TABLE 17. COMPOSITION OF SAMPLE 259-I

Mineral phase	Estimated mass concentration (%)
Tremolite-actinolite fibers	< 1
Tremolite-actinolite prisms	2-4
Sphene	1-3
Diopside	3-7
Augite	2-3
Magnetite, hematite	< 1
Calcite	2-5
Quartz	2-5
Biotite	10-15
Vermiculite	65-72
Other minerals	1-3

The tremolite-actinolite occurred almost exclusively in an unquestionably fibrous crystal habit with very little prismatic tremolite-actinolite present. The fiber bundles were found to be composed of very fine, teasable, flexible fibers. In most of the fiber bundles, the individual fibers were not perfectly parallel to each other and were not as long as the fiber bundles; numerous small groups of short fibers stacked at slight angles to each other both vertically and horizontally comprised the "fiber bundle." Optical properties of the individual fibers included refractive indices greater than 1.610, extinction angles greater than 0 degrees, and pale green color with slight pleochroism.

Other mineral phases (including alteration products) were included in each fiber bundle. In some cases, these other mineral phases were pseudomorphically fibrous. Quartz, calcite, titanite, and diopside were all observed in a fibrous habit. Calcite was the most abundant pseudomorphically fibrous mineral. Approximately 10% of the "2.76 sink" fraction was composed of white fiber bundles, which upon teasing and microscopic examination were found to be composed of 70 to 80% calcite overgrown on 20 to 30% tremolite-actinolite fibers.

The tremolite-actinolite fibers were also observed to be tightly bound to vermiculite plates and growing in between layers of vermiculite. A summary of the EM results for this sample appears in Table 18.

TABLE 18. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE LIBBY, GRACE, GRADE 3

	Fibers of all lengths					Fibers greater than 5.0 μm in length					
	Fiber concentration (10^6 fibers/g)					Fiber concentration (10^6 fibers/g)					
Sample	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
259-1	31.8	23.1-44.7		210	91	12.4	7.1-17.7		190	29	A
	45.8	35.9-59.9	0.4		107	12.8	7.8-17.8	0.4		30	T
	0.9			0.01	2					0	C
259-0	25	8.2-62	2.09	59	12	10	0-21	2.09	43	3	A
	< 2.1	-	2.09	-	0	< 2.1	-	2.09	-	0	C
259-1 Exfoliated	42.8	33.1-58.9		250	100	14.3	7.9-20.7		240	34	A
	43.7	33.8-57.6	0.4		116	14.3	7.9-20.7	0.4		34	T
	0.4			0.1×10^{-2}	1					0	C
259-0 Exfoliated	59	44-74	0.99%	240	59	16	7.9-28	0.99%	190	16	A
	< 1.8	-	0.99%	-	0	< 1.8	-	0.99%	-	0	C

[a] A = amphibole (SAED); C = chrysotile; and T = total.

Sample 282, Libby, Grace, Grade 4, Composite

IITRI Code No. 126, ORF No. 281
Appendix references
Electron microscope I-92-97, II-356-375

Macroscopically, the sample was observed to contain mostly 1- to 4-mm goldish-brown vermiculite flakes. White fiber bundles up to 3 mm in length were visible. Nonmicaceous, nonfibrous mineral phases were also observed; at least three different mineral phases ranging in color from white to emerald green were detected.

The mineralogical composition determined for this sample by polarized light microscopy is listed in Table 19.

TABLE 19. COMPOSITION OF SAMPLE 282-I

Mineral phase	Estimated mass concentration (%)
Tremolite-actinolite fibers	(0.3)-1
Tremolite-actinolite prisms	1-3
Sphene	< 1
Diopside	3-7
Augite	1-2
Hornblende	< 1
Magnetite, hematite	1-3
Calcite	< 1
Quartz	1-3
Biotite	1-3
Vermiculite	78-88
Other minerals	1-3

Tremolite-actinolite was again detected as a significant sample component and was again present in three distinct crystal habits. The truly prismatic tremolite-actinolite was most abundant. Most prismatic fragments had small bundles of fibers or bundles of the thin, lamellated prisms (that could readily fracture to produce particles definable as fibers) attached to them. Practically all bundles composed primarily of truly fibrous tremolite-actinolite contained thick, chunky prisms or the lamellated prisms. All truly fibrous tremolite-actinolite bundles were composed of intergrown fibers; i.e., no bundles were composed of uniform length, parallel fibers. Groups of fibers growing at angles as large as 75 degrees to each other were observed in the same bundle. The lamellated prism bundles, however, did tend to be composed of crystals growing parallel to each other. Bundles composed of both the truly fibrous material and the thicker, lamellated prisms also tended to be composed of nonparallel crystal bundles.

The tremolite-actinolite fiber bundles hand-picked from the sample ranged in color from pure white to deep green. Less than 10% of the fiber bundles were the pure white color; most fiber bundles were pale green and had refractive indices in the middle range reported for the tremolite-ferroactinolite solid solution mineral series. Extinction angles for the truly fibrous crystals and crystal bundles were inclined at least 5 degrees.

No fibrous anthophyllite, prismatic anthophyllite, or talc were detected in this sample. However, some hornblende in a morphology that could be classified as fibrous was detected. The hornblende bundles containing crystals

classifiable as fibers were composed primarily of the thicker, more brittle lamellated prisms.

The 2.76 sink fraction contained a significant fraction of biotite. The other major constituents of this fraction were vermiculite flakes intergrown with tremolite-actinolite, diopside, and iron oxides.

The 2.76 float fraction was relatively free of pyroxene and amphibole mineral fragments. Few flakes of vermiculite intergrown with amphibole mineral phases were detected. A summary of the EM results for this sample appears in Table 20.

TABLE 20. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE LIBBY, GRACE, GRADE 4

Sample	Fibers of all lengths: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fibers greater than 5.0 μm in length: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
282-0	1.0	0-3.2	0.360	1	3	< 0.4	-	0.360	-	0	A
	< 0.4	-	0.360	-	0	< 0.4	-	0.360	-	0	C
282-1 Exfoliated	65.0			460	91	27.1			440	38	A
	72.8		0.7		102	27.8		0.7		39	T
					0					0	C
282-0 Exfoliated	1.8	0.2-3.4	0.446	17	4	0.4	0-1.5	0.446	17	1	A
	< 0.5	-	0.446	-	0	< 0.5	-	0.446	-	0	C

[a] A = amphibole (SAED); C = chrysotile; and T = total.

Sample 264, Libby, Grace, Grade 5, Composite

IITRI Code No. 120, ORF No. 263
Appendix references
Photographs E-5, 18-20, XRD I-126-129
Electron microscope I-26-52, II-44-166

Macroscopically, the sample was observed to be a fine, goldish-brown powder composed of obviously flake-like and fibrous particles. The flake-like particles were generally less than 2 mm in diameter. Fibers up to 3 mm in length were present. At least two other nonvermiculite, nonfibrous mineral phases were observed; one was green in color, while the other was colorless.

The mineralogical composition of the sample determined by PLM analysis of the three density-separated fractions is listed in Table 21.

TABLE 21. COMPOSITION OF SAMPLE 264-I

Mineral phase	Estimated mass concentration (%)
Tremolite-actinolite fibers	2-4
Tremolite-actinolite prisms	2-5
Sphene	1-3
Diopside	6-9
Augite	1-3
Hornblende	< 1
Magnetite, hematite	1-3
Calcite	1-3
Quartz	1-3
Biotite	3-7
Vermiculite	70-74
Other minerals	2-4

Tremolite-actinolite was present in a fibrous morphology. In this sample, however, a significant amount of prismatic tremolite-actinolite was also present. Both fibers and prisms exhibited inclined extinction. There appeared to be some fibers close to the tremolite end member of the series, as refractive indices of some fibers were observed to be at or just slghtly below 1.600.

The tremolite-actinolite fiber bundles occurred as the nonparallel stranded bundles. A higher percentage of the fibers and fiber bundles was found intergrown with vermiculite, biotite, and the other low density minerals in this sample compared to the larger particle samples.

Pseudomorphically fibrous quartz, calcite, diopside, and augite phases were again detected. A summary of the EM results appears in Table 22.

TABLE 22. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE LIBBY, GRACE, GRADE 5

Sample	Fibers of all lengths: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fibers greater than 5.0 μm in length: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
264-I	118	97.5-139		840	93	51.8	8.3-95.3		790	41	A
	135	101-169	6.6		107	55.6	7.2-104	6.6		44	T
					0					0	C
264-0	100	62-150	1.37	600	76	42	25-60	1.37	530	31	A
	< 1.4	-	1.37	-	0	< 1.4	-	1.37	-	0	C
264-I (0)[b]	127	85-240	1.3	1,200	101	49.2	14.6-83.8	1.3	1,100	39	A
					0					0	C
264-0 (I)[b]	91	70-130	1.42	570	69	37	17-57	1.42	500	26	A
	< 1.5	-	1.42	-	0	< 1.5	-	1.42	-	0	C
	27	13-42	1.42	14	19	2.8	0-7.1	1.42	8	2	UF
	36	20-51	1.42	71	25	1.4	0-4.6	1.42	51	1	NAM
	160	120-210	1.42	650	113	41	18-64	1.42	560	29	T
264-I Exfoliated	142	101-177		2,600	121	84.2	45.3-123		2,500	72	A
	149	118-180	1.2		127	85.3	48.4-122	1.2		73	T
264-0 Exfoliated	160	130-200	1.35	1,800	105	78	62-97	1.35	1,700	51	A
	< 1.6	-	1.35	-	0	< 1.6	-	1.35	-	0	C
264-I (0) Exfoliated[b]	119	62-176.4	1.2	350	102	56.6	46.8-66.2	1.2	300	46	A
					0					0	C
264-0 (I) Exfoliated[b]	110	81-130	1.50	2,600	92	42	27-57	1.50	2,500	28	A
	< 1.6	-	1.50	-	0	< 1.6	-	1.50	-	0	C
	1.5	0-4.9	1.50	< 1	1	< 1.6	-	1.50	-	0	TH
	6	0.4-12	1.50	22	4	1.5	0-4.9	1.50	20	1	UF
	22	12-33	1.50	41	15	3.8	0-7.5	1.50	32	2	NAM
	140	110-170	1.50	2,600	92	46	30-63	1.50	2,600	31	T

a A = amphibole; C = chrysotile; T = total; UF = unidentified mineral fiber; NAM = nonasbestos mineral; and TH = tubular morphology, not identifiable as chrysotile.

b The letter in the parentheses indicates that the counting procedure was that normally used by the other laboratory as 264-I (0) are the results obtained by IITRI using the ORF procedure.

Sample 267, Libby, Grace, Grade 5, 1 Day

Appendix references
Photographs E-14, XRD I-153-156

Macroscopically, the sample was composed primarily of fine (0.5 to 3 mm) goldish-brown micaceous flakes. Pale green to white fiber bundles up to 2 mm in length were visible. At least two green, nonmicaceous mineral phases and one colorless, nonmicaceous mineral phase were observed.

The mineralogical composition of the sample, as determined by polarized light microscopy analyses of the various density-separated fractions, is listed in Table 23. Fibrous amphibole--mostly tremolite-actinolite, with some intergrown anthophyllite--was definitely present. No serpentine fibers were detected, however.

TABLE 23. COMPOSITION OF SAMPLE 267-I

Mineral phase	Estimated mass concentration (%)
Tremolite-actinolite fibers	2-5
Tremolite-actinolite prisms	4-8
Anthophyllite (prisms and fibers)	< 1
Sphene	< 1
Diopside	10-15
Augite	1-3
Hornblende	< 1
Magnetite, hematite	1-3
Calcite	1-2
Quartz	1-3
Biotite	< 1
Talc	1-2
Vermiculite	65-70
Other minerals	1-3

The tremolite-actinolite occurred in many different particles but occurred predominantly as irregularly fractured fragments of solid prisms. Prismatic fragments composed of numerous thin, stacked prisms which were capable of fracturing into elongated, parallel-sided fragments definable as fibers were observed but represented less than 1% of the total sample. Truly fibrous bundles composed of very fine, teasable individual fibers, were significant sample components. Typically, the fibrous bundles were composed of short fibers that were not perfectly parallel. Rarely were fiber bundles composed of individual fibers that ran the entire length of the bundle. Obvious fibers were also found attached to (i.e., "growing from") chunky, prismatic fragments and from the lamellated prisms. Both prismatic and fibrous varieties of tremolite-actinolite were found bound to and intergrown with vermiculite plates to a minor extent.

The extinction angles of both prismatic and fibrous varieties of the tremolite-actinolite were on the order of 7 to 18 degrees. Refractive indices of the prismatic variety tended to be greater than those of the fibrous habit. Prism colors were mostly green, while fiber bundle colors ranged from colorless (white) to pale green, depending upon the types and amounts of inclusions present within the bundles.

Anthophyllite fibers and prisms were detected. The fibrous form was found only intergrown with the tremolite-actinolite fibers. Free anthophyllite prisms as well as prisms intergrown with tremolite-actinolite prisms were present. Almost all the tremolite-actinolite fiber bundles that contained anthophyllite also contained talc.

Unlike the 264-I composited grade 5 sample from Libby, this uncomposited sample did not appear to contain other mineral phases in pseudomorphically fibrous habits. None of the fibrous calcite detected in the 264-I sample was found in this sample.

Most of the nonmicaceous contaminant minerals present in this sample were high density materials and were thus found in the TBE sink fraction. The 2.76 density fractions were relatively free of nonvermiculite mineral phases, particularly the 2.76 float fraction.

Sample 291, Libby, Grace, Head Feed Composite

IITRI Code No. 130, ORF No. 290
Appendix references
Photographs XRD I-130-134
Electron microscope I-2-13, II-1-19

Macroscopically, this sample was quite variable in color, particle morphology, and grain size. The overall color was a light brown. Relatively few micaceous flakes were visible to the naked eye; the largest flakes were less than 10 mm in size. Under the stereomicroscope, most of the brownish, fine powder (less than 1 mm) material present was observed to be micaceous. Several large white to pale green elongated (and probably fibrous) rock chunks greater than 20 mm were observed. Obvious mixed phase grains (i.e., mineral phases partially altered) were also present as 1- to 15-mm grains.

Microscopically, the sample was observed to be composed primarily of nonmicaceous, contaminant minerals. The overall sample composition determined by microscopical analyes of the density-separated fractions is presented in Table 24.

TABLE 24. COMPOSITION OF SAMPLE 291-I

Mineral phase	Estimated mass concentration (%)
Tremolite-actinolite fibers	21-26
Tremolite-actinolite prisms	6-9
Sphene	1-3
Diopside	24-29
Augite	2-5
Hornblende	< 1
Magnetite, hematite	3-5
Calcite	3-5
Quartz	4-7
Biotite	1-2
Vermiculite	20-25
Other minerals	3-6

Tremolite-actinolite was a major component of this sample and occurred in both fibrous and prismatic crystal habits. The fibrous habit was found as discrete fiber bundles, fiber bundles intergrown with prismatic amphibole and pyroxene mineral phases, and as small fiber bundles protruding from vermiculite (or other micaceous mineral) plates. Fiber bundles were composed mostly of smaller, shorter irregularly stacked bundles of fibers, rather than as bundles of perfectly parallel, uniform length fibers. Optical properties of fiber bundles identified as tremolite-actinolite indicated that a wide range of chemical compositions was present; i.e., some end member tremolite and ferroactinolite phases as well as the intermediate actinolite were present.

The tremolite-actinolite fibrous phase was a major component of each density fraction because of the multiphase nature of a large percentage of the particles in this sample. Inclusion of lower density phases within each fiber bundle as well as attachment of fiber bundles to lower density mineral grains resulted in a lower than normal bulk density for the tremolite-actinolite.

Some unusual fibrous phases were present. Fiber bundles exhibiting the anomalous blue and pink interference colors typical of crocidolite (riebeckite) asbestos were observed. The refractive indices of these fibers as well as their inclined extinction angles (and XRD data) ruled out crocidolite as the mineral species. The fiber bundles were strongly pleochroic (yellow-green to blue-green), and this undoubtedly caused the anomalous interference colors. Further characterizations by electron microprobe, micro X-ray diffraction, and electron microscopy must be performed in order to fully identify this phase. Possible mineral identities include ferroactinolite, sodium tremolite, and glaucophane.

Identification of all mineral phases present was impossible. Many intermediate, partially altered phases were present in this sample. XRD data suggested that antigorite is present in the low density fraction. A summary of the EM results for this sample appears in Table 25.

TABLE 25. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE LIBBY, GRACE, HEAD FEED

	Fibers of all lengths					Fibers greater than 5.0 μm in length					
	Fiber concentration (10^6 fibers/g)					Fiber concentration (10^6 fibers/g)					
Sample	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
291-I	62.5	41.9-83.3		670	91	26.7	11.5-37.9		630	26	A
	73.4	61.6-85.2	0.7		107	27.4	12.9-41.9	0.7		46	T
	1.4			0.13	2				0.09	1	C
291-O	130	80-190	1.17	690	113	31	18-44	0.562	520	35	A
	1.2	0-3.8	1.17	< 1	1	< 0.6	-	0.562	-	0	C
291-I Exfoliated	73.8	37.7-109.9		590	97	20.5	0-33		540	27	A
	79.9	48.7-111.1	0.6		105	20.5	0-33	0.6		27	T
					8						C

[a] A = amphibole (SAED); C = chrysotile; and T = total.

Sample 294, Libby, Grace, Extractor Waste, Composite

IITRI Code No. 134
Appendix references
Photographs E-15
Electron microscope I-98-102

This sample was quite broad in particle size. It was composed primarily of 0.2- to 15-mm gold to brown micaceous flakes. White fibrous bundles up to 9 mm in length were observed. The fibrous bundles were sufficiently abundant and large in size to allow hand-picking after density separations were conducted. Nonfibrous, nonmicaceous mineral fragments which were mostly green in color were present in diameters up to 6 mm.

The mineralogical composition of the sample is listed in Table 26. Sample components were identified by polarized light microscopy analyses of the hand-picked and density-separated fractions. Fibrous amphibole mineral phases were detected in the analyses, but no fibrous serpentine mineral phases were detected.

TABLE 26. COMPOSITION OF SAMPLE 294-I

Mineral phase	Estimated mass concentration (%)
Tremolite-actinolite fibers	1-4
Tremolite-actinolite prisms	1-3
Sphene	1-2
Diopside	3-7
Augite	< 1
Hornblende	< 1
Magnetite, hematite	1-2
Calcite	1-3
Quartz	4-10
Biotite	6-9
Talc	< 1
Vermiculite	68-76
Other minerals	1-3

The tremolite-actinolite occurred primarily as fibrous crystal bundles and crystal bundles containing both fibrous and prismatic materials. Coarse crystals composed only of bulky, prismatic materials were rare. Tremolite-actinolite fragments composed only of elongated, narrow, thin, lamellated prismatic crystals were also rare but were not as rare as the chunky prismatic crystals. Both prismatic crystal morphologies were observed mostly in conjunction with the fibrous morphology; that is, most of the tremolite-actinolite mineral fragments that contained prismatic material also contained at least 25% truly fibrous material. Fibrous crystal bundles containing mostly fibrous crystals were again observed to contain small bundles of short fibers that were stacked at slight angles to each other both longitudinally and laterally. Single fibers that ran the entire length of the fiber bundle were rarely seen and were only observed in rock fragments that contained at least 35% prismatic materials. The fibers grew parallel to and on top of the prismatic material.

Refractive indices of the fibrous tremolite-actinolite tended to be greater than those of the prismatic tremolite-actinolite crystals. Practically all fiber bundles exhibited a green coloration and pleochroism in plane polarized light. Prismatic crystals tended to be more strongly colored than the fibrous crystals. Prismatic crystals also tended to be more blue-green than green. Extinction angles of both the prismatic and fibrous crystal habits were greater than zero.

Intergrowth of tremolite-actinolite and pyroxene minerals with vermiculite was greater in this Libby sample than it was in most of the other Libby samples included in this group of 10 lesser priority vermiculite samples. This is reflected by the relatively high weight percentage of the 2.76 sink fraction.

Fibrous phases in addition to tremolite-actinolite were detected. Some pseudomorphically fibrous calcite was found intergrown in tremolite-actinolite fiber bundles. Pseudomorphically fibrous diopside and (probable) hornblende were also detected. Traces of fibrous anthophyllite intergrown with talc within fibrous tremolite-actinolite bundles were also observed. There were two additional fibrous phases present that could not be identified because they were present in such low concentrations and could not be isolated for further studies. One fibrous type exhibited the anomalous interference colors and higher refractive indices associated with the glaucophane-riebeckite series amphiboles. The other fibrous phase exhibited the lower refractive indices and anomalous interference colors this analyst has observed in chrysotile samples containing biotite and vermiculite. A summary of the EM results for this sample appears in Table 27.

TABLE 27. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE LIB87, GRACE, EXTRACTOR

	Fibers of all lengths					Fibers greater than 5.0 μm in length					
	Fiber concentration (10^6 fibers/g)					Fiber concentration (10^6 fibers/g)					
Sample	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
294-I Exfoliated	55.0			420	82	24.8			400	37	A
	67.7		0.7		101	25.5		0.7		38	T
	0.7			3.4×10^{-3}	1					0	C

[a] A = amphibole (SAED); C = chrysotile; and T = total.

Sample 297 Libby, Grace, Baghouse, Mill Dust, Composite

IITRI Code No. 136, ORF No. 296
Appendix references
Photographs E-17
Electron microscope I-103-108, II-376-388

The sample was a brownish-green, very fine powdered mineral dust. Obviously micaceous flakes as large as 4 mm in diameter were observed. Obivously fibrous crystals up to 2 mm in length were also detected.

Density separations in heavy liquids did not result in clean separations of the various mineral phases. Fine particle sizes resulted in temperature-induced turbulent motion of particles rather than strict density settling. The particles were also extremely agglomerated and thus behaved with the composite densities of the component particles.

The mineralogical composition of the sample, as determined by the polarized light microscopy analyses of the various density-separated fractions, is presented in Table 28.

TABLE 28. COMPOSITION OF SAMPLE 297-I

Mineral phase	Estimated mass concentration (%)
Tremolite-actinolite fibers	8-12
Tremolite-actinolite prisms	2-6
Sphene	1-3
Diopside	3-6
Augite	2-5
Hornblende	< 1
Magnetite, hematite	1-3
Calcite	1-3
Quartz	2-5
Biotite	1-3
Talc	< 1
Vermiculite	55-61
Other minerals	2-5

Tremolite-actinolite was a major sample component. Bundles composed of truly fibrous crystals as well as lamellated prisms and chunky prismatic fragments of tremolite-actinolite were detected. Single crystals of tremolite-actinolite in morphologies classifiable as fibers were not unexpectedly abundant, as the sample obviously was fine particle material produced from fracture and abrasion of larger mineral grains. Both the truly fibrous bundles

and lamellated prism types of tremolite-actinolite would be expected to give rise to single crystals morphologically definable as fibers. Again, the distinction between fiber-like amphibole crystals produced from particles macroscopically definable as fibrous and fiber-like crystals produced from mineral grains composed of thin, narrow, lamellated prisms, may be immaterial. It was certainly not possible to define the origins of all the fiber-like tremolite-actinolite single crystals present in the sample.

Anthophyllite was again detected as a very trace (< 0.1%) sample component. Fibrous hornblende and the unidentified fibrous blue-green amphibole were also detected again.

Traces of a mineral with morphological and optical properties similar to nonfibrous serpentine were detected in the 2.76 float fraction. Concentration of this possible serpentine was estimated to be well below 0.1% of the sample. The low concentration precluded further isolation for verification of the proposed identity. A summary of the EM results for this sample appears in Table 29.

TABLE 29. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE LIBBY, GRACE, MILL DUST

	Fibers of all lengths					Fibers greater than 5.0 μm in length					
	Fiber concentration (10^6 fibers/g)					Fiber concentration (10^6 fibers/g)					
Sample	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
287-0	100	93-140	1.20	4,600	95	48	40-59	1.20	4,600	61	A
	< 1.3	-	1.20	-	8	< 1.3	-	1.20	-	8	C
287-1 Enfoliated	777			35,000	100	545			34,000	70	A
	905		7.8		117	606		7.8		78	T
					8					8	C

a A = amphibole (SAED); C = chrysotile; and T = total.

Sample 288, Libby, Grace, Screening Plant Dust, Composite

IITRI Code No. 135, ORF No. 287
Appendix references
Photographs E-16
Electron microscope I-108-113, II-389-402

Macroscopically, the sample was observed to be a very fine, pale green powder. Obvious micaceous flakes up to 2 mm in diameter were present. From the bulk density of the sample, it appeared that micaceous type minerals were the primary sample components.

Density separations produced a deeper green, powdery fraction (sinks in tetrabromoethane), a brownish-green fraction with some micaceous flakes (sinks in 2.76 density liquid), and a gold-colored fraction obviously composed primarily of micaceous flakes (2.76 floats fraction). The mineralogical composition of the sample, as determined by polarized light microscopy analyses of the three density-separated fractions, is presented in Table 30. Separations of the density fractions were not very clean, in part due to the very small grain sizes, but mostly due to the intergrowth of high density phases with low density phases.

TABLE 30. COMPOSITION OF SAMPLE 288-I

Mineral phase	Estimated mass concentration (%)
Tremolite-actinolite fibers	2-5
Tremolite-actinolite prisms	1-4
Sphene	< 1
Diopside	3-6
Augite	1-2
Hornblende	< 1
Magnetite, hematite	1-3
Calcite	1-3
Quartz	4-7
Biotite	1-3
Talc	< 1
Vermiculite	68-78
Other minerals	1-4

Identification of mineral phases was somewhat hindered by the relatively small particle sizes of the fractured mineral fragments. Numerous shards of vermiculite were present and could easily be mistaken for fibrous mineral types on morphology only. The vermiculite shards could easily be distinguished from the fibrous amphiboles on the basis of refractive index, however.

Although the mineral fragments in the sample were quite abraded and fractured, three distinctly different morphologies of the tremolite-actinolite mineral phase were observed. The chunky, prismatic crystals that would not fracture to produce fragments definable as fibers were the least abundant tremolite-actinolite phase present. Fragments composed of elongated, narrow, thin, lamellated tremolite-actinolite prisms were as abundant as the bundles of nonparallel intergrown, truly fibrous tremolite-actinolite crystals. Morphologies of the very small (less than 10 μm wide) single tremolite-actinolite crystals that could be classified as fibers on the basis of aspect ratios suggested that equal proportions of the larger lamellated prisms and true fiber bundles had been abraded to produce the single crystals. That is, many of the "fiber-like" single crystals were more platey than true fibers would be expected to be. However, at this small particle size, the origins of particles classifiable as fibers--either from lamellated prisms or true fiber bundles--are only speculation and may well be immaterial.

In addition to the tremolite-actinolite fibrous amphibole, fibrous anthophyllite was detected by its parallel extinction angles and different refractive indices. Fibrous anthophyllite was well below 0.1% of the sample mass; it was most frequently found in association with talc.

Other fibrous phases present included a morphology of hornblende that could be considered fibrous, and pseudomorphically fibrous quartz and calcite. The unidentifiable blue-green amphibole with the anomalous interference colors similar to glaucophane-riebeckite series amphiboles was again detected.

The 2.76 float fraction contained a mineral phase with optical and morphological properties consistent with nonfibrous serpentine. Insufficient numbers of particles were available for further identification studies. A summary of the EM results for this sample appears in Table 31.

TABLE 31. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE LIBBY, GRACE, SCREENING DUST

	Fibers of all lengths					Fibers greater than 5.0 μm in length					
	Fiber concentration (10^6 fibers/g)					Fiber concentration (10^6 fibers/g)					
Sample	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
224-0	300	248-364	1.54	2,000	192	100	72-140	1.54	2,700	67	A
	< 1.6	-	1.54	-	0	< 1.6	-	1.54	-	0	C
224-I Exfoliated	1,000		19.6	41,000	92	1,090			42,000	53	A
	2,100				197	1,150		19.6		53	T
					6						C

a A = amphibole (SAED); C = chrysotile; and T = total.

Sample 430, Enoree, South Carolina, Grace, Grade 3, Composite

IITRI Code No. 121, ORF No. 429
Appendix references
Photographs E-7-8, XRD I-135-138
Electron microscope I-60-65

Macroscopically, the sample was observed to contain 1- to 5-mm black to brownish-gold micaceous flakes, and 1- to 3-mm fragments of nonmicaceous minerals. The nonmicaceous minerals were white, pale green, or reddish-brown in color. No obviously fibrous phases were detected in the stereomicroscopic examination.

The composition of this sample as determined by PLM analyses of the density-separated fractions is listed in Table 32.

TABLE 32. COMPOSITION OF SAMPLE 430-I

Mineral phase	Estimated mass concentration (%)
Anthophyllite	< 1
Tremolite-actinolite	2-4
Augite	< 1
Hornblende	1-2
Apatite	1-2
Magnetite, hematite	1-2
Calcite	< 1
Quartz, feldspars	4-6
Talc	1-2
Vermiculite	80-90
Other minerals	1-2

As is evident from Table 32, the sample was composed primarily of vermiculite. Relatively little contaminant, nonvermiculite mineral matter was present.

Both tremolite-actinolite and anthophyllite amphiboles were detected. The tremolite-actinolite occurred almost exclusively in a very bulky, prismatic morphology. However, small elongated, parallel-sided particles could fracture from these prisms to yield particles classifiable as "fibers." So few large particles of anthophyllite were observed that it is impossible to confidently state whether or not truly fibrous anthophyllite was present. Certainly, elongated fiber-like particles of anthophyllite were observed.

The 2.76 float density-separated fraction contained some unusual, not totally characterizable material. Irregular, light green particles composed of microcrystalline material rather similar to serpentine minerals were present. This material was obviously an alteration state intermediate between amphibole and later-stage products, and may well include serpentine minerals, though none were identifiable as such. A summary of the EM results for this sample appears in Table 33.

TABLE 33. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE EMORY, SOUTH CAROLINA, GRACE, GRADE 3

	Fibers of all lengths					Fibers greater than 5.0 μm in length					
	Fiber concentration (10^6 fibers/g)					Fiber concentration (10^6 fibers/g)					
Sample	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
430-I	1.0			0.55	9	0.2			0.23	2	A
	4.1	0.5-7.9	0.1		30	0.2		0.1		2	T
	0.1			5×10^{-4}	1						C
430-0	2.7	0.5-4.9	0.299	< 1	9	< 0.3	-	0.299	-	0	A
	< 0.3	-	0.299	-	0	< 0.3	-	0.299	-	0	C
430-I Exfoliated	3.1		0	3.7	12	0.5			3.1	2	A
	9.8		0.3		34	1.3		0.3		5	T
					0					0	C
430-0 Exfoliated	2.4	0-5.4	0.402	1	6	< 0.5	-	0.402	-	0	A
	< 0.5	-	0.402	-	0	< 0.5	-	0.402	-	0	C

[a] A = amphibole (SAED); C = chrysotile; and T = total.

Sample 433, Enoree, South Carolina, Grace, Grade 4, Composite

IITRI Code No. 127, ORF No. 432
Appendix references
Electron microscope I-114-119, II-403-420

Macroscopically, the sample was observed to be composed of 0.5- to 4-mm goldish-brown flakes of micaceous mineral and 0.2- to 2-mm white, brown, tan, and green nonmicaceous minerals. No obviously fibrous phases were detected in the macroscopic examination.

The mineralogical composition of the sample, as determined by polarized light microscopy analyses of the density-separated fractions, is listed in Table 34.

TABLE 34. COMPOSITION OF SAMPLE 433-I

Mineral phase	Estimated mass concentration (%)
Fibrous mixed amphibole	< 1
Anthophyllite-prismatic	1-3
Tremolite-actinolite	1-4
Sphene, ilmenite	< 1
Augite	< 1
Apatite	1-3
Hornblende	2-5
Magnetite, hematite	1-2
Rhodonite, pyrolucite	< 1
Calcite	< 1
Quartz, feldspars	3-8
Talc	1-3
Vermiculite	75-81
Other minerals	2-5

Both tremolite-actinolite and anthophyllite amphibole mineral phases were detected in the sample. Neither amphibole was found in a bulk grain morphology that could be considered fibrous. That is, the as-received mineral grains were definitely prismatic crystals which were, for the most part, stout, single crystal prisms. Less than 10% of each amphibole occurred as grains composed of the elongated, thin, narrow lamellated prisms that could readily fracture to produce particles definable as fibers. Lamellations tended to be imperfect; thus, fractured fragments, though elongated, did not have parallel sides and frequently had unevenly terminated ends.

Tremolite-actinolite prisms were generally pale green and pleochroic, and exhibited inclined extinction. The anthophyllite was colorles (in transmitted light), had refractive indices lower than the tremolite-actinolite, and exhibited parallel extinction. Tremolite-actinolite was occasionally found intergrown with hornblende. The anthophyllite and tremolite-actinolite prisms were never found intergrown with each other in the same mineral fragment in this sample.

The relatively high proportion of the 2.76 sink density-separated fraction reflects the degree of intergrowth of the amphibole and pyroxene mineral phases with the vermiculite. In general, the vermiculite plates of this sample were more irregular, strained, and intergrown with other mineral phases than were the vermiculite plates of most of the Libby, Montana, samples. At least two other micaceous mineral phases that could not be identified were present in addition to the vermiculite. As these phases were micaceous, they were included in the mass accounting for vermiculite. A summary of the EM results for this sample appears in Table 35.

TABLE 35. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE ENOREE, SOUTH CAROLINA, GRACE, GRADE 4

	Fibers of all lengths					Fibers greater than 5.0 μm in length					
	Fiber concentration (10^6 fibers/g)					Fiber concentration (10^6 fibers/g)					
Sample	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
423-I	1.6			6.5	16	0.5			5.3	5	A
	4.7		0.3		4	0.5		0.1		5	T
				0	0					0	C
423-C	2.7	0.1-5.3	0.244	25	11	0.2	0-0.8	0.244	29	1	A
	< 0.3	-	0.244	-	0	< 0.3	-	0.244	-	0	C
423-I Exfoliated	3.1			1.4	8	0.4			0.94	1	A
	7.1		0.4		18	0.4		0.4		1	T
					0						C
423-C Exfoliated	2.7	0.9-4.5	0.269	2	10	< 0.3	-	0.269	-	0	A
	< 0.3	-	0.269	-	0	< 0.3	-	0.269	-	0	C

[a] A = amphibole (SAED); C = chrysotile; and T = total.

Sample 427, Enoree, South Carolina, Grace, Grade 5, Composite

IITRI Code No. 119, ORF No. 426
Appendix references
Photographs E-8-10, 21-23, XRD I-139-142
Electron microscope I-66-78, II-204-334

The sample was a goldish-brown powder composed of less than 2-mm flake-like particles. No obviously fibrous phases were detected in the macroscopic examination. Submillimeter grains of nonmicaceous gold, green, colorless, and white minerals were observed in the stereomicroscopic examination.

The mineralogical composition of the sample determined by PLM analyses of the density-separated fractions is listed in Table 36.

TABLE 36. COMPOSITION OF SAMPLE 427-I

Mineral phase	Estimated mass concentration (%)
Fibrous mixed amphibole	< 1
Anthophyllite	4-6
Tremolite-actinolite	2-4
Sphene, ilmenite	1-3
Hornblende	2-5
Apatite	1-2
Magnetite, hematite	< 1
Rhodonite, pyrolucite	1-2
Calcite	< 1
Quartz, feldspars	3-6
Talc	1-3
Vermiculite	72-78
Other minerals	1-3

Definitely fibrous mineral phases were detected in the tetrabromoethane sinks fraction. However, the fibers were well below 10% of the TBS fraction and thus were less than 1% of the total sample. Analysis of selectively removed fibers indicated that both anthophyllite and tremolite-actinolite were present within the fiber bundles. The anthophyllite was identified by its parallel extinction and its slightly lower refractive indices compared to the tremolite-actinolite.

The anthophyllite and tremolite-actinolite occurred primarily in very clearly prismatic crystal habits. However, grinding of the prisms did produce parallel-sided, elongated particles which could be classified as fibers.

Talc was found both as free plates and incorporated within the fiber bundles. The talc incorporated within the fiber bundles tended to be fibrous in morphology.

Some pseudomorphically fibrous mineral phases were found in this sample. Some of the sphene (titanite) and fluorapatite were present as fractured fragments morphologically characterizable as fibrous. A summary of the EM results for this sample appears in Table 37.

TABLE 37. SUMMARY OF ELECTRON MICROSCOPE RESULTS FOR SAMPLE ENOREE, SOUTH CAROLINA, GRACE, GRADE 9

Sample	Fibers of all lengths: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fibers greater than 9.0 μm in length: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
427-I	6.6			1.5	4	0.1			0.01	1	A
	5.6	2.9-7.3	0.1		20	1.3		0.1		9	T
				6						8	C
427-O	17	8.1-25	1.27	37	13	2.6	0-6.4	1.27	32	2	A
	2.6	0-6.4	1.27	< 1	2	1.3	0-4.1	1.27	< 1	1	C
427-I (O)[b]	3.8	0-8.3		4.8	42	0.5			2.7	7	A
	0.07		0.07	1×10^{-4}	1			0.07		0	C
427-O (I)[b]	31	13-48	1.25	130	24	2.6	0-6.4	1.25	93	2	A
	2.6	0-6.4	1.25	< 1	2	< 1.3	-	1.25	-	0	C
	5.2	0-14	1.25	< 1	4	< 1.3	-	1.25	-	0	TH
	13	11-36	1.25	4	10	< 1.3	-	1.25	-	0	UF
	75	54-100	1.25	270	61	9.8	0-19	1.25	340	7	HAM
	440	100-180	1.25	500	389	12	0.8-22	1.25	440	9	T
427-I, Exfoliated	3.5			4.1	7	0.5			2.6	1	A
	0.5		0.5		17	1.5		0.5		3	T
					0					0	C
427-O, Exfoliated	2.9	0.9-4.9	0.253	120	10	1.5	0-3.0	0.253	120	5	A
	< 0.3	-	0.253	-	0	< 0.3	-	0.253	-	0	C
427-I (O) Exfoliated[b]	3.2			7.3	12	1.3			4.9	3	A
			0.3					0.3		1	T
					0					0	C
427-O (I) Exfoliated[b]	2.4	0.4-4.3	0.299	8	8	0.3	0-1.0	0.299	6	1	A
	0.9	0-2.9	0.299	< 1	3	< 0.3	-	0.299	-	0	C
	7.2	3.4-9.0	0.299	7	24	0.3	0-1.0	0.299	1	1	UF
	7.8	4.7-11	0.299	23	26	0.9	0-1.9	0.299	14	3	HAM
	18	15-21	0.299	36	61	1.3	0.3-2.6	0.299	22	5	T

a A = amphibole; C = chrysotile; T = total; UF = unidentified mineral fiber; HAM = nonasbestos mineral; and TH = tubular morphology, not identifiable as chrysotile.

b The letter in the parentheses indicates that the counting procedure was that normally used by the other laboratory as 264-1 (O) are the results obtained by IITRI using the ORF procedure.

Sample 436, Enoree, South Carolina, Grace, Head Feed, Composite

IITRI Code No. 131, ORF No. 435
Appendix references
Photographs E-10-12, XRD I-143-147
Electron microscope I-53-59, II-167-203

Macroscopically, the sample was observed to be quite varied in grain size, grain morphologies, and grain colors. Black to gold micaceous flakes up to 5 mm in diameter were major components. Dark to pale green glassy chunks up to 3 mm in diameter were present. Colorless to white irregular glassy fragments, some with obvious iron-staining, were as large as 15 mm. Milky white to light green irregular chunks were also as large as 15 mm.

The composition of the sample determined by PLM analyses of the density-separated fractions is presented in Table 38. This sample was primarily non-micaceous contaminant minerals, with less than 50% vermiculite.

TABLE 38. COMPOSITION OF SAMPLE 436-I

Mineral phase	Estimated mass concentration (%)
Fibrous mixed amphiboles	< 1
Anthophyllite-prismatic	1-3
Tremolite-actinolite	6-9
Sphene	2-4
Hornblende	11-15
Apatite	2-4
Magnetite, hematite	1-3
Rhodonite, pyrolucite	1-2
Calcite	1-2
Quartz, feldspars	23-28
Talc	3-5
Vermiculite	32-40
Other minerals	1-3

Fibrous amphibole mineral phases were detected, mostly in the tetrabromoethane sinks fraction, but were less than 1% of the total sample. Both anthophyllite and tremolite-actinolite fibrous amphibole phases were detected. In addition, it is likely that fibrous hornblende was also incorporated within the fiber bundles.

The three major amphibole types present, anthophyllite, tremolite-actinolite, and hornblende, occurred predominantly as prisms. Fracture of hornblende prisms to yield particles classifiable as fibers is unlikely. However, the prisms of anthophyllite and tremolite-actinolite were obviously layered and cleavable to particles definable as fibers.

Talc was again rather abundant and was also found as fracture fragments that might be classified as fibers.

The milky green, rough textured, irregular mineral grains were isolated from the TBS fraction and analyzed separately. Morphologies of the crushed fragments produced in grinding ranged from irregular to elongated prisms. Color and extinction characteristics (as observed on paralled-sided fragments) were consistent with tremolite-actinolite, but refractive indices were slightly lower than the indices of the glassy, obviously prismatic fragments of tremolite-actinolite observed in the sample. X-ray diffraction studies of this phase indicated this material was a sodium tremolite. A summary of the EM results for this sample appears in Table 39.

TABLE 39. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE ENOREE, SOUTH CAROLINA, HEAD FEED - 100 MESH

Sample	Fibers of all lengths: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fibers greater than 5.0 μm in length: Fiber concentration (10^6 fibers/g) Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
436-I	0.3			0.49	12	0.1			0.43	3	A
	2.2	0.5-3.9	0.83		82	0.2		0.3		8	T
					6					6	C
436-O	12	7.1-16	0.160	22	73	1.6	0.1-1.6	0.160	16	6	A
	0.3	0-0.8	0.160	< 1	2	0.2	0-0.5	0.160	< 1	1	C
436-I, Exfoliated	1.3			0.81	3					0	A
	5.1		0.4		12	0.4		0.4		3	T
					6					0	C

[a] A = amphibole (SAED); C = chrysotile; and T = total.

Sample 439, Enoree, South Carolina, Grade 3, Commercially Exfoliated

IITRI Code No. 133, ORF No.
Appendix references
Electron microscope I-120-121

The sample was typical in appearance of expanded vermiculite used as packing material or soil conditioning material. Individual particles were obviously composed of multiple, stacked vermiculite plates. Colors of the stacks ranged from white to tan to brown to light green. Diameters of the plates ranged from 1 to 5 mm. Lengths of the expanded stacked plates were quite variable and ranged up to 15 mm. Non nonmicaceous mineral phases were detected in the gross, stereomicroscopic inspection of the sample.

Density separations did not yield much higher density (greater than 2.76) material. Table 40 lists the mineralogical composition of the sample determined by the polarized light microscopy analyses.

TABLE 40. COMPOSITION OF SAMPLE 439-I

Mineral phase	Estimated mass concentration (%)
Fibrous mixed amphibole	< 1
Anthophyllite-prismatic	< 1
Tremolite-actinolite	< 1
Sphene	< 1
Augite	< 1
Apatite	1-3
Hornblende	< 1
Magnetite, hematite	1-2
Rhodonite, pyrolucite	< 1
Calcite	< 1
Quartz	1-3
Talc	1-2
Vermiculite	85-95
Other minerals	1-3

Fluorapatite was the primary nonmicaceous mineral constituent of both the tetrabromoethane and 2.76 sinks density-separated fractions. Apatite crystals were significantly larger in size and more abundant than any other nonmicaceous mineral phase detected.

Particles classifiable as fibers on a morphological basis, upon high magnification inspection, were found to be mostly vermiculite shards and scrolls. Refractive indices were a major characteristic observed to distinguish vermiculite "fibers" from amphibole fibers since vermiculite refractive indices are significantly lower than tremolite-actinolite and anthophyllite refractive indices.

Tremolite-actinolite and anthophyllite were present as coarsely prismatic material and as fine fractured particles classifiable as fibers. The prismatic crystals each comprised less than 10% of each sink fraction and were thus each less than 0.1% of the total sample. The fiber-like crystals were present at a count rato of one per 1,000 particles; on a mass basis, therefore, their concentrations would have to be in the parts per million range. A summary of the EM results for this sample appears in Table 41.

TABLE 41. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE ENOREE, SOUTH CAROLINA, GRADE 3, COMMERCIAL EXFOLIATION

	Fibers of all lengths					Fibers greater than 5.0 μm in length					
	Fiber concentration (10^6 fibers/g)					Fiber concentration (10^6 fibers/g)					
Sample	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
439-F	11.7		1.5		0 8 0			1.5		0 0 0	A T C

[a] A = amphibole (SAED); C = chrysotile; and T = total.

Sample 442, Enoree, South Carolina, Grade 4, Commercially Exfoliated

This sample was a fine-grain, expanded vermiculite. The expanded, stacked vermiculite plates visible in this sample ranged in diameter from 0.5 to 3 mm. Lengths of the stacked plates ranged from 1 to 5 mm. Particle colors were white, tan, brown, and greenish brown. No nonmicaceous mineral phases were detected in the macroscopic inspection.

Density separations of this sample also produced relatively little high density (greater than 2.76) material. The mineralogical composition of the sample determined in the polarized light microscopy analyses of the various density fractions is presented in Table 42.

TABLE 42. COMPOSITION OF SAMPLE 442-I

Mineral phase	Estimated mass concentration (%)
Fibrous mixed amphibole	< 1
Anthophyllite-prismatic	< 1
Tremolite-actinolite	0.5-1
Sphene	< 1
Augite	< 1
Apatite	1-2
Hornblende	< 1
Magnetite, hematite	1-2
Rhodonite, pyrolucite	< 1
Calcite	< 1
Quartz	1-2
Talc	< 1
Vermiculite	85-95
Other minerals	1-2

Tremolite-actinolite was the primary nonmicaceous mineral type in both the tetrabromoethane and 2.76 sinks fractions. It occurred primarily as coarse, chunky prisms. Up to 10% of the tremolite-actinolite occurred as overall prismatic fragments composed of elongated, thin, narrow lamellated prisms. This crystal form undoubtedly produced many of the small, fiber-like crystals observed. The larger anthophyllite fragments present occurred only as the chunky prisms.

The very small (less than 10 μm diameter) amphibole crystals present in morphologies definable as fibers were both anthophyllite and tremolite-actinolite. It was impossible to determine if these fine, fiber-like crystals were abraded from large bundles of truly fibrous material or were fractured from the lamellated prisms. Number concentrations of the fine, fiber-like amphibole crystals were greater in this sample compared to sample 439-I. However, mass concentrations must be considered to be again in the parts per million range.

Sample 573, Enoree, South Carolina, Patterson, Ungraded, Composite

IITRI Code 124, ORF No. 572
Appendix references
Photographs E-13, 24-25, XRD I-148-152
Electron microscope I-79-83, II-335-375

Macroscopically, the sample was observed to have a wide size range and to be a brownish-gold material with some obviously micaceous flakes. Brownish-gold, nonmicaceous grains ranged up to 10 mm in size, while the micaceous

flakes were 7 to 8 mm in maximum dimension. Fragments of nonmicaceous minerals up to 20 mm in diameter were present. Colors of the nonmicaceous minerals were milky white, milky green, and glassy green. No obviously fibrous phases were observed in either the unmagnified or stereomicroscopic examinations.

The composition of the sample, as determined by PLM analyses of the density-separated fractions, is listed in Table 43.

TABLE 43. COMPOSITION OF SAMPLE 573-I

Mineral phase	Estimated mass concentration (%)
Fibrous mixed amphiboles	< 1
Anthophyllite	4-8
Tremolite-actinolite	8-12
Sphene, ilmenite, rutile	1-2
Hornblende	1-3
Apatite	1-2
Magnetite, hematite	1-2
Rhodonite, pyrolucite	< 1
Calcite	< 1
Quartz, feldspars	26-32
Talc	12-16
Vermiculite	33-38
Other minerals	1-3

This sample appears to have been exposed to some type of heat treatment. Glassy agglomerates were observed in the total sample and were, of course, concentrated in the 2.76 floats fraction.

No obviously fibrous bundles were observed in the stereomicroscopic examination of the TBE fraction. Small, elongated, coarse fibrous to prismatic white particles were observed in the TBE fraction; however, they were in greater abundance in the 2.76 sink fraction. In the TBE, this particle type was less than 1% of the fraction, while in the 2.76 sink the prismatic to coarse fibrous phase represented 10 to 20% of the fraction mass. These particles were generally not teasable with a fine needle and thus are not in a true fibrous habit. However, gentle crushing and grinding produced long, thin parallel-sided particles which would be classifiable as fibers.

The TBE fraction contained numerous pale green, prismatic amphibole mineral particles which were determined to be tremolite-actinolite. Again, even these clearly prismatic particles could be fractured to yield particles definable as fibers. Although the anthophyllite comprised 10 to 20% of this fraction, practically all of it also occurred in an obviously prismatic crystal

habit. While fracture of the prismatic anthophyllite could yield fragments classifiable as fibers, this fracture was not readily accomplished; irregular, jagged fragments tended to be produced.

The prismatic to coarse fibrous mineral phases found in abundance in the 2.76 sink fraction were isolated and carefully examined. The particles were found to be composed almost exclusively of talc and anthophyllite. Tremolite-actinolite was only a trace constituent of this fraction. Grinding of the particles resulted in ready fracture of both the talc and anthophyllite into long, thin, parallel-sided fragments classifiable as fibers. Larger fragments showed splintered ends suggestive of fiber bundles.

Unlike the Grace samples from South Carolina, the Patterson sample contained predominantly rutile rather than sphene titanium phases. Some of the rutile was found in elongated, thin crystal habits. A summary of the EM results for this sample appears in Table 44.

TABLE 44. SUMMARY OF ELECTRON MICROSCOPY RESULTS FOR SAMPLE ENDREE, SOUTH CAROLINA, PATTERSON, UNGRADED

	Fibers of all lengths					Fibers greater than 5.0 μm in length					
	Fiber concentration (10^6 fibers/g)					Fiber concentration (10^6 fibers/g)					
Sample	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Mean	95% Confidence interval	Concentration equivalent to 1 fiber detected	Estimated mass concentration (ppm)	No. of fibers counted	Fiber type[a]
573-I	0.83		0.83	2.7×10^{-4}	1						A
	0.8				23	0.83		0.83		1	T
	0.83			1.4×10^{-4}	1						C
573-O	1.7	0.6-2.9	0.244	27	7	0.5	0-1.2	0.244	25	2	A
	< 0.3	-	0.244	-	0	< 0.3	-	0.244	-	0	C
573-I, Exfoliated	0.5			2.6	3	0.2			2.4	1	A
	2.7		0.2		21	0.5		0.2		2	T
	0.2			2.3×10^{-5}	1					0	C
573-O, Exfoliated	1.1	0.1-2.0	0.265	4	4	0.3	0-0.9	0.265	4	1	A
	< 0.3	-	0.265	-	0	< 0.3	-	0.265	-	0	C

[a] A = amphibole (SAED); C = chrysotile; and T = total.

Air Sample, Phase Contract Results

The results of the examination of the air sample filters by phase contrast analysis are presented in Table 45.

TABLE 45. RESULTS OF THE PHASE CONTRAST ANALYSIS OF AIR SAMPLES COLLECTED AT THREE VERMICULITE SITES

	Sample	Sample vol. (ℓ)	Fibers/cc ORF	Fibers/cc IITRI
Libby, Grace				
106	Field blank[a]	-	< 0.02	0.04
133	Field blank[a]	-	0.03	0.05
131	Front loader	303	0.02	0.04
148	Pit haul driver	297	< 0.01	0.01
138	Mine analyst	294	1.5	1.9
141	Bottom operator	276	1.2	0.4
130	No. 2 operator	285	3.1	9.7
139	Dozer operator	270	0.02	0.2
101	Shuttle truck	385	0.1	0.2
104	Screening plant, DW	390	0.08	0.5
111	Screening plant, DW	368	0.1	0.02
108	Trailer court	169	0.03	ND[b]
136	No. 5 substation	111	0.03	0.02
South Carolina, Grace				
312	Field blank[a]	-	< 0.02	0.04
346	Field blank[a]	-	< 0.02	0.02
340	Mill monitor	340	0.03	0.03
321	Mill lab technician	478	0.07	0.2
301	Dragline operator	240	< 0.01	ND[b]
347	No. 4 bagger	314	0.06	0.1
330	No. 3 bagger	285	0.1	0.05
328	Mill (ENE) downwind	287	0.05	0.04
335	Mill (N) crosswind	80	0.04	ND[b]
307	Mine (N) crosswind	291	< 0.01	0.02
323	Mine (E) downwind	154	0.01	0.02
338	Mine (W) upwind	264	0.03	0.01
310	Truck driver	257	< 0.01	0.3
300	Screening plant floor	354	0.06	0.14
South Carolina, Patterson				
505	Field blank[a]	-	< 0.02	< 0.01
533	Field blank[a]	-	< 0.02	0.02
508	Payload operator	255	< 0.01	0.04
520	Plant foreman	252	0.01	0.3
542	Bagger/forklift	249	< 0.01	0.1
513	(NE) downwind	188	< 0.01	ND[b]
506	Control off-site	274	< 0.01	ND[b]
515	(SE) crosswind	299	0.01	0.01
528	(SW) upwind	147	0.02	ND[b]

a Values for blanks were calculated assuming a 100-liter sample.

b ND: No fibers detected (100 grids).

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APPENDIX A

STUDY PROTOCOL FOR THE COLLECTION AND ANALYSIS OF VERMICULITE AND RELATED SAMPLES FOR THE EVALUATION OF FIBER CONTENT WITH EMPHASIS ON ASBESTIFORM FIBERS

TASK 32
STUDY PROTOCOL FOR THE COLLECTION AND ANALYSIS OF VERMICULITE AND RELATED SAMPLES FOR THE EVALUATION OF FIBER CONTENT WITH EMPHASIS ON ASBESTIFORM FIBERS

I. Background

In December 1978, the vermiculite industry submitted information to the EPA regarding health problems experienced by employees who were processing asbestos-contaminated vermiculite. The original submission indicated that bloody pleural effusions had been detected in 4 of 350 employees; symptomatology and clinical findings in the employees were similar to those found in individuals with asbestos-related diseases. Subsequent follow-up studies by the Occupational Safety and Health Administration (OSHA) revealed an even higher prevalence of health problems among the employees.

Vermiculite is a hydrated magnesium-iron-aluminum silicate which has been mined in the United States since 1929. After mining, vermiculite is processed to remove impurities, including asbestiform minerals; however, all contaminants are not removed. Information suggests that the three major domestic deposits in Montana, South Carolina, and Virginia contain asbestiform minerals. Some impurities, including asbestos, may remain as a contaminant in processed vermiculite.

Although vermiculite may contain fibrous materials, the health effects from vermiculite itself are unknown at this time. A priority review of asbestos-contaminated vermiculite, completed by the Office of Testing and Evaluation in June 1980, suggested that the asbestos in vermiculite may be responsible for the reported adverse health effects, and it concluded that certain information gaps needed to be filled before an in-depth risk assessment on vermiculite could be initiated.

Several projects have been initiated to fulfill the information gaps and complete the preregulatory analysis on vermiculite. A control options analysis has been initiated to determine regulatory strategy to control asbestiform mineral-contaminated vermiculite, and a substitute analysis is in preparation to evaluate replacements for vermiculite products. Work has also been initiated on a materials balance to show the mass flow of vermiculite along with the release of any associated asbestiform mineral, and the development of a mineralogy profile with a sampling and analysis protocol of vermiculite is underway to characterize the fibrous materials within vermiculite.

From the available information on the composition of vermiculite, it seems there is the possibility that asbestos contamination of vermiculite does occur, but that it may be difficult to assess the magnitude of the contamination. Therefore, the objective of this protocol is to specify the sampling and analysis procedure to determine the composition of vermiculite, particularly the amount of asbestiform minerals[1] present in the vermiculite. This

[1] For practical analysis purposes, the specific identification of asbestiform minerals will be limited to chrysotile, the amphiboles, and vermiculite scroll.

will provide the needed information on the risk to the population exposed to asbestiform minerals from vermiculite at each of the various stages of its commercial distribution.

The protocol will be conducted in two phases. The first phase will be an in-depth analysis of the asbestiform fibers present in and associated with vermiculite ore, ore concentrates, and beneficiated vermiculite from the four major vermiculite mines in the United States and of beneficiated vermiculite from the ports of entry. Both bulk and air samples will be collected and analyzed. The second phase will be a similar analysis of bulk and air samples from a representative number of exfoliation plants in the United States. The exfoliation plants where sampling will occur will be statistically chosen by Exposure Evaluation Division (EED) to include all the major sources of vermiculite.

II. Preparation for Sampling

A. Inventory Supplies

1. All necessary equipment for sampling bulk vermiculite and air will be gathered and inventoried.

2. Filters to be used for the collection of airborne particles will be assembled and labeled before samples are obtained.

3. Calibration of the pumps will be performed prior to their shipment to the sampling site and recalibrated in the field.

4. All supplies will be packed and shipped to the vermiculite sampling site at least 2 days in advance of the arrival of the crew.

B. Site Investigation

1. Survey site - Upon arrival at the site, the crew chief and other designated persons will survey the site to determine the location of the facility, its boundaries, and the locations of various operations within the facility.

2. Select sampling points - The crew chief and other designated persons will select appropriate points for the collection of ore samples and airborne particulates. Officials of the host plant will be invited to participate and assist in the survey and selection of sampling points.

III. Sampling

A. Bulk Material

1. Basis for selection of protocol - No American Society for Testing Materials (ASTM) method was found that is directly applicable to this situation. The following related methods are used for guidance.

a. American National Standards Institute (ANSI)/ASTM D 75-71 (1978) Standard Methods of Sampling Aggregates.

b. ASTM Designation: D 2234-72 Standard Methods for Collection of a Gross Sample of Coal.

c. ANSI/ASTM E 105-58 (1975) Standard Recommended Practice for Probability Sampling of Materials.

d. ASTM Designation: C 702-72 Standard Methods for Reducing Field Samples of Aggregate to Testing Size.

e. ASTM Designation: C 516-75 Standard Specifications for Vermiculite Loose Fill Insulation.

f. BS 812 (British Standards Institution) Methods for Sampling and Testing of Mineral Aggregates, Sands and Fillers.

g. Other Considerations - The minimum quantity of any sample should be 5 to 10 times the anticipated analytical needs. The analytical needs will vary with particle size and range from approximately 40 g for fine material to 1,000 g for 25-mm particle size. Therefore, sample size minimums should range from 400 g to 10 kg.

Each sample may consist of a composite of individual sampling increments representing different times and/or locations. Increments will be sampled and stored separately with a composite made under laboratory conditions by combining representative fractions of each increment.

2. Samples to be collected - The objective of sampling is to obtain samples that are representative of the operations or sites. It is anticipated that properties of the materials of similar types will vary with time, operation and specific mine site origin. Therefore, to obtain representative samples, it is necessary that composite samples be prepared of a given sample type from individual sample increments, each representing a specific sample time or site. It is likely that a historical sample collection is maintained (by the mine company) from several operation points within the facility. If these historical samples are available, it would be helpful to obtain selected increment samples for both the preparation of a time averaged composite and a comparison of present to past conditions.

The number of increment samples to be collected must depend on the variability of the sample and availability of increment sources, with a decision made by an experienced sampler depending upon increment availability and proper sampling procedures. All decisions will be documented with copies sent to the EPA task manager.

a. Raw ore and ore concentrates (Phase I)

(1) A bulk sample of the raw vermiculite ore representing different parts of the mine.

(2) A bulk sample of the concentrated ore before beneficiation.

(3) A bulk sample of dust from the dust collection equipment where such equipment exists.

(4) A water sample from washings and dust control operations.

(5) A bulk sample of concentrated ore blend (beneficiation feed) before beneficiation.

b. Beneficiated vermiculite (Phase I)

(1) A bulk sample of each of five grades of beneficiated vermiculite.

(2) A bulk sample of material from one to three intermediate beneficiation processing steps.

(3) A bulk sample of tailing from the beneficiation process.

(4) A bulk sample of dust from dust collection equipment.

(5) A water sample from washing and dust control operations.

c. Exfoliated plant samples (Phase II)

(1) A bulk sample of each of the five grades of vermiculite before exfoliation.

(2) A bulk sample of each of five grades of exfoliated vermiculite.

(3) A bulk dust sample from dust collection equipment and other appropriate related material.

B. Air Samples (Phases I and and II)

1. General considerations - Airborne particulate samples will be collected at designated points inside and outside the plant boundaries. The sampling will generally follow the EPA method described in Electron Microscope Measurement of Airborne Asbestos Concentrations - A Provisional Methodology Manual, EPA-600/2-77-178, Revised June 1978. This method recommends polycarbonate 0.4 μm Nuclepore® filters when possible, but allows for the use of cellulose acetate (Millipore®) filters.

There are advantages and disadvantages to the use of either Nuclepore® or Millipore® filters. The sample collected on the smooth polycarbonate

(Nuclepore®) suface has poor retention efficiency and the sample may be lost or redistributed during transport. The cellulose acetate (Millipore®) filters requires an ashing procedure and reconstitution on a polycarbonate filter for TEM analysis. Ashing and reconstitution is an extra step in the procedure but has the potential advantage of eliminating interfering organic particle analysis. This reduces the need of multiple time sampling to obtain a range of filter loadings. Asbestos contamination has been reported in some lots of both Nuclepore® and Millipore® filters.

The current consensus of leaders in the field is to favor the use of Millipore® filters for the type of sampling and transport that will be required on this program.

The potential presence of asbestos fibers in the filters themselves will require careful attention to the selection and analysis of filter blanks and field blanks.

2. Control blanks

a. Filter blanks - Four filters from each package of 100 filters, one from each box of 25, will be selected by random numbers as filter blanks. The four filters will be quartered and one-fourth of each combined as a composite sample.

b. Field blanks - One of every 10 filters will be a field blank, subjected to all processing conducted with an actual air sample except for the sampling itself.

3. Sampling procedure - All sampling, fixed and personal, will be taken using 37 mm 0.45 μm Millipore® filters backed with 5 μm Millipore® filters and a Millipore® support pad. The sampling rate will be approximately 2 liter/min with the exact rate determined periodically throughout the sampling period by the use of calibrated flow meters.

Sampling will be scheduled for 8 hr (or longer for ambient and background samples). However, if the flow is found to reduce during sampling, indicating that the filter is loaded, sampling will be stopped and the time and flow rate recorded.

4. Air samples will be collected - Personal air zone samples and fixed samples located at targeted areas will be taken. The use of personal samples will depend on the individual work patterns and on the cooperation of the host company. When possible, individuals at each work station will be equipped with personal samplers.

When possible, air samples will be taken which correspond to the bulk samples (Section III-A-2). The following air samples will be taken. Any variation from these sampling locations will be documented.

a. Air samples taken at operations before beneficiation (Phase I).

(1) An air sample at the mine during mining.

(2) An air sample at dumping or crushing operation.

(3) Air samples around the mining facility.

(4) Air samples downwind of dusty operations.

(5) Air samples along shipping lanes.

(6) An air sample as a background control within the geographic region.

b. Air samples taken from the ore beneficiation operations. (Where mining and beneficiation are at the same general location, several of the samples may be the same.) (Phase I)

(1) An air sample at each of selected work stations in the beneficiation operation.

(2) Air samples around the beneficiation plant.

(3) Air samples at grading (screening) operations.

(4) Air samples downwind from dusty operations.

(5) Air samples along shipping lanes.

(6) An air sample as a background control within the geographic region.

c. Air samples taken from the exfoliation operation. (Phase II)

(1) An air sample from each of selected work stations in the exfoliation operations.

(2) Air samples around the exfoliation plant.

(3) Air samples downwind from dusty operations.

d. A meteorological station will be installed on-site to collect air speed and direction data throughout the sampling period.

IV. Sample Handling

A. Bulk Samples

The increment samples will be shipped to a central laboratory. Each increment sample will be divided by appropriate procedures (riffle divided or cone and quarter). Part of each increment will be retained and the

remainder combined with other appropriate increments to form a composite sample. The composite will be mixed and split (riffle or cone and quartered) to provide appropriate split analytical samples. The composite samples will be properly designated and submitted for analyses.

B. Air Samples

1. Special handling - When sampling is completed, the filter cartridge will be turned to a position with the filter horizontal and the collection surface up, the cartridge disconnected from the pump, the cartridge cover replaced, and the inlet and exit holes plugged. This horizontal filter position will be maintained during transport and storage. The cartridge will be placed in a special container for transport.

2. Each filter will be divided and each portion will be taped to the bottom surface of the petri dish and delivered to different laboratories to provide for replicate analysis.

V. Sample Analysis

A. Bulk Sample Analysis

The analysis protocol for the bulk vermiculite samples will include parallel approaches which, to a degree, support one another. However, because of the great differences in the detection limits of the different methods, the justification of some approaches is their simplicity as preliminary screening procedures rather than their sensitivity. X-ray diffraction of the unfractionated samples is an example of a simple procedure with limited sensitivity. These methods may serve to identify some samples with gross quantities of asbestos and eliminate the need for continued analysis.

1. Unexfoliated vermiculite, before and after beneficiation

a. Examine the sample as received with a low power (30X) stereomicroscope for quantities of visible fibers.

b. If fibers are observed, estimate the weight (%) of fibrous material. If appropriate, remove (hand pick) the asbestos from the sample and weigh.

c. Identify the isolated asbestiform mineral by appropriate means (PLM, XRD, etc.).

d. To isolate the fine fibers from vermiculite, start with a sample quantity depending on particle size. Place the sample in a specified beaker size and add 10 times the sample weight of prefiltered isopropyl alcohol.

The sample quantities, isopropyl alcohol volume and beaker sizes to be used are as follows:

Sample	Grams	Volume IPA	Tall Form Beaker (ml)
Grades 1 and 2	40	400	1,000
Grades 3 and 4	20	200	400
Grade 5[a]	40	400	1,000
Unbeneficiated material and other tailings, etc.	40	400	1,000

a Grade 5 is expected to have more variability than the other grades.

Place the beaker in an ultrasonic bath, stir, allow the large particles to settle (during ultrasonic treatment) and withdraw aliquot portions from near the center of the liquid for optical microscopic analysis (i.e., PLM) and to prepare a series of Nuclepore® filters for EM analysis. Serial dilution may be required to obtain optimum filter loading.

e. The Nuclepore® filter with suspended fines will be used to prepare a TEM grid by the EPA carbon-coated Nuclepore® filter technique.

f. Make fiber count - Determine chrysotile or amphiboles. Count 100 fibers or 10 grid of 200 mesh screen. Determine the limit of detection and count more grids if necessary.

g. Identify specific amphiboles using selected area electron diffraction or zone axis selected area electron diffraction plus energy dispersive X-ray analysis.

h. Exfoliate a portion of the beneficiated vermiculite by sprinkling no more than a one particle thick layer of sample, in a preheated (800°C) shallow container and place the container back into a 800°C oven for 5 sec. Examine the exfoliated sample as described in No. 2.

2. Exfoliate vermiculite (for laboratory expanded samples of Phase I and for Phase II) - An important feature of the analytical procedure to achieve high microfiber detection sensitivity is the fractionation of the sample to remove much of the interfering vermiculite, thereby greatly enriching whatever asbestiform fibers that may be present. The basis of fractionation is the floatation on water of the exfoliated vermiculite and the wetting and sinking of the asbestos and other fibers. This assumes that a proportionally high fraction of the fibers are not physically attached to the vermiculite particles. This is a reasonable assumption but one that will be verified by the examination of representative samples of the fraction that floats.

Starting with a sample quantity depending on particle size, or grade,

Vermiculite Grade	Sample Weight (g)	Water Volume (ml)
1 and 2	40	2,000
3 and 4	20	1,000
5	40	2,000

and proceed as follows:

a. Float separation - Place the expanded vermiculite in a 2,000 ml plastic beaker and add water. Stir for 30 sec and skim off the vermiculite and drain on a 50-mesh screen. Collect the drain water and return it to the beaker. Discard the vermiculite.[2]

b. Disperse the "sink" material with ultrasonic treatment. Remove an aliquot during treatment for a preliminary PLM examination and for TEM analysis. Double dilution may be necessary to obtain proper grid loading.

c. Examine preparation by PLM as a preliminary parallel examination.[3]

d. Prepare TEM grid by EPA carbon-coated Nuclepore® filter technique.

e. Fiber count - Determine chrysotile, total amphiboles and vermiculite scrolls. Count 100 fibers or 10 grids of 200-mesh screen. Determine limit of detection and count more grids if necessary.

f. Identify specific amphiboles using SAED plus energy dispersive X-ray analysis.

3. Miscellaneous bulk samples

a. Dust samples

(1) A preliminary examination of the dust sample will be made by optical microscopy including PLM for the identification of gross quantities of asbestiform fibers. If gross quantities of fibers are identified, the quantities will be estimated and the analysis terminated.

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[2] Selected samples will be examined to verify the absence of asbestos in this fraction.

[3] If PLM examination reveals a gross quantity of identifiable asbestiform fibers, the quantity should be estimated and the analysis terminated. (Modified during the project to continue analyzing.)

(2) If the sample is not adequately characterized by PLM, a portion of the sample will be dispersed in water and filtered for EM analysis.

b. Wash water samples - The solids present will be dispersed in the water and aliquots filtered for appropriate optical and EM analysis.

B. Air Samples

1. Portions of selected filters will be used to determine fiber count by the standard NIOSH procedure using phase microscopy.

2. The major analysis of the air samples will basically follow that specified in the EPA document, "EPA-600/2-77-178, Revised June 1978, Electron Microscope Measurement of Airborne Asbestos Concentrations - A Provisional Methodology Manual.

APPENDIX B

DETAILED ANALYSIS PROCEDURES AS SUBMITTED BY IITRI

PROCEDURES

BULK SAMPLE ANALYSIS

Quantitative analysis requires that valid and rigorous procedures be used during all phases and steps of a procedure and that these procedures be well-defined before work on the first sample is begun. The approach and logic used by IITRI was based on:

- A study protocol prepared by MRI,
- Discussions of the protocol with MRI, and
- Discussion on procedures with Ontario Research Foundation (ORF).

The bulk sample procedure is presented in Figure B-1. Where we note that the first operation is, as with any sample, sample log-in. The bulk sample is then subdivided for two distinct series of sequential steps. The first begins with analysis of the sample "as received" for gross (defined for this study as > 1% by weight) fiber contamination and characterization by polarized light microscopy. Samples which are not found to be grossly contaminated are moved into the steps of isopropyl alcohol beneficiation and electron microscopy analysis for fiber content.

A parallel screening test for the second series of steps is whether the sample received is an exfoliated vermiculite or not. If it is exfoliated, no work is needed; if not, the sample is thermally exfoliated, the product is beneficiated, and the "sink" fraction analyzed by electron microscopy.

In the subsections which follow, IITRI describes the procedures used for:

- Sample splitting
- Optical microscopy
  - Preliminary inspection
  - Sample separations
  - Polarized light microsocpy
  - X-ray diffraction
- Electron microscopy
  - Beneficiation
  - Sample preparation
  - Electron microscopy analysis

[1] Task 32--Study Protocol for the Collection and Analysis of Vermiculite and Related Samples for the Evaluation of Fiber Content with Emphasis on Asbestiform Fibers (Revised November 13, 1980).

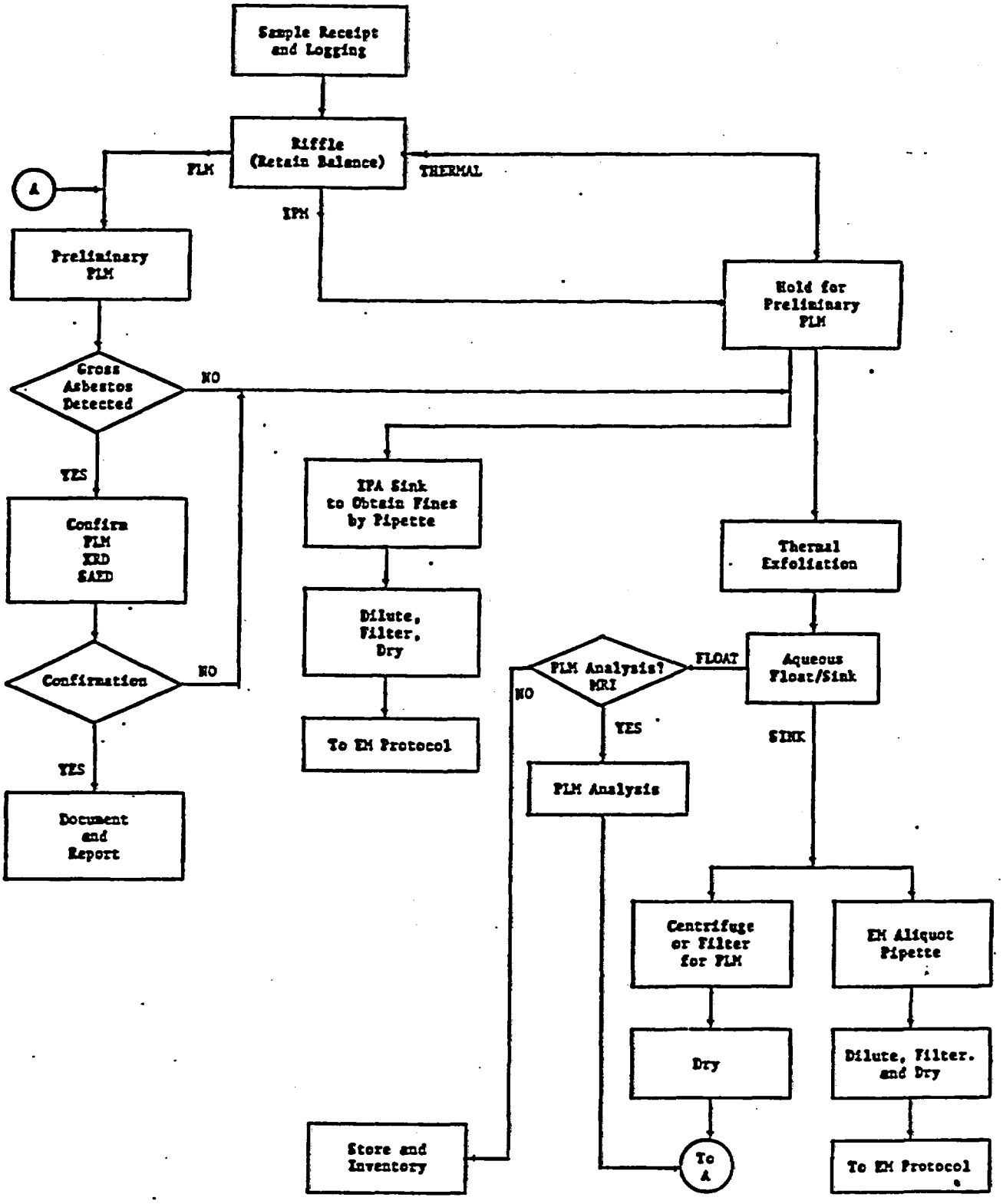

Figure B-1. Flow chart for bulk sample analysis.

SAMPLE SPLITTING

The samples were split into aliquots using a spinning riffler.[2] The riffler is a rotating tray containing sample receivers. As the tray rotates, the receivers extract a sample from the flowing powder stream. This time-averaged sample consisting of many small aliquots produces a sample free of biases due to segregation variation in aerodynamic diameter and the powder's flow properties.

Each fraction collected was placed in a clean, glass cream jar, labeled with the IITRI sample number and submitted for analysis or stored. IITRI riffled a minimum of four fractions from each sample--one each for PLM, alcohol beneficiation, thermal exfoliation, and a back-up sample. The target size for each sample was:

- Twenty grams for vermiculite Grades 3 and 4.
- Forty grams for all others, including vermiculite Grades 1, 2, and 5.

OPTICAL MICROSCOPY

The objectives of the polarized light microscopy analyses were to:

- Determine if fibers were present,
- Identify the fibrous phases detected,
- Determine the concentrations of asbestiform phases in the bulk sample, and
- Identify the prismatic mineral phases present that could fracture to yield "fibrous" particles.

To achieve these objectives, several sample preparation steps and supplementary analyses are used as integral parts of the polarized light microscopy analysis. The sample separation steps enhance the (semi-)quantitative aspects of microscopical analyses which rely heavily on estimations of component concentrations. The supplementary analyses, principally x-ray diffraction, were conducted to establish irrefutable identities of phases--especially those in a fibrous habit.

Preliminary Inspections

The bulk sample portions submitted for polarized light microscopy (PLM) were first inspected with a low power stereomicroscope to determine the number of different mineral phases present, the associations of the various phases, and the presence of fibrous phases. This preliminary inspection also served to determine which sample separation step (hand-picking of fibrous phases, or

[2] ASTM C702 71T, Tentative Method for Reducing Field Samples of Aggregate to Testing Size.

heavy liquid separation) should proceed first. Notations on sample color, texture and general particle size ranges were made at this time.

Sample Separations

The objective of the sample separations was to concentration any fibrous phases to facilitate both the phase identification and quantitation tasks. Subsamples for the separation procedures were obtained by coning and quartering* the sample fraction submitted for PLM analysis. The entire PLM sample fraction was poured out of its container onto a clean piece of foil and quartered with a broad-bladed spatula. The desired subsample size (one or two quarters) was retained on the foil and the remainder of the PLM sample was returned to its container. For those samples that received a duplicate separation analysis, the coning and quartering was repeated.

Hand-Picking--

When the preliminary inspection revealed the presence of several bundles of fibers at least 1 mm in diameter and 3 mm in length, hand-picking of the fibrous phase(s) with a fine-pointed tweezers was the first separation step performed. The separation subsample of the PLM sample was weighed on a piece of tared foil and then spread to a monolayer of particles. While viewing through the stereomicroscope, the fibers were tweezed from the subsample and placed in a tared weighing pan. Mixed particle types containing at least 25% fibrous material, as well as totally fibrous particles were tweezed. The pan containing the fibrous phase as well as the foil containing the nonfibrous remainder of the subsample were then reweighed (to 0.1 mg) and the mass percent of "pickable" fibrous material was calculated.

When smaller bundles were present, hand-picking was done either after the first heavy liquid separation step or, for some samples, was not feasible. The procedure for hand-picking fibers from the "sinks" fraction of the first heavy liquid separation is essentially the same as for the bulk subsamples.

Heavy Liquid Separation--

Nonvermiculite mineral phases, particularly amphiboles and pyroxenes, were separated from the vermiculite bulk samples on the basis of density using a simple sink-float method. The densities of the mineral phases must differ by at least 0.2 g/cm^2 for this method to work. Table B-1 lists the specific gravities of vermiculite, some of the amphibole minerals, and other mineral contaminants commonly associated with vermiculite.

* See Reference 2, page B-3.

TABLE B-1. SPECIFIC GRAVITIES OF SELECTED MINERALS

Mineral	Chemical formula	Specific gravity
Vermiculite	$(Mg,Ca)_{0.8}(Mg,Fe,Al)_{3.0}(Al,Si)_4O_{10}(OH)_4$	2.4
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	2.8-3.2
Chrysotile	$Mg_3Si_2O_5(OH)_4$	2.5-2.6
Serpentine	$Mg_3Si_2O_5(OH)_4$	2.3-2.6
Talc	$Mg_3Si_4O_{10}(OH)_2$	2.7-2.8
Anthophyllite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$	2.85-3.2
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$	3.1-3.3
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	3.0-3.2
Ferroactinolite	$Ca_2Fe_5Si_8O_{22}(OH)_2$	3.2-3.3
Cummingtonite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$	3.1-3.3
Grunerite	$Fe_7Si_8O_{22}(OH)_2$	3.6
Diopside	$CaMgSi_2O_6$	3.2
Hornblende	$(Ca,Na)_{2-3}(Mg,Fe,Al)_5Si_6(Si,Al)_2O_{22}(OH_2)$	3.0-3.4
Quartz	SiO_2	2.65
Olivine	$(Mg,Fe)_2SiO_4$	3.27-4.37

The density separation technique is based on the principal that particles with a greater density than the liquid they are suspended in will sink while particles with densities equal to or less than the liquid density will float in the liquid. Mineral powder samples subjected to this float-sink procedure should be composed of single phase grains of fairly uniform size and less than 1 to 2 mm in diamter. As particle size approaches subsieve size (i.e., less than 37 μm), other forces including friction, particle shape, and thermal turbulence influence the settling characteristics of particles as much as density. The separation of most bulk samples will improve if grinding or sieving is performed prior to using the float-sink procedure. While this would have been true for the vermiculite samples, these steps were omitted to preserve the integrity of the sample.

Two density separations were performed on each subsample yielding three fractions based on density differences. The separation subsample was first suspended in 1,1,2,2-tetrabromoethane (TBE), specific gravity of 2.97; the TBE "sinks" were the first density separation fraction recovered. The TBE "floats" were then suspended in a TBE/isopropanol mixture (specific gravity of 2.76) yielding two other density-separated fractions, the "2.76 sinks" and the "2.76 floats." The procedure is described in detail below.

The density subsamples were dried for 24 hr at 90°C; then accurately weighed in tared 250-ml beakers. Approximately 200 ml of tetrabromoethane were added, and the mineral powder slurries were vigorously agitated with a spatula. The slurries were allowed to stand undisturbed for 12 to 24 hr. The top 160 to 175 ml of tetrabromoethane containing the "floats" were then

decanted into a 400-ml beaker and tetrabromoethane and isopropanol were added to produce 300 ml of 2.76 specific gravity liquid. This slurry was agitated and allowed to separate for 12 to 24 hr until migration of particles in the 2.76 sp. gr. liquid ceased. The top 200 to 250 ml of liquid containing the "2.76 floats" were decanted into a clean beaker.

The separated fractions were recovered by filtering each suspension through a tared, 0.22 μm pore size, Millipore® membrane filter. The recovered mineral fractions were dried for 24 hr at 90°C and weighed. Since losses of materials were unavoidable during the decanting and handling, the calculations of the mass percent for each density fraction represented in the total sample are based on the summed masses of recovered materials, rather than on the subsample mass determined at the start of the density separations. For samples from which fibers were hand-picked before the density separations, the mass of the hand-picked fibers was added to the mass of the TBE fraction for calculation of the mass percents of each density separation fraction represented in the total bulk sample.

The actual losses occurring in the heavy liquid separation steps were determined to be 2.2 to 5.5%. Duplicate separations performed on two of the samples indicated the density fraction data were reproducible to within 5%.

Polarized Light Microscopy

A portion of the unseparated sample and of each separation fraction were dispersed in a standard immersion oil (n_D = 1.515) on a glass slide for PLM analysis. Mineral phases present were identified, at least as to mineral group, by morphological properties and by observation of optical properties; including extinction angles, birefringence, refractive indices, color and pleochroism. Individual particle types removed from subsamples by hand-picking were mounted in other standard refractive index liquids to allow precise determination of particle refractive indices. Comparison of the unknown mineral particle properties with those of known reference samples and published handbook values allowed identification of various mineral types.

Individual phase concentrations were microscopically estimated in the density separated subsamples on the basis of relative particle sizes and frequency. Mass concentration ranges for individual mineral phases were described as:

Primary	> 25%
Major	5 to 25%
Minor	0.5 to 5%
Trace	< 0.5%

The concentrations of the individual mineral phases in the total bulk sample were obtained by multiplying the microscopically estimated concentration of the phase in the separation fraction by the mass fraction the subsample represented of the total sample. For many samples, individual mineral phases occurred in small concentrations in all the density-separated fractions. Multiple-phase particles also contributed to the presence of high density

mineral phases in the two lower density fractions. Thus, the concentrations of individual phases within the total sample were determined by summing the concentration determined for each density-separated fraction.

X-Ray Diffraction

Positive identification of mineral phases, particularly fibrous amphiboles, by polarized light microscopy, is difficult. Therefore, to clearly establish identities of major and fibrous mineral phases, x-ray diffraction (XRD) analyses were conducted on selected separation subsamples and individual phases hand-picked from separation subsamples. The major objective of the XRD analyses was identification of the fibrous phases.

IITRI used the thin film technique, since this is most suitable for the very small quantities of materials available from hand-picking. The thin films were prepared by filtering the isopropanol suspended material through a silver membrane (25 mm diamter, 0.45 μm pore size). The XRD samples were ground to -325 mesh in a diamonite mortar prior to the filtration. As implied above, this technique provides an XRD pattern for material quantities as low as 0.1 mg; its drawback is that quantitation is not practical due to preferred orientation of many minerals including amphibole fibers.

Diffraction patterns were obtained with a Rigaku brand, rotating copper anode diffractometer operated at 50 kilovolts and 100 milliamps. The CuK_{α} x-ray lines, with an averaged wavelength of 1.54184 A, were thus generated. Most patterns were run at a scan rate of 2°/min. After conversion of the 20 diffraction angles to d-spacings in angstroms, the sample diffraction patterns were compared to standard diffraction patterns published by the Joint Committee on Powder Diffraction Standards for mineral identifications.

ELECTRON MICROSCOPY

The objectives of the electron microscopy analysis were to (a) determine if respirable asbestos fibers were present; (b) identify the fibers present within the limitations of the EPA Provisional Method;[3] (c) determine the number concentration of respirable asbestos fibers in the bulk sample; and (d) estimate the mass concentration of "respirable" fibers in the bulk sample.

The steps required to achieve these objectives are:

- Beneficiation of vermiculite samples,
- Sample preparation, and
- Electron microscopy analysis.

[3] Electron Microscope Measurement of Airborne Asbestos Concentrations: A Provisional Methodology Manual, EPA-600/2-77-178. Available from U.S. Environmental Protection Agency, Office of Research and Development Technical Information Staff, Cincinnati, Ohio 45268, Samudra, A., et al.

Beneficiation

Two beneficiation procedures were used for the samples; one used isopropanol and the other water as a working fluid. Each is described below.

Isopropanol Beneficiation--

The isopropanol beneficiation procedure was used for those samples whose asbestos fiber concentration, as determined during the PLM analysis, was less than 1% by weight, and to samples 259-I, 264-I, and 291-I* at the specific request of MRI.

This beneficiation required particle-free isopropanol, a sonic bath and tall form beakers. The weighed sample was placed in a tall form beaker of appropriate size; a volume approximately equal to 10 times the sample weight of filtered isopropanol was added and the beaker and contents put in an ultrasonic bath.

The ultrasonic bath was turned on, the mixture was stirred using a clean spatula, the large particles were allowed to settle, and aliquots were withdrawn from the center of the liquid column. The aliquots were diluted with a sufficient quantity of prefiltered isopropanol to permit filtration (30 to 50 ml). Each aliquot was quantitatively transferred to a Nuclepore® filter for electron microscopy analysis.

Aqueous Beneficiation--

One of the objectives of the study is to determine the fate of the asbestos which may be in the run-of-the-mine graded vermiculite. To determine the fate of the asbestos, IITRI exfoliated the graded vermiculite samples by exposing them in an 800°C oven, beneficiated the resulting exfoliated samples, and used electron microscopy to determine the asbestos content of the sink fractions.

Thermal exfoliation is used to prepare expanded vermiculite products. This treatment can readily be simulated in the laboratory. A monolayer of unexfoliated vermiculite is sprinkled into a preheated shallow quartz container which is inserted into an 800°C oven for 5 sec. After the 5 sec expire, the dish is removed, permitted to cool and the exfoliated vermiculite is stored for analysis. The process is repeated until all of the sample is exfoliated.

The exfoliated sample still contains all of the components originally present; however, most of the vermiculite phase can now be removed by an aqueous float process. In the float process, the exfoliated vermiculite is placed in a container, 1 or 2 liters of filtered, distilled water is stirred for 30 sec and the "vermiculite floats" removed and drained on a 50 mesh, U.S. Standard sieve. The drain water is collected and returned to the original container, and the vermiculite floats are discarded.

The water (in its container) is then placed in the sonic bath, sonicated, and aliquot samples are removed with a pipette. The procedure used to

* Midwest Research Institute sample numbers.

prepare filters is identical to that used in the isopropanol beneficiation, except that filtered, distilled water is substituted for isopropanol.

Sample Preparation

The basic procedures IITRI used to analyze the samples are documented in Electron Microscope Measurement of Airborne Asbestos Concentrations: A Provisional Methodology Manual;[3] however, four samples were analyzed using a modified protocol. Both protocols use identical sample preparation procedures, which are discussed below followed by a description of the analytical protocols.

The membrane on which the sample is deposited was air-dried overnight in a Class 100 clean workbench; a wedge-shaped portion of the filter was cut, carbon-coated, and 0.3 mm diameter circle was then removed with a punch from the wedge for transfer to a 200 mesh copper transmission electron microscopy grid. The Jaffe washer technique was used to transfer the sample to the grid.

In the Jaffe washer technique, a stack of 40 clean, 4.4 cm diameter, paper filters is placed in a clean glass petrie dish. Spectroscopic grade chloroform is then added until the level is at the top of the stack of filter paper. Several small (but larger than the 0.3 mm diameter grid) pieces of 60 or 100 mesh stainless steel (SS) screen are placed on the stack of filter paper. An orientation mark is placed on the outside of the petri dish, and a "map" showing the location of each piece of SS mesh is drawn. A sample to be transferred is placed, carbon-coated side down, onto a transmission electron microscope grid and the pair is placed on the center of a piece of SS mesh. The sample identification is noted on the "map." The procedure is repeated until the washer is filled or all samples to be prepared are in place.

The chloroform level is maintained at the top surface of the stack of filter paper for the 24 to 72 hr required to dissolve the Nuclepore® membrane. The preparation is completed by allowing the residual chloroform to evaporate from the grid, then placing the grid in a labeled grid storage box. All of the procedures described are performed in a Class 100 clean workbench.

Electron Microscopy Analysis

EPA Provisional Method--

The prepared samples are examined using a JEOL 100C analytical electron microscope. The electron microscope (EM) is used in the transmission mode to screen the sample prior to the analysis and to perform the enumeration and sizing of each fiber located in the selected grid opening(s). The scanning transmission electron microscopy (STEM) mode is used to obtain nondispersive x-ray data at a tilt angle of 40°.

[3] See Reference 3, page B-7.

Prior to analysis of the sample, it is inspected at low (500X) magnification to assure that the majority (80%) or more) of the grid openings are clear and the carbon film intact. The particle loading is also determined at this time. Any sample found overloaded, damaged, or not adequately cleared is not used in the analytical process, but is reprepared from either the original suspension or the filter, as appropriate.

The accepted preparations are immediately counted by randomly selecting a grid opening(s) and counting, sizing, and classifying each fiber found in the grid opening. The fibers are classified as chrysotile asbestos, amphibole asbestos, not asbestos, ambiguous, and no pattern based on morphology and the selected area diffraction (SAD) pattern. The SAD patterns are not recorded (except a few for documentation) or indexed. The comparison is visual and if the pattern is obviously compatible with one of the asbestos minerals, the fiber is so classified. A nondispersive x-ray pattern is often used as an aid in the classification, particularly when nonasbestos phases capable of providing false positive fiber identification are known (by PLM, XRD, or from geological sources) to be present.

Similarly, fibers whose SAD pattern characteristics differ significantly from asbestos pattern characteristics are classified as "not asbestos," and those providing no pattern* or indeterminate patterns are classified as "no pattern" or "ambiguous" fibers, respectively. These data are recorded, with the size data taken for each fiber, and is reported for each fiber observed.

The fiber enumeration and sizing is continued until approximately 100 fibers have been completed or 10 grid openings have been examined. The data are taken from two different TEM grids whenever possible.

Modified Provisional Method--

IITRI analyzed four samples using a modified Provisional Method to count the fibers. The method was modified to facilitate obtaining statistically valid counts, which in turn permits estimation of confidence limits for the analysis. The modifications are based on discussions with Dr. E. Chatfield and one of our objectives is to provide data for comparison of our results with duplicate anayses at Ontario Research Foundation (ORF).

As previously stated, the modifications affect the analysis of the sample during electron microscopy--not during preparation. The specific changes are in the loading requirement and the fiber identification criteria.

The difference in loading requirement is in the basis for selection of a grid. IITRI selects grids for analysis based on total loading of particles. We have found that this basis facilitates particle and fiber identification, although it can cause low fiber counts in samples containing asbestos at the part per million concentration level.

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* Fibers which are too close to another particle or to the edge of the grid frequently are "ambiguous."

The ORF procedure bases grid selection of a fiber loading (with, of course, an upper limit fixed by total particle loading) of, ideally, 10 asbestos fibers per grid opening. Since the objective is to obtain statistically valid counts, this procedure also calls for counting on four grids prepared from different areas of the filter. This enhances the statistical validity of the data.

It is obvious that using the higher loading requires screening many more fibers when the ORF procedure is followed; thus, the IITRI method, which involves classification of each fiber encountered, must be modified. The ORF procedure allows screening on the basis of morphology and other information known about the samples. As an example, vermiculite scrolls and plates are common nonasbestos "fibers" in vermiculite samples. However, they have much lower contrast than do amphibole fibers and prisms and are readily distinguished by an experienced analyst scanning the vermiculite samples. Thus, the nonasbestos fibers are passed over, chrysotile is identified on the basis of its unique morphology and amphibole fibers are identified by morphology and the compatibility of the fibers' SAD pattern with known amphibole patterns.

The ORF procedure results in three classifications of fibers analyzed: chrysotile, amphibole, and unidentified fibers.

Data Reduction--

The data from each procedure is reduced using similar procedures. The fiber concentration in fibers per gram is computed based on the original weight of vermiculite from which the sample was prepared. It is computed using Equation 1:

$$C_N = \frac{N_{f,i}}{n_g \cdot A_g} \frac{A_f}{W_s} \cdot \frac{V_T}{V_A} \qquad (1)$$

where C_N = Concentration, fibers per gram
$N_{f,i}$ = Number of fibers of type i counted
n_g = Number of grid openings counted
A_g = Area of one grid opening, cm^2
A_f = Area of filter from which grid was made, cm^2
W_s = Weight of sample, g
V_T = Total volume of benification fluid
V_A = Aliquot volume used for filter preparation.

IITRI and ORF used similar but different grids. Those used by IITRI were extremely uniform in opening areas and not all openings were measured. ORF used a different grid which was not as uniform and measured each grid opening that was counted.

The total mass of fibers is estimated using a right circular prism model to compute a volume, then multiplying by a density and summing over each fiber type. This calculation is shown in Equation 2. The mass concentration, f_g/g, is computed by substituting the total fiber mass estimate into Equation 1, for N_f.

$$M_f = \sum_{i=1}^{n} \frac{\pi}{4} \times d^2 \times \ell \times e \times 10^3 \qquad (2)$$

where: M_f = Estimated total fiber mass, f_g
d^2 = Fiber diameter (projected width), μm
ℓ = Fiber length, μm
e = Mineral density, g/cm^3: chrysotile = 2.6 g/cm^3
amphibole = 3.0 g/cm^3

Fiber detection limits for any sample can also be computed using Equation 1. To do this, the value of 1 is substituted for N_f, equivalent to assuming 1 fiber is detected. All detection limits reported herein are in fibers per gram.

When high fiber loadings are encountered, or when the ORF alternate procedure is used, the average fiber count per grid opening and the standard deviation (S) are determined. These values are computed using standard methods based on a normal distribution and the fiber count data are then given with 95% confidence limits.

Airborne Fiber Analysis--

The enumeration and measurement of airborne fibers is accomplished using two well-defined and established techniques. The first is the NIOSH specified phase contrast fiber enumeration by optical microscopy. The procedures are described in detail in DHEW (NIOSH) Publication No. 79-127. The second analytical method is the U.S. EPA's Provisional Methodology, described in EPA-600/2-77-178, revised June 1978. The NIOSH procedure is summarized below, since it was used for analyses on this program; the EPA electron microscope procedures are identical to the procedure described as Sample Preparation and Electron Microscopy Analysis (EPA Provisional Method) in the bulk sample procedures.

Sample Preparation

Samples to be submitted for phase contrast enumeration are collected on cellulose acetate (Millipore® or equivalent) filters using an open face filter holder. The sample is prepared for enumeration using one of two techniques--dissolving the filter in a solution of dimethyl phthalate and diethyl oxalate containing clean, dissolved membrane for viscosity control[4] or by collapsing the membrane pore structure using a solution of hexane/1,2-dichloroethane/p-dioxane and rendering the collapsed membrane transparent by exposure to acetone vapors.[5] Both techniques end by covering the sample with a cover slip, with the latter technique requiring a 1.505 refractive index oil. IITRI uses the second procedure because it provides a permanent mount with no restrictions on the count-time frame. This preparation procedure is routinely used by IITRI for proficiency analytical testing (PAT) fiber enumeration.

[4] Contained in P&CAM 239, recommended by NIOSH.
[5] Millipore® Procedure, TS018.

Fiber Enumeration

The fibers on the filter are enumerated using the following protocol. A Porton Graticule is used to define counting areas. A minimum of 20 areas and a maximum of 100 areas are counted. After 20 areas have been counted, the enumeration of fibers is topped when 100 fibers have been enumerated. Fibers are enumerated using the following rules:

- Fiber is entirely within counting area
  Count--1 fiber if length > 5 μm

- Fiber has one end in counting area
  Count--1/2 fiber if length > 5 μm

- Fiber crosses two sides of counting area
  Count--no fiber

- Fiber does not enter counting area
  Count--no fiber

Note: All fibers--defined as particles having parallel sides, length to diameter ratio ≥ 3 and length > 5 μm--are enumerated by the NIOSH procedure. Thus, if the probability is high that nonasbestos fibers are present, the NIOSH procedure can overstate the actual asbestos fiber concentration. The reason for the possible over statement is the fact that phase contrast illumination does not allow the analyst to identify the individual fibers.

The fiber count data are converted to airborne fiber concentration using Equation 3:

$$F_c = \frac{f_c A_f}{a_c V_s} \qquad (3)$$

where: F_c = Airborne fiber concentration, fibers/cc
f_c = Number of fibers enumerated
a_c = Total counting area, cm^2
A_f = Area of filter used for sample collection, cm^2
V_s = Volume of air sampled, cc

APPENDIX C

AIR SAMPLES FLOW RATES AND SAMPLE VOLUMES

The Dupont Model 4000 personal air samplers were calibrated before and after each day of sampling. The calibration was done with a 500-ml soap bubble meter and a stop watch. The sampler calibration values are given in Table C-1.

The data for the volume calculation for the various personal air samples are given in Table C-2.

The flow rates for the stationary samplers were measured at the beginning of sampling, periodically during sampling and at the end of sampling. The data for the stationary samplers are given in Table C-3.

TABLE C-1. PERSONAL SAMPLER CALIBRATIONS (EACH VALUE REPRESENTS A MINIMUM OF THREE DETERMINATIONS)

Sampler ID	Grace, Libby Montana		Enoree, North Carolina								
			Grace Mill			Grace Mine			Patterson		
	Pre-sampling[a]	Post-sampling	Pre-sampling	Post-sampling	Avg[a]	Pre-sampling	Post-sampling	Avg[a]	Pre-sampling	Post-sampling	Avg[a]
186172	2.13	1.91	2.02	2.07	2.04						
186173	2.12	1.92	1.96	1.94	1.95						
186174	2.09	1.96	1.99	2.00	2.00						
186175	2.12	1.93	1.98	2.01	2.00						
1-7328	2.07	1.89	2.02	2.04	2.03	1.94	1.99	1.97			
2-7334	2.16	2.13	2.00	2.04	2.02	1.98	1.92	1.95	1.94	1.93	1.93
6-7329	2.12	1.99	2.02	2.07	2.04	1.95	2.00	1.98	1.95	1.94	1.94
7-7317	2.19	1.99	2.01	2.00	2.01				1.93	1.93	1.93

a Values used to calculate sample volume.

TABLE C-2. DATA FOR VOLUME CALCULATIONS FOR PERSONAL SAMPLES

Sample no.	Sampler ID	Flow (ℓ/min)	Time sampled (min)	Volume (ℓ)
101	1-7328	2.07	186	385
121	186173	2.12	429	909
125	7-7317	2.19	264	578
126	186175	2.12	278	589
128	2-7334	2.16	266	575
129	186172	2.13	270	575
130	7-7317	2.19	130	285
131	186174	2.09	145	303
135	186174	2.09	283	591
138	186172	2.13	138	294
139	2-7334	2.16	125	270
141	6-7329	2.12	130	276
146	6-7329	2.12	261	555
148	186175	2.12	140	297
300	2-7334	2.02	175	354
301	6-7329	1.98	121	240
304(S)[a]	186174	2.00	438	876
305	186172	2.04	141	288
306	6-7329	1.98	362	717
308	7-7317	2.01	203	408
310	2-7334	1.95	132	257
314	186173	1.95	146	285
315	1-7328	1.97	127	250
320	2-7334	1.95	280	546
321	7-7317	2.01	238	478
322	186173	1.95	241	470
324	1-7328	1.97	31	61
330	1-7328	2.03	141	285
322(S)[a]	2-7334	2.02	202	408
336	6-7329	2.04	205	418
337	186175	2.00	246	492
339	186172	2.04	302	616
340	6-7329	2.04	181	369
341(S)[a]	2-7334	2.02	79	160
347	186175	2.00	157	314
349	1-7328	2.03	251	507

(continued)

TABLE C-2 continued

Sample no.	Sampler ID	Flow (ℓ/min)	Time sampled (min)	Volume (ℓ)
504	2-7334	1.93	185	357
508	7-7317	1.93	132	255
511	6-7329	1.94	194	376
516	7-7317	1.93	188	363
517	2-7334	1.93	192	371
519	7-7371	1.93	177	342
520	6-7329	1.94	130	252
521	6-7329	1.94	184	357
542	2-7334	1.93	129	249

a 304(S), 332(S), and 341(S) were stationary samples.

TABLE C-3. VOLUME CALCULATIONS FOR STATIONARY SAMPLES

Sample no.	Average flow (ℓ/min)	Time sampled (min)	Volume (ℓ)
102	0.97	270	261
103	1.04	182	189
104	2.19	178	390
107	1.90	109	207
108	1.16	146	169
111	2.08	177	368
112	2.05	301	616
113	1.39	143	199
115	0.79	321	253
116	0.90	174	156
119	1.00	128	128
120	2.20	299	658
122	2.36	179	422
123	1.47	166	244
124	0.88	343	302
132	0.96	362	348
134	1.94	404	784
136	0.97	114	111
145	1.09	386	421
147	1.41	387	545
149	1.14	369	420
302	0.74	321	239
307	1.31	222	291
309	1.04	321	334
313	1.81	329	595
316	1.85	314	582
318	1.18	320	378
323	1.54	100	154
328	2.37	121	287
329	2.13	387	823
331	1.52	128	195
334	1.08	124	134
335	0.85	94	80
338	1.94	136	264
342	1.58	327	516
343	2.36	328	774
344	1.05	84	88
345	1.77	122	216
350	0.87	331	288
351	1.26	332	420
352	1.45	352	511
353	1.96	322	632
354	1.59	324	515

(continued)

TABLE C-3 continued

Sample no.	Average flow (ℓ/min)	Time sampled (min)	Volume (ℓ)
502	1.67	351	585
503	1.46	144	210
506	2.23	123	274
513	1.30	145	188
515	1.70	175	299
518	1.76	342	601
523	1.72	348	599
525	2.19	342	748
527	2.13	345	735
528	1.02	144	147
531	2.08	144	300
540	2.04	343	701

APPENDIX D

INCREMENT BULK SAMPLES COLLECTED AND COMPOSITED

Most of the samples submitted for anaysis were composites of increment samples. To prepare the composite samples each increment sample was riffled to obtain a representative fraction of the increment. Approximately equal weight fractions of each increment fraction were combined to make a composite sample. The composite sample was then mixed and riffled to produce four equal samples. One of the fourths was set aside and retained as a control. One of the fourths was again riffled to produce two-eights of the original composite. The two-eighths were combined with the two-fourths so that the composite was divided into 1/4, 3/8, and 3/8 of the original. The "1/4" was retained at MRI: one "3/8" was sent to IITRI; the other "3/8" was sent to Ontario (ORF) for analysis.

Each of the increment samples was assigned a sample ID number. Tables D-1, D-2, and D-3 lists the increment samples from the three collection locations that were processed into composites. Table D-4 lists the samples that were not processed.

TABLE D-1. INCREMENT AND COMPOSITE SAMPLES FROM LIBBY, MT, GRACE

Sample description	Date collected	Sample ID	Sample weight (g)	Weight for composite (g)
Grade 1	10/7/80	151	1,030	126
Grade 1	10/8/80	152	1,002	125
Grade 1	10/9/80	153	1,002	126
Grade 1	10/10/80	154	1,000	125
Grade 1	10/13/80	155	1,001	125
Grade 1	10/14/80	156	999	125
Grade 1	10/15/80	157	1,002	125
Grade 1	10/16/80	158	1,009	125
Grade 1	10/17/80	159	1,000	125
Grade 1	10/21/80	160	798	125
Grade 1	10/23/80	161	991	125
Grade 1	Composite	270		
Grade 2	10/7/80	162	1,001	125
Grade 2	10/8/80	163	1,006	125
Grade 2	10/9/80	164	1,004	125
Grade 2	10/10/80	165	1,004	125
Grade 2	10/13/80	166	1,004	125
Grade 2	10/14/80	167	1,002	125
Grade 2	10/15/80	168	956	125
Grade 2	10/16/80	169	1,002	125
Grade 2	10/17/80	170	1,002	125
Grade 2	10/21/80	171	873	125
Grade 2	10/23/80	172	992	125
Grade 2	Composite	276		
Grade 3	10/7/80	173	999	133
Grade 3	10/8/80	174	1,002	113
Grade 3	10/9/80	175	1,002	121
Grade 3	10/10/80	176	1,002	122
Grade 3	10/13/80	177	1,003	127
Grade 3	10/14/80	178	997	124
Grade 3	10/15/80	179	1,003	129
Grade 3	10/16/80	180	1,000	124
Grade 3	10/17/80	181	997	124
Grade 3	10/21/80	182	1,000	124
Grade 3	10/23/80	183	964	125
Grade 3	Composite	259		

(continued)

TABLE D-1 continued

Sample description	Date collected	Sample ID	Sample weight (g)	Weight for composite (g)
Grade 4	10/7/80	184	1,000	125
Grade 4	10/8/80	185	1,004	125
Grade 4	10/9/80	186	997	125
Grade 4	10/10/80	187	1,002	125
Grade 4	10/13/80	188	1,001	125
Grade 4	10/14/80	189	1,000	125
Grade 4	10/15/80	190	1,000	125
Grade 4	10/16/80	191	1,022	125
Grade 4	10/17/80	192	1,000	125
Grade 4	10/21/80	193	999	125
Grade 4	10/23/80	194	1,002	125
Grade 4	Composite	282		
Grade 5	10/7/80	195	1,000	125
Grade 5	10/8/80	196	1,001	125
Grade 5	10/9/80	197	1,005	124
Grade 5	10/10/80	198	999	125
Grade 5	10/13/80	199	998	129
Grade 5	10/14/80	200	1,000	129
Grade 5	10/15/80	201	1,000	124
Grade 5	10/16/80	202	1,000	126
Grade 5	10/71/80	203	997	124
Grade 5	10/21/80	204	995	126
Grade 5	10/23/80	205	1,000	125
Grade 5	Composite	264		
Head feed[a]	10/8/80	223	958	125
Head feed[a]	10/9/80	224	965	125
Head feed[a]	10/10/80	225	955	125
Head feed[a]	10/13/80	226	951	125
Head feed[a]	10/14/80	227	953	125
Head feed[a]	10/15/80	228	947	125
Head feed[a]	10/16/80	229	949	125
Head feed[a]	10/17/80	230	950	125
Head feed[a]	10/23/80	231	1,000	125
Head feed[a]	Composite	291		

(continued)

TABLE D-1 continued

Sample description	Date collected	Sample ID	Sample weight (g)	Weight for composite (g)
Extractor	10/8/80	250	870	125
Extractor	10/9/80	251	860	125
Extractor	10/10/80	252	852	125
Extractor	10/13/80	253	860	125
Extractor	10/14/80	254	860	125
Extractor	10/15/80	255	893	125
Extractor	10/16/80	256	887	125
Extractor	10/17/80	257	890	125
Extractor	Composite	294		
Dust, screening plant	10/8/80	206	1,008	125
Dust, screening plant	10/9/80	207	1,000	125
Dust, screening plant	10/10/80	208	998	125
Dust, screening plant	10/13/80	209	1,230	125
Dust, screening plant	10/14/80	210	996	125
Dust, screening plant	10/15/80	211	965	125
Dust, screening plant	10/17/80	212	980	125
Dust, screening plant	Composite	288		
Dust, mill baghouse	10/8/80	215	1,006	125
Dust, mill baghouse	10/9/80	216	998	125
Dust, mill baghouse	10/10/80	217	1,003	125
Dust, mill baghouse	10/13/80	214	1,009	125
Dust, mill baghouse	10/14/80	218	977	125
Dust, mill baghouse	10/15/80	219	989	125
Dust, mill baghouse	10/16/80	220	1,002	125
Dust, mill baghouse	10/17/80	221	1,004	125
Dust, mill baghouse	Composite	297		

a All "head feed" samples contained rocks too large to pass through the channels in the riffle box. These were separated out, weighed separately, and retained at MRI.

TABLE D-2. INCREMENT AND COMPOSITE SAMPLES FROM ENOREE, SC, GRACE

Sample description	Date collected	Sample ID	Sample weight (g)	Weight for composite (g)
Grade 3	10/27/80	389	1,538	120
Grade 3	10/28/80	390	2,584	120
Grade 3	10/29/80	391	2,445	125
Grade 3	10/30/80	392	1,900	125
Grade 3	10/31/80	393	2,584	125
Grade 3	11/1/80	394	2,682	125
Grade 3	11/2/80	395	2,788	126
Grade 3	Composite	430		
Grade 4	10/27/80	396	1,490	125
Grade 4	10/28/80	397	2,450	125
Grade 4	10/29/80	398	2,380	125
Grade 4	10/30/80	399	2,390	125
Grade 4	10/31/80	400	2,715	125
Grade 4	11/1/80	401	2,610	125
Grade 4	11/2/80	402	3,005	125
Grade 4	Composite	433		
Grade 5	10/27/80	403	1,729	123
Grade 5	10/28/80	404	2,459	126
Grade 5	10/29/80	405	2,590	119
Grade 5	10/30/80	406	2,185	125
Grade 5	10/31/80	407	2,700	125
Grade 5	11/1/80	408	2,490	125
Grade 5	11/2/80	409	2,770	129
Grade 5	Composite	427		
Mill feed + 100 mesh	10/27/80	375	451	225
Mill feed + 100 mesh	10/28/80	378	881	225
Mill feed + 100 mesh	10/29/80	379	776	225
Mill feed + 100 mesh	10/30/80	381	709	225
Mill feed + 100 mesh	10/31/80	384	958	225
Mill feed + 100 mesh	11/1/80	386	836	225
Mill feed + 100 mesh	11/2/80	388	792	225
Mill feed + 100 mesh	Composite	436		
Grade 3 exfoliated	11/5/80	424	203	
Analysis ID		439		
Grade 4 exfoliated	11/5/80	422	260	
Analysis ID		442		

TABLE D-3. INCREMENT AND COMPOSITE SAMPLES FROM ENOREE, SC, PATTERSON

Sample description	Date[a] collected	Sample ID	Sample weight (g)	Weight for composite (g)
Ungraded	11/6/80	567	1,770	250
Ungraded	11/6/80	568	1,700	250
Ungraded	11/6/80	569	1,186	250
Ungraded	11/6/80	570	1,780	250
Ungraded	Composite	573		

a Increments taken at 2 hr intervals.

TABLE D-4. BULK SAMPLES THAT WERE COLLECTED BUT NOT SUBMITTED FOR ANALYSIS

Sample description	Number of increments
Grace, Libby, under 90 mesh	9
Grace, Libby, coarse tails	9
Grace, SC, mill feed, under 100 mesh	7
Grace, SC, dryer composite	7
Grace, SC, wet scrubber discharge	1
Grace, SC, composite total tails	1
Grace, SC, Lanford mine composite	1
Grace, SC, Foster mine composite	1
Grace, SC, No. 4 concrete aggregate, stabilized	1
Grace, SC, No. 3 masonry insulation	1
Patterson, SC, raw ore prescreen	1
Patterson, SC, raw ore postscreen	3
Patterson, SC, raw ore multiple grab from main ore pile	1
Patterson, SC, main waste pile	4
Patterson, SC, preexfoliated waste	4
Patterson, SC, bagged product	4

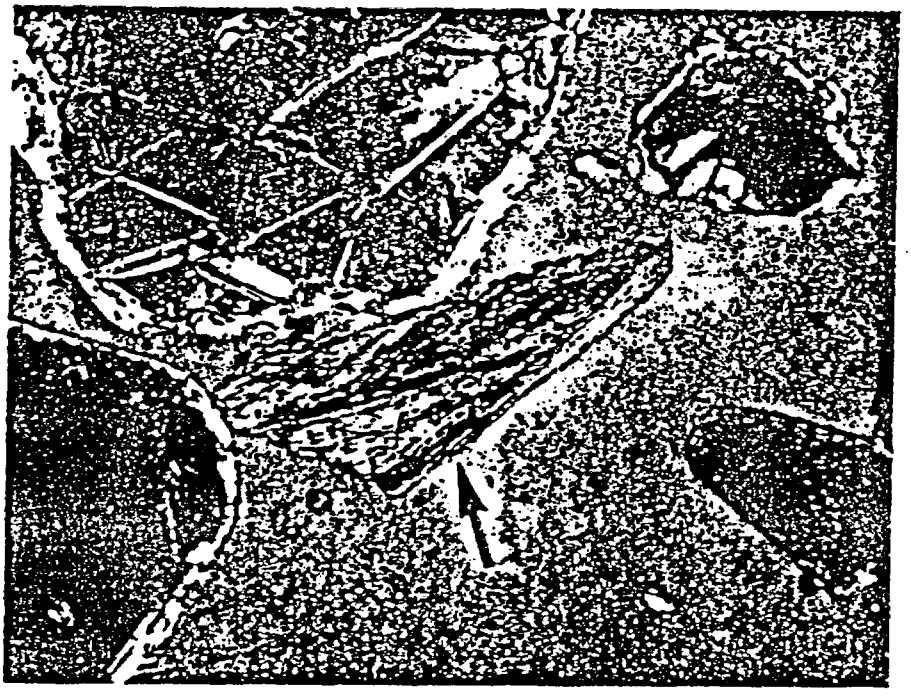
APPENDIX E

PHOTOMICROGRAPHS AND TEM MICROGRAPHS OF SELECTED SAMPLES

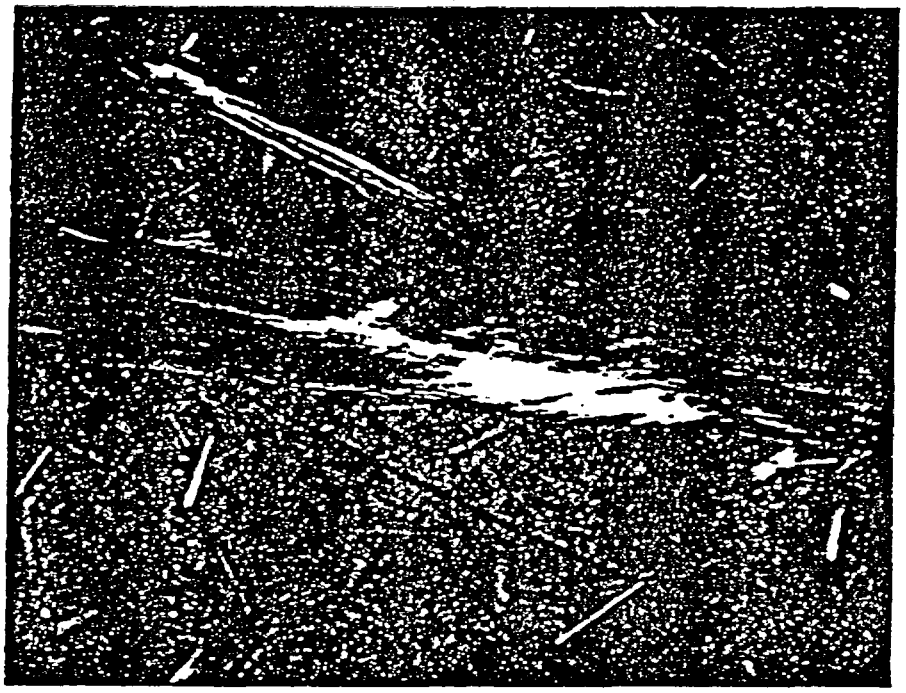
1. Photomicrographs (IITRI) (p. E-2 to E-17) of selected samples. All photomicrographs were taken with slightly uncrossed polars unless otherwise indicated.

2. TEM micrographs (ORF) (p. E-18 to E-25) of selected samples to illustrate the types of particles observed in samples of vermiculite from the various locations represented in this study. It should be noted that these micrographs were taken using specimen grids prepared for illustration purposes only and the particle loadings are considerably heavier than those required for TEM evaluation.

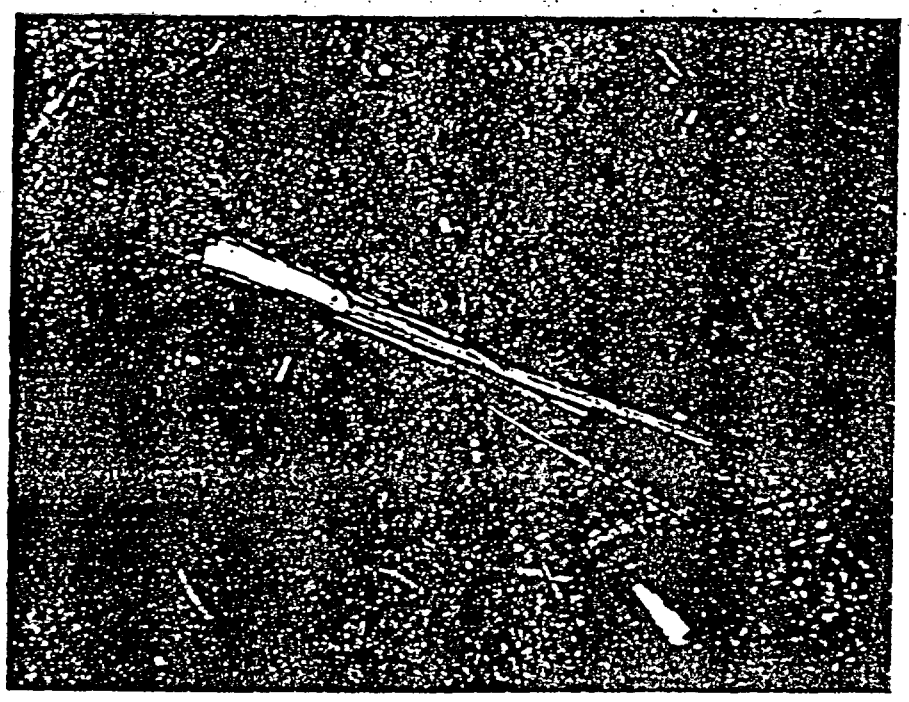
259-I-TBS; 52X. Unevenly fractured fragments of dark green diopside and augite.



259-I-2.76 float; 84X. Large flakey particles are vermiculite with white stress lines. Arrow points to a flake of talc intergrown with tremolite-actinolite fibers.



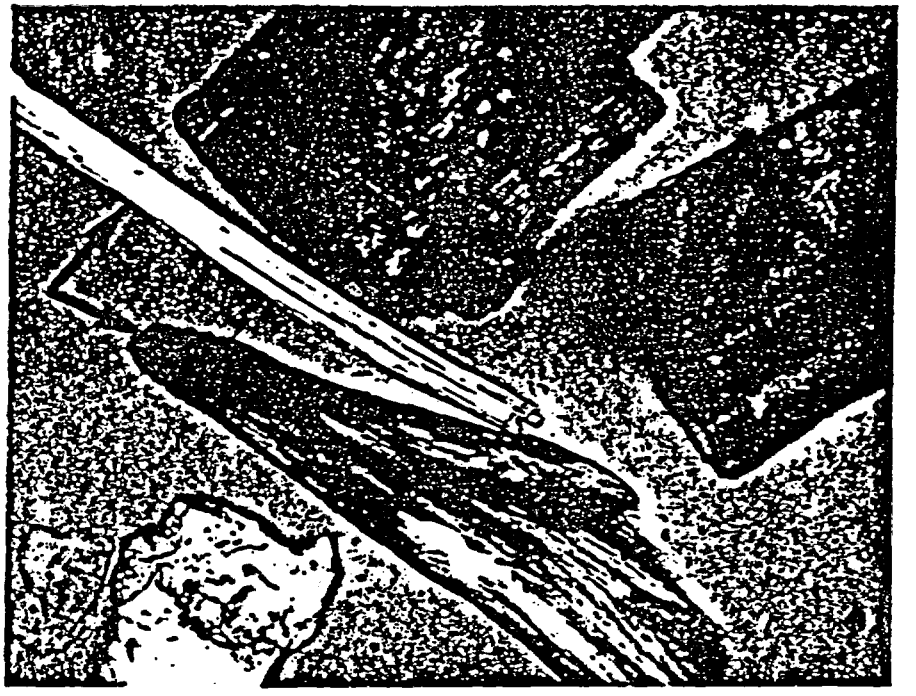
259-I-TBS-Fibers (ground); 208X. Large bundle in the center is unquestionably fibrous tremolite-actinolite. Note the (white) interference colors of fibers growing at angles to the main fiber bundle which has been rotated to an extinction position (and is therefore gray).



259-I-TBS-Fibers (ground); 208x. This parallel-lamellated prism morphology of tremolite-actinolite was found within hand-picked fiber bundles.

259-I-2.76 sink; 208X. Calcite (bright white) growing in a pseudomorphically fibrous crystal habit within tremolite-actinolite fiber bundles. Some calcite crystals (arrows) could be fractured to yield "fibers".

259-I-2.76 float; 84X. Arrow points to a flake of lamellated quartz. The flakey, lamellated morphology was caused by the quartz forming inbetween vermiculite plates.

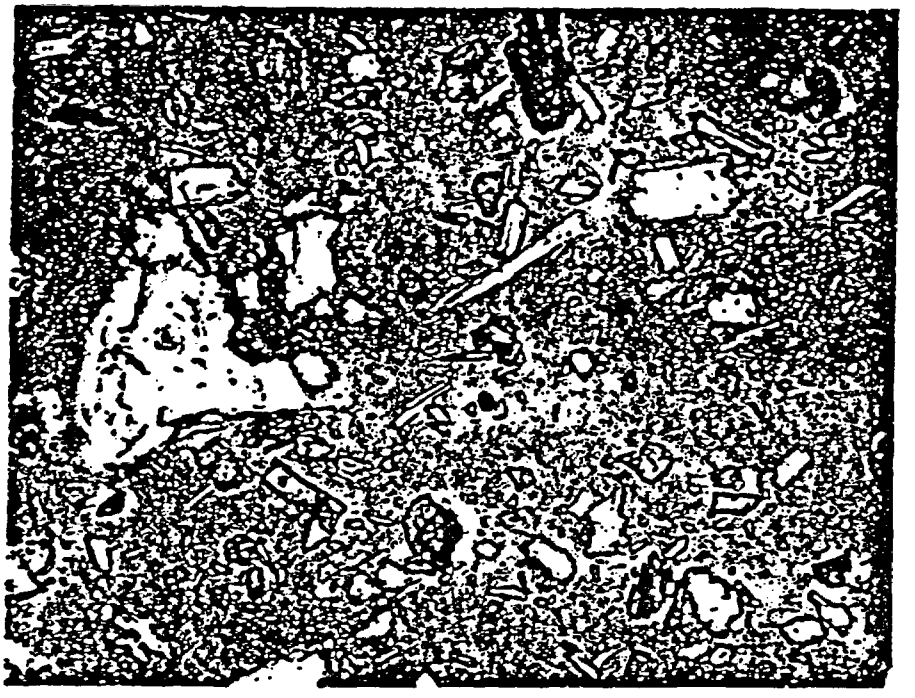


264-I-TBS; 208X. Arrows point to tremolite-actinolite in two different crystal habits--the parallel, lamellated prisms and truly fibrous material. The mottled coloring of the fiber bundle is due to the various angles at which the individual fibers are intergrowing with each other.

264-I-TBS; 208X. The circle outlines one tremolite-actinolite particle which contains 2 different crystal habits--the parallel, lamellated prisms on one end and matted, intergrown fibers (white portion) on the other end.

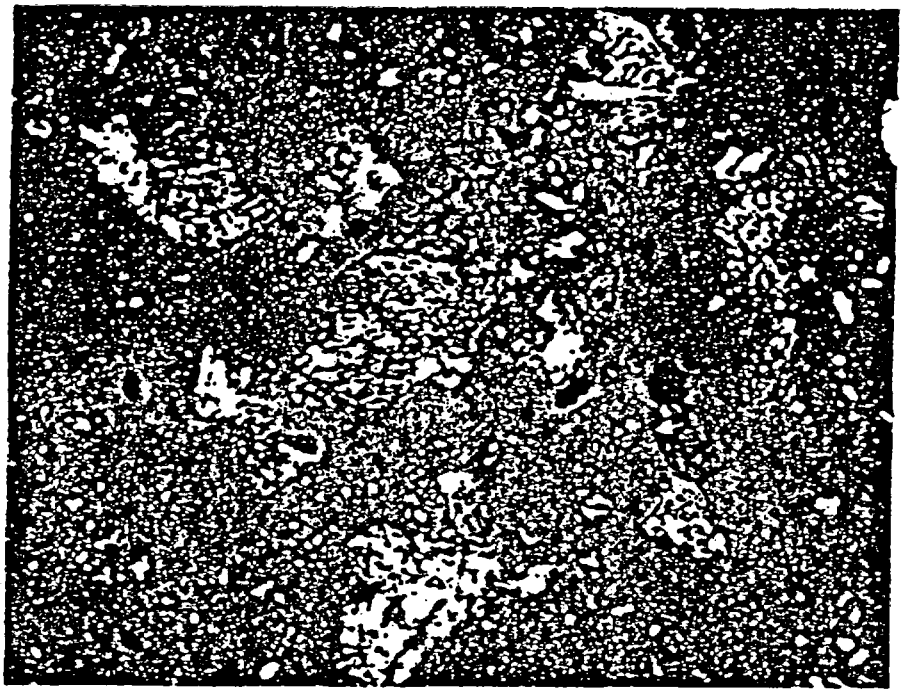
264-I; 84X. The large elongated particle in the center is fibrous tremolite-actinolite with inclusions(arrows) of prismatic tremolite-actinolite. The large flakey white particle (arrow) is a sheet of quartz adhering to vermiculite and was apparently growing inbetween vermiculite plates.

291-I; 84X. The friability of the tremolite-actinolite fiber bundles is demonstrated here. Simple dispersion of the sample resulted in abrasion of numerous smaller fiber bundles from the large bundles present.



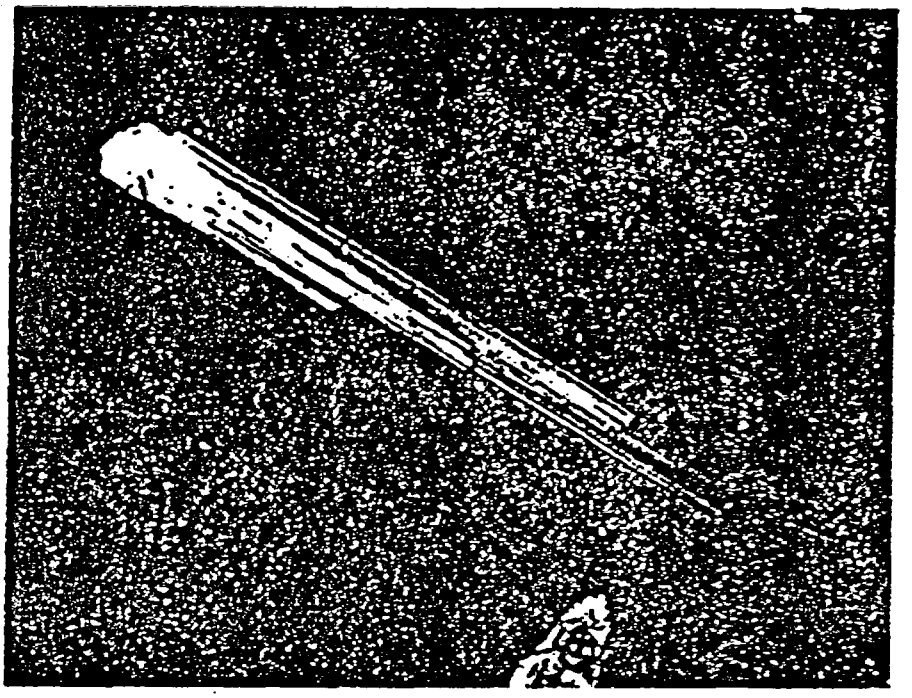
430-I-TBS (minimal grinding); 208X. The tremolite-actinolite, hornblende and anthophyllite amphibole fragments are mostly irregular to chunky prisms. Some slender prisms which could yield particles classifiable as fibers are present.

430-I-2.76 sink (after grinding); 208X. Most of the prismatic to near fibrous amphibole separated into this density fraction because it was so intimately intergrown with vermiculite and talc.

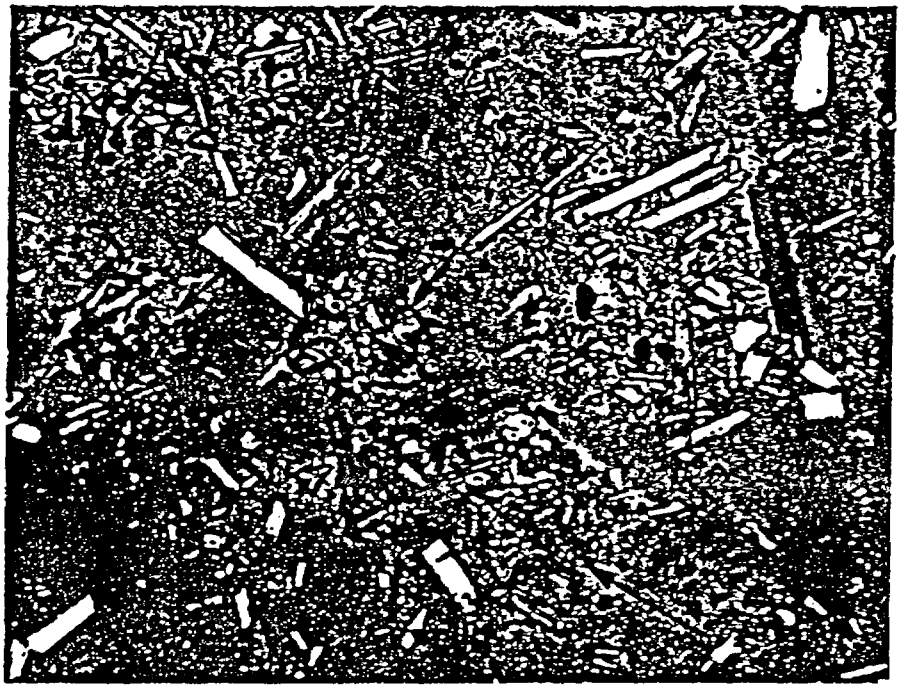


430-I-2.76 float (ground); 208x. Although optical and morphological properties of the mottled phase depicted were consistent with serpentine minerals XRD data ruled out serpentine as its identity. Mixed layer vermiculite-hydrobiotite was identified in the XRD work.

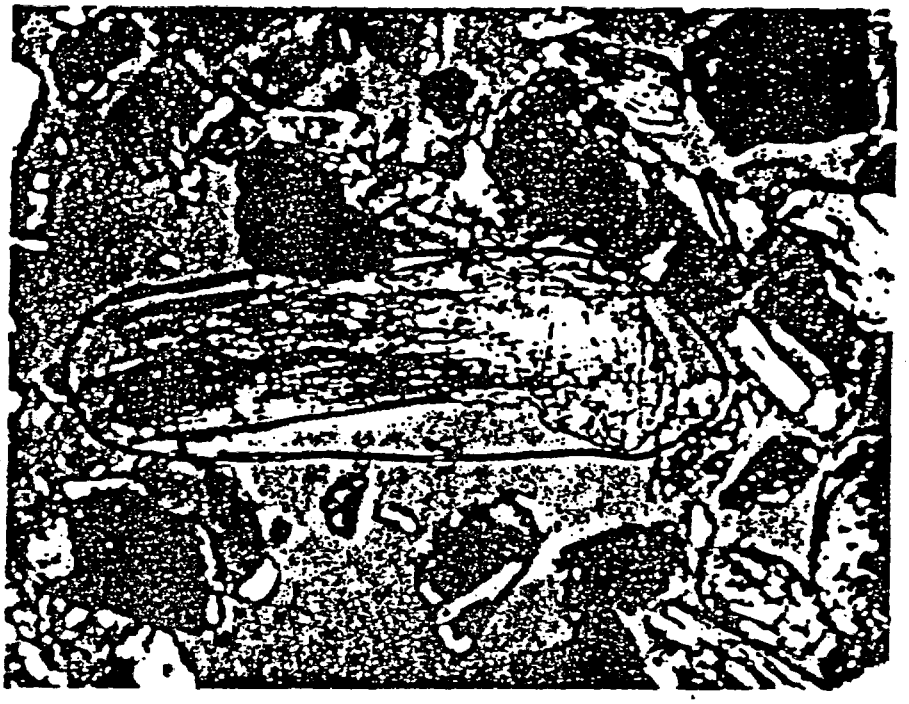
427-I-TBS; 84X. Several large lamellated, parallel prisms of tremolite-actinolite and anthophyllite are visible.



427-I-TBS (ground); 208X. Crushing of the large amphibole prisms produced prisms with splinter fragments that could morphologically be defined as fibers.

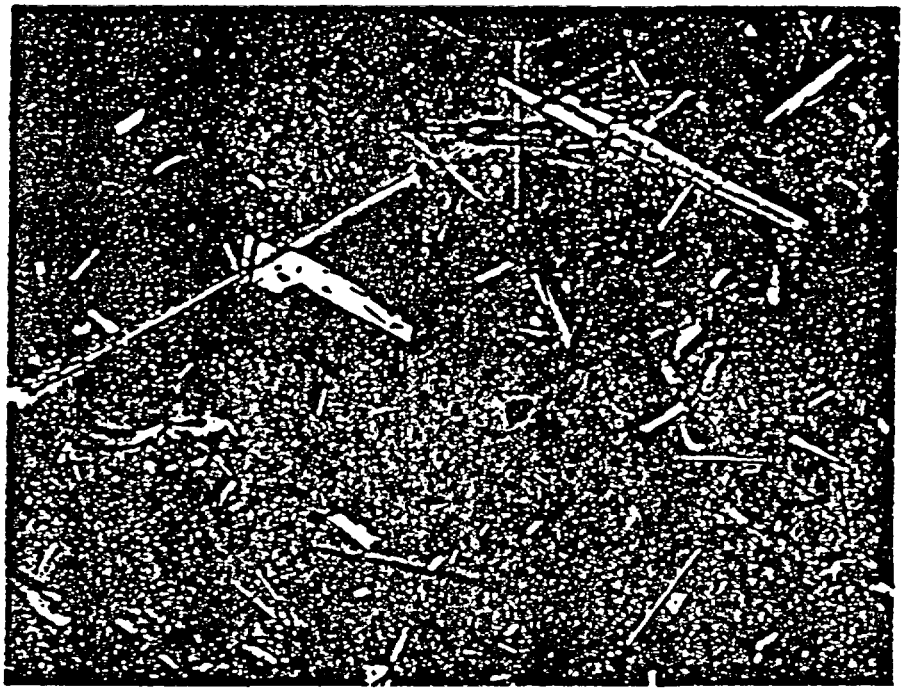


427-I-TBS-Fibers (ground); 208X. Crushing of coarse "fibers" produced mostly prismatic material. Arrows point to the numerous vermiculite and talc plates intergrown within "fiber" bundles.

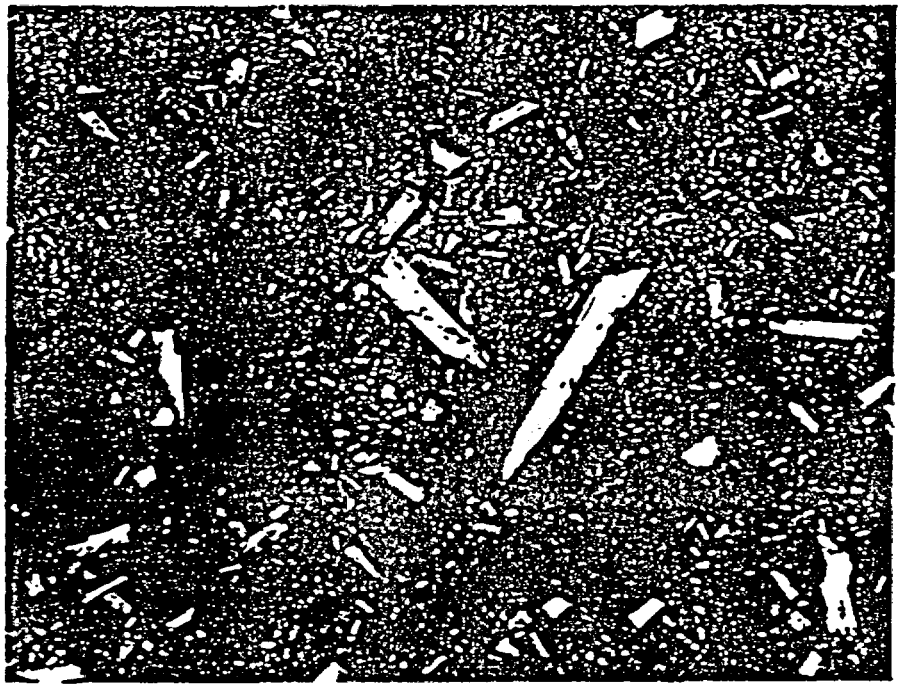


427-I-2.76 sink; 208X. The white portion of the circled particle is talc. The remainder is (lamellated) prismatic anthophyllite. Numerous flakes of talc intergrown with anthophyllite were found in this fraction.

436-I; 82X. The amphiboles are mostly chunky and prismatic in this sample. Arrow points to tremolite composed of rather thick, lamellated prisms.

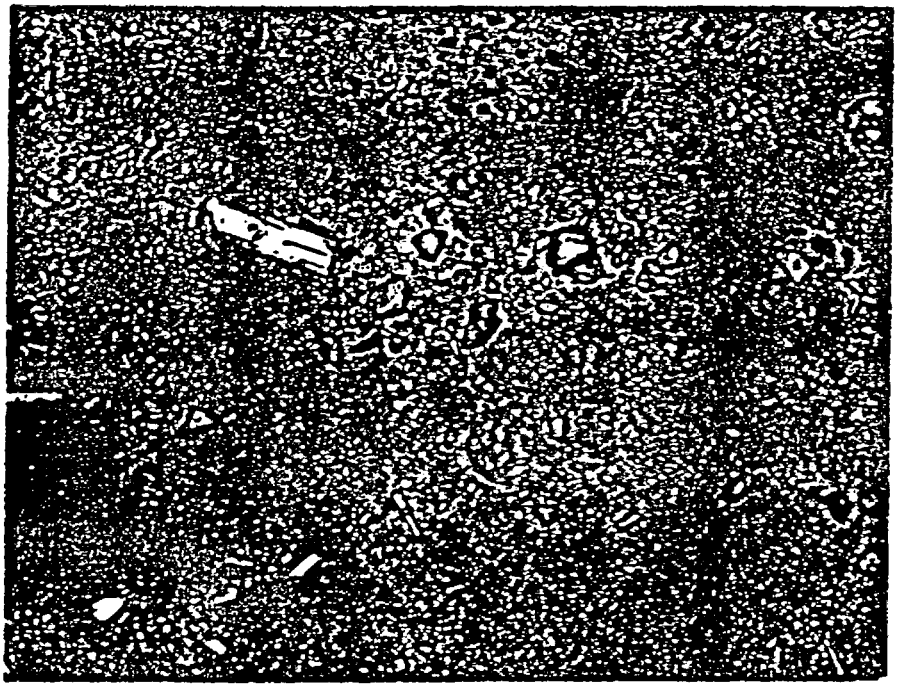


436-I-Fibers (ground); 208X. Truly fibrous amphibole as well as very chunky, prismatic particles were produced when particles macroscopically classifiable as fiber bundles were ground.



436-I-TBS-green, glassy (ground); 208X. This phase was a mixture of hornblende and tremolite-actinolite. The amphiboles' morphologies were predominantly chunky prisms.

436-I-TBS-milky green (ground); 208X. Mineral grains composed of this tremolite-hornblend mixture were irregular in shape and rough. Appearances of crushed fragments indicated that the grains were composed of agglomerated smaller crystals which themselves were irregularly grown.

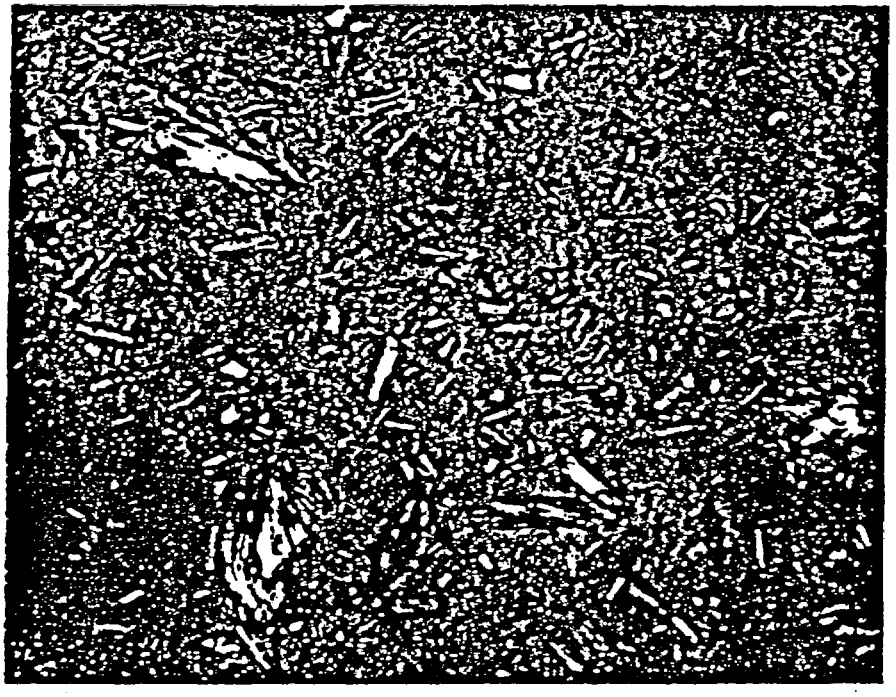


436-I-TBS-colorless, glassy (ground); 208X. The predominant material is fluorapatite--high contrast, conchoidally fractured particles.

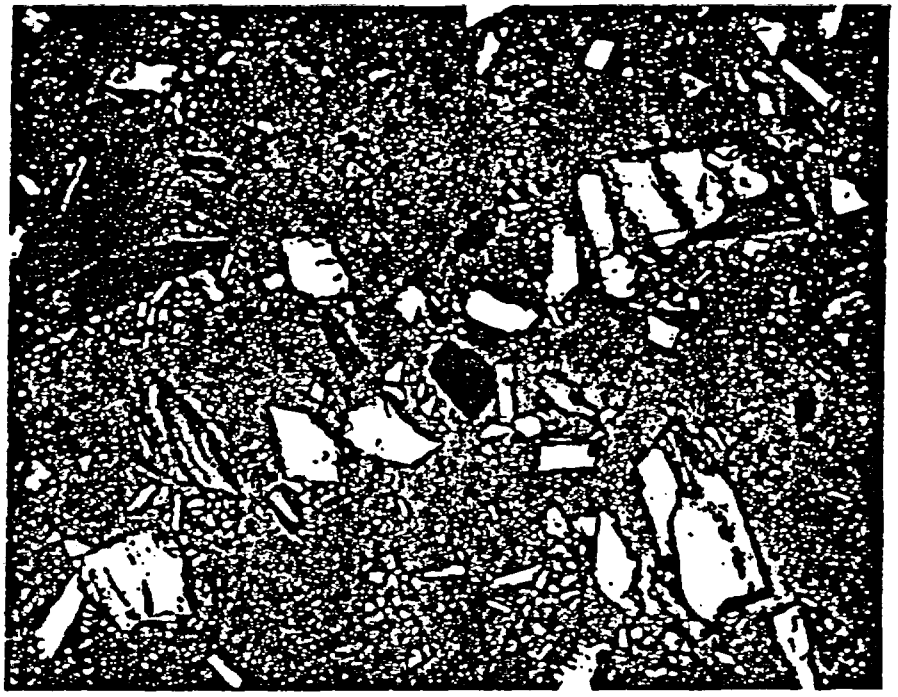
573-I-TBS; 82X. Non-vermiculite phases were mostly chunky, prismatic amphiboles, iron oxides (black) and fluorapatite (rounded, gray particles).

573-I-TBS (ground); 208X. Grinding did result in fracture of some amphibole grains into elongated fragments morphologically classifiable as fibers. Most of the amphibole fragments retained chunky, prismatic morphologies.

267-I-TBS; 82X. Fibrous and prismatic amphiboles (arrows) are present with diopside.

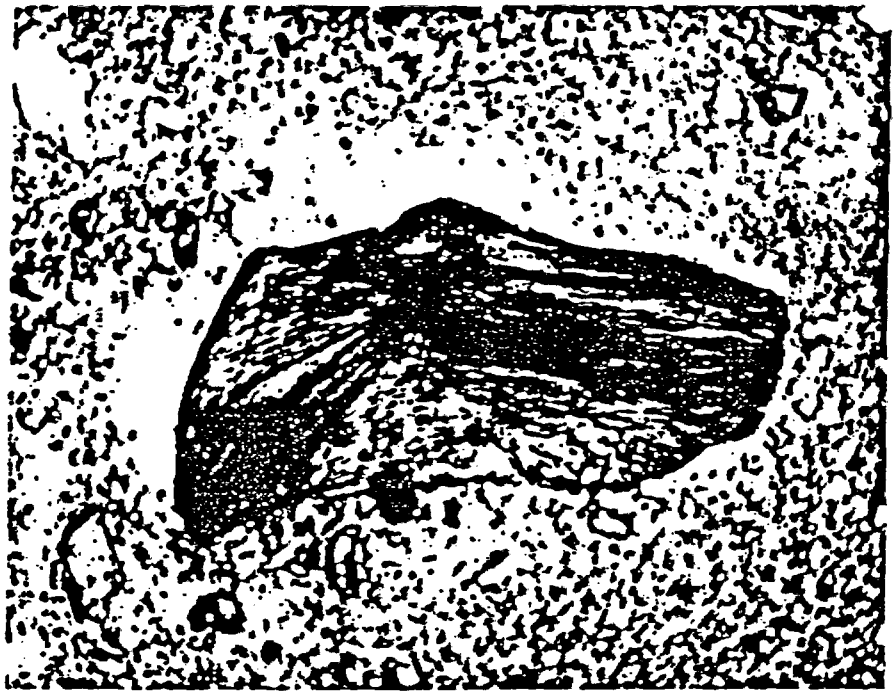


276-I-TBS-milky green (ground); 208X. Like the milky green mineral grains of 436-I, the milky green grains of this sample were composed of multiple, poorly formed amphibole crystals. Unlike the 436-I sample, the individual crystals in this sample exhibited mostly fibrous morphologies.

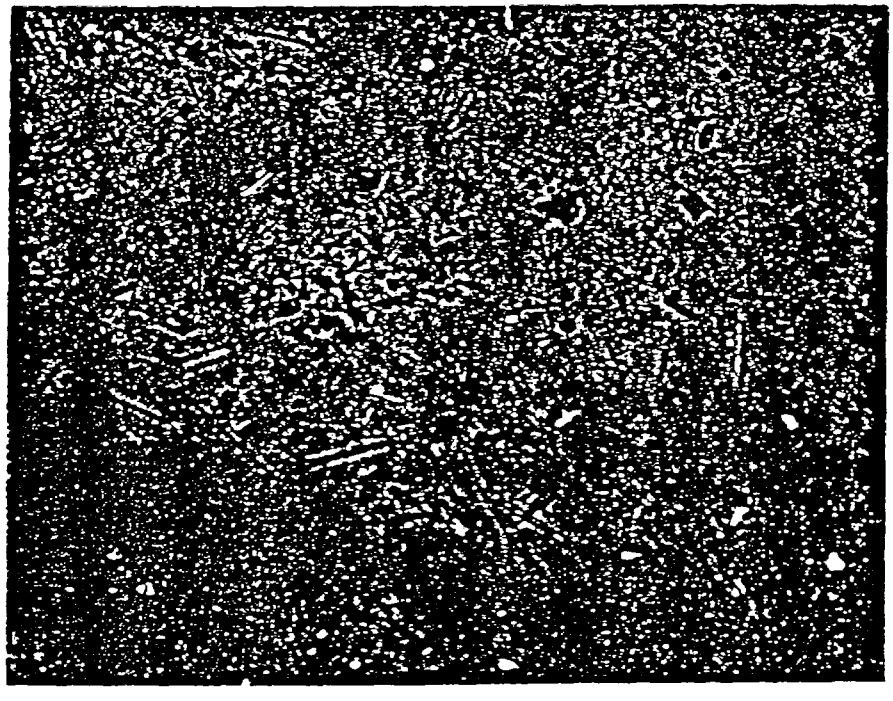


276-I-TBS-dark green glassy (ground); 208X. The pyroxene, diopside, exhibits some conchoidal as well as prismatic fracture patterns.

294-I-TBS; 82X. Small amphibole fiber bundles and large amphibole prisms are present. Note the layered crystal growth of the fractured tremolite-actinolite fragment (arrow).



288-I; 52X. The mottled coloring of this large tremolite-actinolite fiber bundle is due to the non-parallel, radiating growith pattern of the individual fibers in the bundle.



288-I (fines); 208X. Much abrasion and disintegration of large fiber bundles has obviously occurred in the processing of the vermiculite, as indicated by the numerous very fine fibers present.

297-I; 208X. The fine, single fibers here were abraded from larger tremolite-actinolite fiber bundles.

Transmission electron micrograph showing typical particulate matter found in water suspension after laboratory exfoliation of Sample 264-0, Grace, Libby, Montana, Grade 5 (composite).

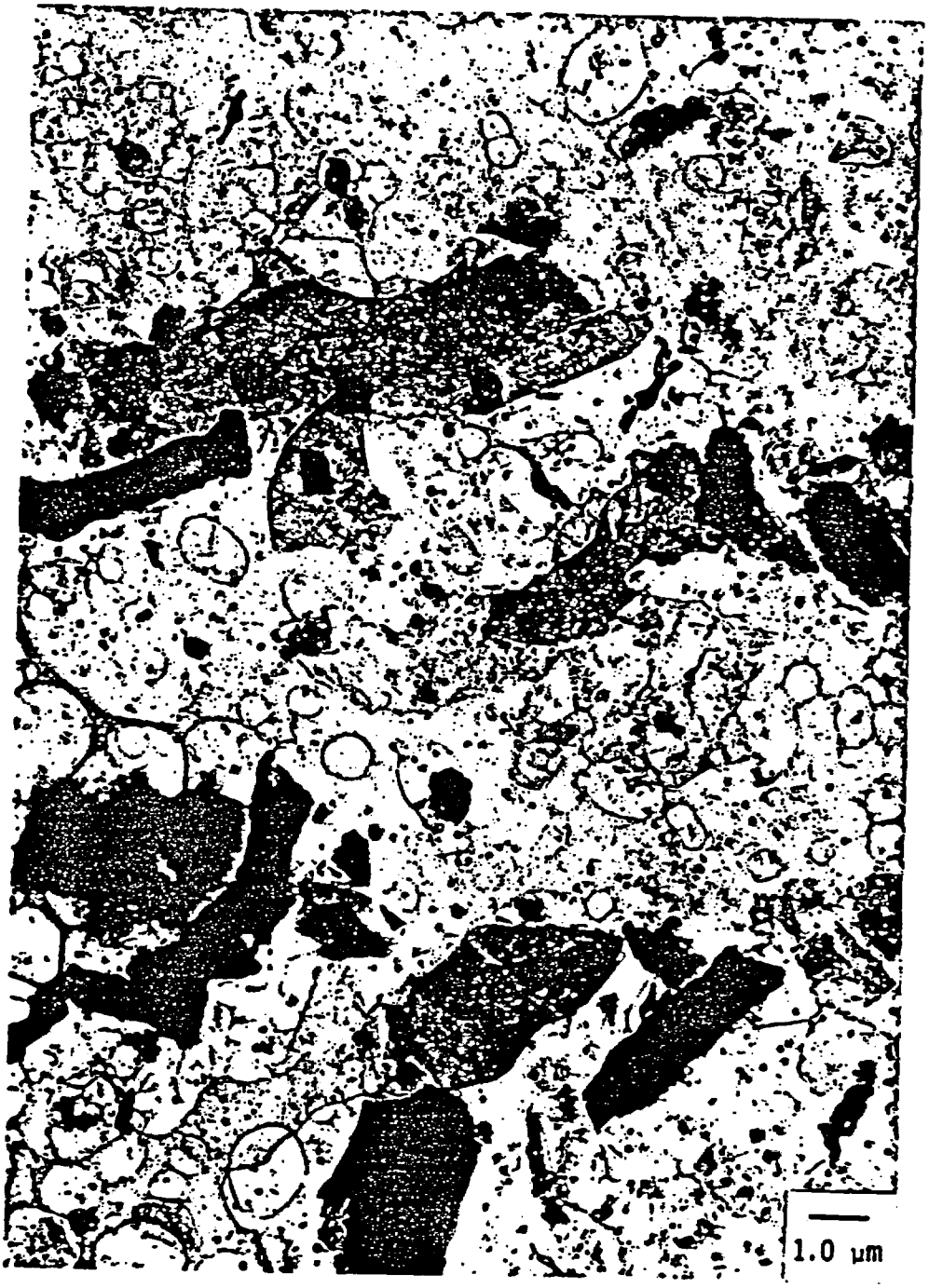
Transmission electron micrograph showing typical particulate matter found in water suspension after laboratory exfoliation of Sample 264-O, Grace, Libby, Montana, Grade 5 (composite).

Transmission electron micrograph showing typical particulate matter found in water suspension after laboratory exfoliation of Sample 264-0, Grace, Libby, Montana, Grade 5 (composite).

Transmission electron micrograph showing typical particulate matter found in water suspension after laboratory exfoliation of Sample 427-O, Grace, Enoree, South Carolina, Grade 5 (composite).

Transmission electron micrograph showing typical particulate matter found in water suspension after laboratory exfoliation of Sample 427-O, Grace, Enoree, South Carolina, Grade 5 (composite).

Transmission electron micrograph showing typical particulate matter found in water suspension after laboratory exfoliation of Sample 427-O, Grace, Enoree, South Carolina, Grade 5 (composite).



Transmission electron micrograph showing typical particulate matter found in water suspension after laboratory exfoliation of Sample 573-0, Patterson, Enoree, South Carolina, Ungraded, Dried Ore (composite).

Transmission electron micrograph showing typical particulate matter found in water suspension after laboratory exfoliation of Sample 573-0, Patterson, Enoree, South Carolina, Ungraded, Dried Ore (composite).