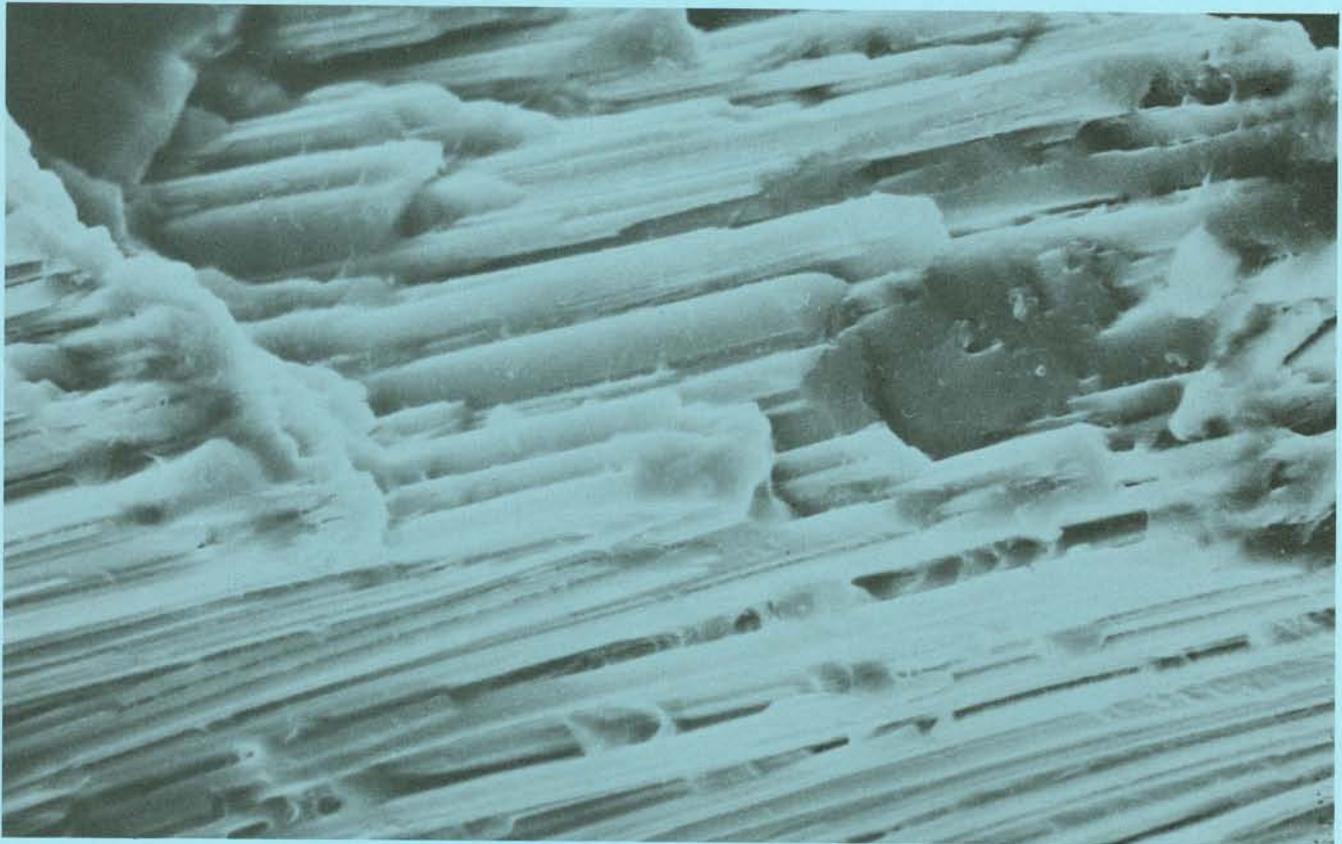




**New Jersey Geological Survey
Geologic Report 15**

**Asbestiform and Non-Asbestiform Amphiboles,
Cadmium and Zinc in Quarry Samples from
Franklin and Sparta, Sussex County, New Jersey**



Thomas H. Kean, *Governor*
Richard T. Dewling, Ph.D., P.E., *Commissioner*

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CADMIUM, AND ZINC IN QUARRY SAMPLES OF
MARBLE FROM FRANKLIN AND SPARTA,
SUSSEX COUNTY, NEW JERSEY**

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by
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CONTENTS

	Page
Abstract	1
Introduction	1
Acknowledgments	1
Quarry locations and products	1
Quarry mineralogy	3
Asbestos mineralogy and habit	3
Previous work on asbestos-related minerals in New Jersey marbles	3
Methods	4
Measurement of amphibole content	4
Measurement of fiber dimensions	5
Measurement of regulatory asbestos fiber content	5
Measurement of potentially respirable fiber content using PLM	5
Characterization of fibers and measurement of respirable fiber content by electron microscopy	6
Measurement of zinc and cadmium content	6
Results	8
Insoluble mineral content	8
Amphibole habit	8
Total amphibole content	8
Origin of fibers	9
Electron microscopic characterization of amphibole fiber	11
Cadmium and zinc content	16
Environmental studies	17
Discussion	17
Asbestos	17
Cadmium and zinc	17
References cited	18

ILLUSTRATIONS

Figure	Page
1. SEM images of tremolite particles	2
2. Amphibole peak from step-scanning XRD of insoluble residue of pulverized marble sample from Franklin (CH3)	8
3. Ternary diagram for EDXS data showing relative intensities of elemental maxima from Mg, Fe, and Al	9
4. PLM aspect-ratio frequency data for crushed tremolite-actinolite grains from Franklin and Sparta	9
5. PLM aspect-ratio frequency of regulatory fibers from crushed tremolite-actinolite from Franklin and Sparta	10
6. PLM aspect-ratio frequency data for regulatory amphibole fibers in pulverized marble samples	11
7. Ternary diagrams showing relative intensities (percent) of EDXS maxima from TEM examinations	12
8. TEM aspect-ratio frequency data for amphibole fiber from two pulverized marble samples (LC2 and CH3) and worn marble chips (PF)	13
9. TEM length-frequency data for amphibole fibers from two pulverized marble samples (LC2 and CH3) and worn marble chips (PF)	13
10. TEM images of amphibole fibers	14
11. TEM width-frequency data for amphibole fibers from two pulverized marble samples (LC2 and CH3) and worn marble chips (PF)	15
12. Plot showing relationship between width and aspect-ratio data for TEM measurements from two pulverized marble samples	15
13. Plot showing relationship between cadmium and zinc concentrations in crushed marble samples ...	16

TABLES

Table	Page
1. Descriptions of selected samples	7
2. Concentrations of insoluble mineral and amphibole in selected samples	7
3. Summary of PLM fiber counts	10
4. PLM length and aspect-ratio distribution data	10
5. Zinc and cadmium content of selected samples	16

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ABSTRACT

Crushed marble samples from two quarries in Franklin and Sparta, Sussex County, were analyzed for amphibole content using x-ray diffraction. Regulatory asbestos fiber content was measured using light microscopy. Respirable amphibole fiber content was determined using electron and light microscopy. Cadmium and zinc were measured using atomic absorption.

Total amphibole content ranged from 0.1 to 0.9 percent by weight. Regulatory asbestos fibers were measured at 16.9 and 42.0 fibers per milligram in pulverized marble samples from the quarries in Franklin and Sparta, respectively. Respirable amphibole was measured by light microscopy at 8.6 and 7.6 regulatory fibers per milligram in the same respective samples. A substantial amount of amphibole fiber was also found in worn and weathered gravel composed of marble.

Observations under light and electron microscopes indicate that most of the fibers in the crushed stone samples are derived from prismatic to acicular amphibole. Amphibole of semiasbestiform to asbestiform habit accounts for a small but discernable portion of the total fiber content. Most fibers are the result of cleavage, although there is some evidence for fibrillar development in some of the amphibole.

Habit-type is important in interpreting the data on amphibole content presented here. Most of the amphibole fibers noted, although considered asbestos for regulatory purposes, are derived from amphibole which does not meet mineralogical or commercial criteria for asbestos, and which cannot be equated with asbestos in physical or biological terms. In interpreting actual asbestos content, content of fibers of aspect ratio greater than 20 seems to be a more reasonable criterion than content of fibers above the regulatory limit of 3.

Average cadmium concentration in Sparta crushed stone samples was relatively high, about 660 ppb. At Franklin, cadmium is much lower, averaging about 67 ppb. Zinc averaged 111 ppm at Sparta and 26 ppm at Franklin. Sphalerite and aragonite were identified as cadmium-bearing mineral species in the stone.

Cadmium in pulverized carbonate rocks bears further study as a source of cadmium in soils to which such limestones are applied.

INTRODUCTION

The primary purpose of this report is to provide information on the quantity and types of mineral fiber present in stone and stone products from quarries in Precambrian marble at Franklin and Sparta, New Jersey. Analyses are also presented for cadmium and zinc in these stone products. Both cadmium and asbestos are subject to environmental and occupational regulation. These substances were selected for study on the basis of published and unpublished data on the mineralogy and chemistry of marbles in the area.

Acknowledgments

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Malcolm Ross, U. S. Geological Survey, reviewed a later version. David Calvert and James Kerner of Lehigh University assisted in the electron microscopy. The cooperation of the Limestone Products Corporation during the sampling period is also gratefully acknowledged. Parts of this investigation were conducted in conjunction with the author's graduate research in geology at Rutgers, under the general guidance of Prof. J. H. Puffer.

QUARRY LOCATIONS AND PRODUCTS

The Limestone Products Corporation of America owns and operates two quarries in the Precambrian marble of Sussex County, New Jersey. The larger quarry is the Limecrest (or Sparta) quarry, located on Limecrest Road in Sparta (41° 3.25'N; 74° 40.90'W). The other is the Franklin quarry, located on Cork Hill Road in Franklin, (41° 5.50'N; 74° 35.91'W). Products of the quarries include agricultural and garden limestone, filler, gravels, animal grit and feed additives.

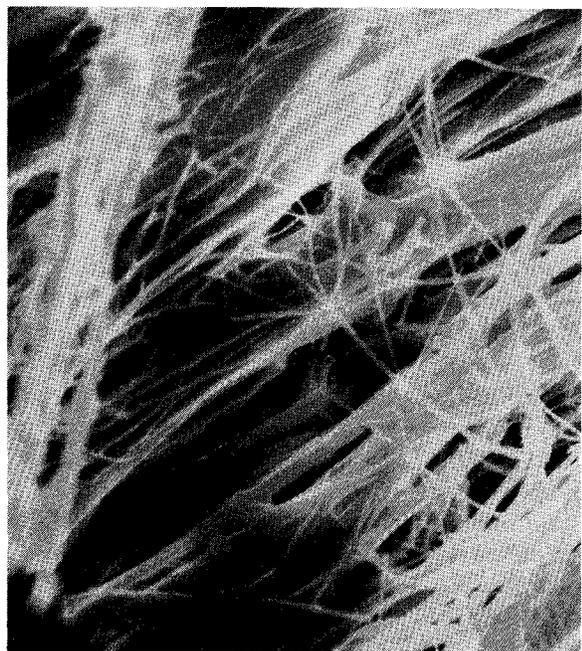
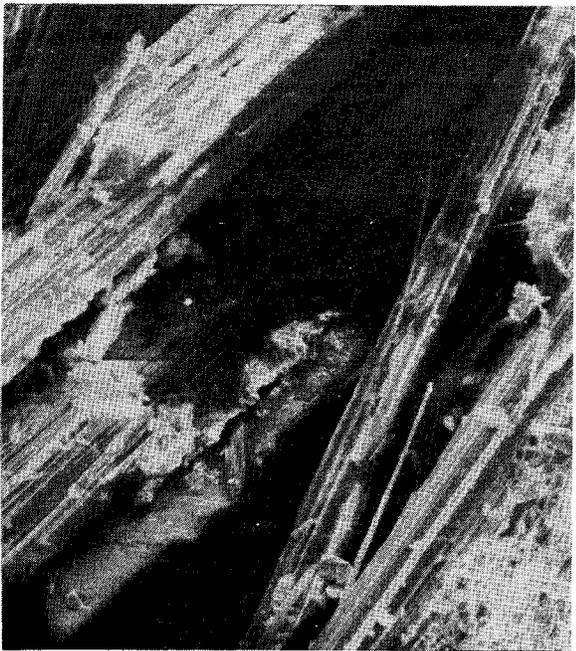
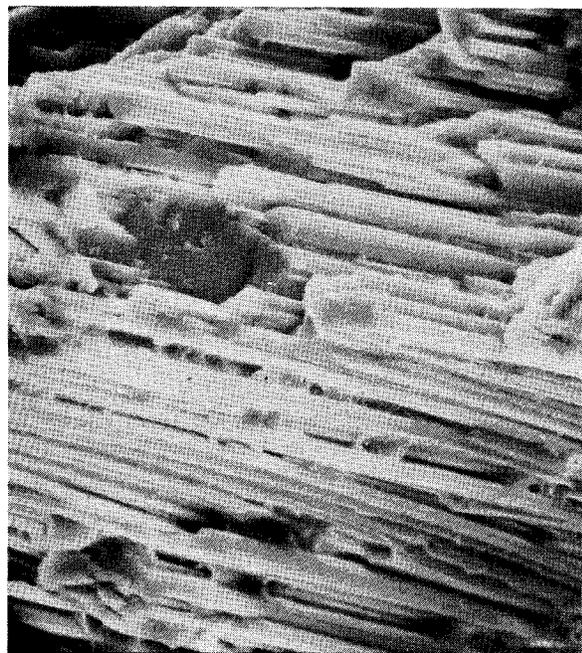
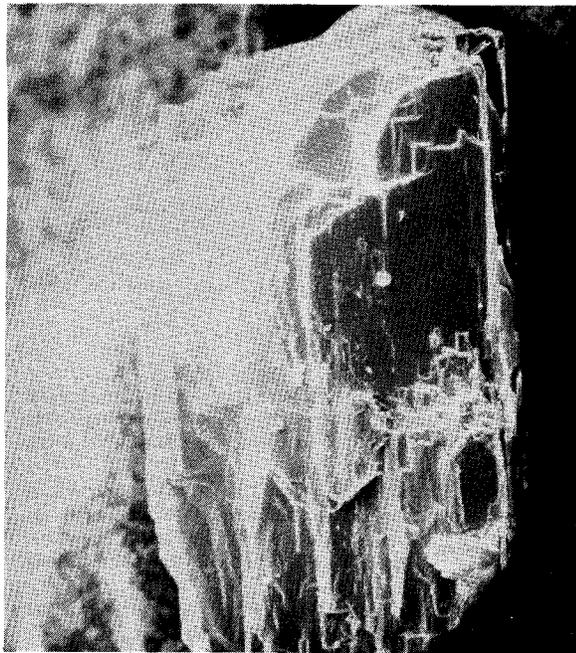


Figure 1. Scanning electron microscope images of tremolite particles. a) prismatic, Franklin, 300X. b) acicular, Sparta, 2000X. c) semiasbestiform, Sparta, 300 X. d) asbestiform, Sparta, 3000X.

QUARRY MINERALOGY

At both the Franklin and Sparta quarries, the stone is typically a gray to white marble composed primarily of calcite and dolomite. Graphite and phlogopite are usually present as minor constituents. Also commonly present are tremolite-actinolite minerals, hornblende, sericite, talc, chondrodite, norbergite, pyrite, chalcocopyrite, sphalerite, and fluorite. Less common or more locally distributed minerals include galena, bornite, spinel, and corundum.

At the Sparta quarry pegmatite is abundant. The pegmatite is composed mostly of microcline, quartz, and hornblende. Chalcocopyrite, pyrite, fluorite, and sphalerite occur locally and generally in small quantities. Galena has been reported (Widmer, 1962) but was not noted in examinations done for this report.

A distinctive mineral assemblage occurs in reaction zones near boundaries between pegmatite intrusions and marble. This assemblage includes chondrodite-norbergite minerals, scapolite, phlogopite, hornblende, and clinopyroxene. Hydrothermal alteration is pronounced at places within these zones. Among the types of alteration are chloritization of pyroxene and serpentinization of chondrodite.

The stone at the Franklin quarry is almost exclusively marble. Chondrodite- and norbergite-bearing marble are abundant in some sections of the quarry. No pegmatite was noted. Sulfide assemblages occur in minor concentrations and include sphalerite-galena-fluorite and chalcocopyrite-sphalerite-bornite.

ASBESTOS MINERALOGY AND HABIT

The commercial product known as asbestos can consist of naturally-occurring asbestiform varieties of any of 6 minerals: the serpentine mineral chrysotile and the amphibole minerals crocidolite (riebeckite-magnesioriebeckite), amosite (cumingtonite-grunerite), anthophyllite, tremolite, and actinolite. Characteristically, commercial asbestos is composed of fibers which are bundles or aggregates of smaller fibrous units known as fibrils. This is referred to as polyfibrillar structure or, simply, fibrillar structure.

Non-asbestiform amphiboles are marked by two good directions of cleavage intersecting at approximately 55°. The cleavage gives rise to cleavage-bound fibers on crushing of these amphiboles. With increasingly well developed cleavage, tendency to produce fibers on crushing increases.

Four principal habit types can be recognized in amphiboles (Campbell and others, 1979; Palekar and others, 1979): 1) prismatic: having no outward fibrous form, 2) acicular: having a coarsely fibrous

appearance, 3) semiasbestiform: composed of fine fibers that can be separated with difficulty, and which are stiff except where very fine, and 4) asbestiform: composed of flexible and easily separated fibers. The habit-types (figure 1) are intergradational and frequently intergrown.

Pronounced cleavage marks the difference between prismatic and acicular amphibole. The difference between acicular and semiasbestiform amphibole is in the development of fibrillar structure. More pronounced development of fibrillar structure is accompanied by increased separability of fibers, marking the difference between semiasbestiform and asbestiform fibers. The development of fibril separability is accompanied by development of flexibility in asbestiform amphibole. The terms listed above are defined and used differently by different authors. Terms used in this report should be interpreted only within the context of the definitions given above.

PREVIOUS WORK ON ASBESTOS-RELATED MINERALS IN NEW JERSEY MARBLES

The occurrence of amphiboles in the Precambrian marble of Sussex County has been documented mostly in connection with mineral collecting activities in and around Franklin Borough. Widespread occurrence of coarsely crystalline, prismatic tremolite-actinolite minerals is characteristic of the marble (Hague and others, 1956). Crystals of edenite (an amphibole of the hornblende group) are also abundant. Edenite is very similar in appearance and properties to minerals of the tremolite-actinolite series (Palache, 1935). Other members of the hornblende group such as pargasite and hastingsite have also been noted in the area (Palache, 1935; Frondel, 1972). Tremolite, actinolite, and edenite have been described from both quarries (Kushner, 1974; Wood, 1962). Asbestiform tremolite-actinolite minerals have been described from the marble in the Franklin area (Palache, 1935). An unspecified variety of asbestos has been reported from the quarry at Sparta (Widmer, 1962; Wood, 1969).

Asbestos in the Precambrian marble of New Jersey has been described in detail by Germine (1981) and Germine and Puffer (1981). Chemical analyses of asbestos composed of tremolite-actinolite minerals from the Sparta quarry were presented by Germine (1981). Preliminary results of this study were presented by Germine (1982). Germine and Puffer (1981) did not note chrysotile asbestos in either quarry, although it was identified in Precambrian marble from elsewhere in the state. A single occurrence of slip-fiber chrysotile, on pegmatite, was noted in examinations of the Sparta quarry done for this study.

The most notable concentration of asbestos in New Jersey marbles is on the northeast end of Jenny Jump Mountain (about 16 miles southwest of the Sparta quarry in Independence and Al-lamuchy Townships, Warren County). Asbestos was reportedly once mined in this area (Valiant, 1903). Little is known about these "asbestos mines," and it is doubtful that they ever produced commercial quantities of asbestos.

METHODS

Quarry stone was sampled to determine distribution and mineralogy of amphiboles. Loose stone was examined over the entire floor area of both quarries. Because of safety requirements no quarry walls were examined closely. Product samples were grab samples taken from freshly-opened 50 pound bags.

Specimens collected in the quarries were identified mineralogically using standard optical and x-ray diffraction techniques. Product samples were analyzed as follows: (1) total amphibole content was determined semi-quantitatively by step-scanning x-ray diffraction (XRD), (2) amphiboles were characterized on the basis of mineralogy and habit with binocular polarized light microscopy (PLM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), (3) amphibole fiber content was quantitatively determined and habit-types were described on the basis of aspect-ratio data, (4) potentially respirable fiber content was determined on the basis of fluid-dynamic properties, and (5) cadmium and zinc were measured using atomic absorption spectroscopy.

Measurement of Amphibole Content

Total amphibole content was measured using step-scanning x-ray diffraction (XRD) determinations of the area under the amphibole diffraction maximum at about $10.5^{\circ}2\theta$. Tremolite-actinolite and hornblende minerals show strong diffraction peaks at about $10.5^{\circ}2\theta$, and analyses at this angle therefore reflect combined tremolite-actinolite and hornblende content (total amphibole content). Step-scanning was done at intervals of 0.01° to 0.05° and for periods ranging from 10 to 140 seconds per reading. One to several sets of readings were taken for each sample. Longer and more numerous counts were taken for samples with low peak intensity above background than for those with greater intensity peaks.

The standard employed for measurement of amphibole content in unknowns was IARC (International Agency for Research on Cancer) tremolite. Similar analyses have been performed successfully using the same standard (Rohl and others, 1976). In determination of amphibole content, the area beneath the amphibole peak and above a datum drawn through the base of the peak was measured

by planimeter 5 times for each sample. These measurements were averaged and amphibole content of the sample was determined by reference to the standard. In determining amphibole content, a linear relationship was assumed between amphibole concentration and areas beneath peaks. The average area for two sub-samples of the IARC tremolite-actinolite standard was used as a basis for estimates of concentration. Assumption of a linear relationship between intensity and mineral concentration is a recognized practice in analyses of this type (Zussman, 1967). Errors may occur due to introduction of undefined variables, in particular matrix absorption of x-rays and preferred orientation of mineral particles in x-ray mounts. To avoid error due to interfering peaks of other minerals, continuous scans were run on representative samples and all mineral species were identified.

The lower limit of detection of tremolite-actinolite by step-scanning XRD is about 0.1 percent by weight (Rohl and others, 1976). Amphibole was concentrated in the unknowns to produce samples with concentrations well above the detection limit. Concentration was accomplished by dissolution of carbonates using dilute HCl (less than 1N). Such a solution can also dissolve or partially dissolve other relatively soluble components such as sphalerite, but does not significantly affect the amphiboles.

Unknowns to be analyzed were split, weighed on an analytical balance, and immersed in dilute HCl. After removal of all soluble components, residues were separated from the solution by filtration. The filtrate was washed, first in water and then in acetone, dried, and weighed to determine the percent of insoluble content in the unknowns. The residues were then mixed with acetone, ground to a fine powder with an agate mortar and pestle, and applied to clean glass slides.

Standard samples were analyzed by step-scanning XRD in the same manner as dried residues. Reproducibility was tested in separate residue preparations from a single sample (CH4). During step-scanning analyses, the standard was run at regular intervals to check for instrumental drift. A second standard of pure prismatic tremolite from Gouverneur, New York, was analyzed to determine if prismatic tremolite would give different quantitative data using the analytical technique described. The prismatic sample gave a peak with a 3 percent greater area than the asbestiform sample. This is not a significant difference. It may be due to statistical variation or to a minor talc impurity in the asbestiform standard.

In order to identify mineral species and determine the mineral chemistry of amphiboles in the bulk samples, grains were picked from two of the coarser-grained crushed stone samples and analyzed under the scanning electron microscope using

energy dispersive x-ray spectroscopy (EDXS). Relative intensities for Fe, Mg, and Al peaks were measured from spectra and plotted on ternary diagrams along with reference samples of known amphiboles from Precambrian marbles from elsewhere in the Reading Prong.

Measurement of Fiber Dimensions

Polarizing light microscope (PLM) measurements were made on amphibole fibers from quarry products and from amphibole samples collected from the quarries and crushed in the laboratory. Samples representing each of the major habit types (prismatic, acicular, semi-asbestiform, and asbestiform) found in the quarries were ground to a gritty powder of similar consistency to the pulverized quarry products. The dimensional characteristics of fragments from these reference samples were used to infer the origin of fibers in products in terms of mineral habit before crushing. This procedure was of critical importance in that the mineral habit of the particle from which a fiber is derived may have a great deal to do with the fiber's potential adverse effects (Campbell and others, 1977; Campbell and others, 1979). Fiber length and width were measured using an eyepiece reticle calibrated against a micrometer slide. Fiber width measurements were used solely to determine if the particles were regulatory fibers (see "Measurement of Regulatory Asbestos Fiber Content" below). Aspect ratio was estimated by comparing fibers with visual scales showing fibers of graduated aspect ratio. This method of determining aspect ratio is more reliable than determination using length and width measurements because fiber widths are generally too low to be accurately measured by PLM (see Campbell and others, 1979). The estimation of dimensional ratios on the basis of reference images has been described by Rittenhouse (1943) and Metz (1980).

Measurement of Regulatory Asbestos Fiber Content

A regulatory asbestos fiber is defined by the U.S. Bureau of Mines as an amphibole or chrysotile particle with length greater than 5 microns, width less than 3 microns and aspect ratio (length to width ratio) greater than 3 (Campbell and others 1979). OSHA regulations (Fed. Reg. 9002, 1975, p. 47652-47660 OSHA) differ in using a 5 micron width cutoff. The membrane filter method of fiber counting (described below) was used in analyses of fiber content. This same basic method is used by federal regulatory agencies in work on environmental samples (Anderson and Long, 1980; Goodwin, 1978).

Counts and measurements to obtain OSHA regulatory fibers per gram were conducted on 2 to 4 sub-

samples for each unknown using the following procedure:

1. Splitting and weighing of a product sample. Samples were used as received with no further grinding or processing.
2. Dissolution of carbonate in dilute HCl.
3. Filtration of insoluble residue suspensions using 0.45 micron Millipore (type HA). This method of filtration has been outlined by Anderson and Long (1980).
4. Ashing of a measured section of loaded Millipore filter on a clean glass slide with overlying cover slip. The sample mass represented on the slide is calculated by multiplying the percentage of the filter ashed by the original mass of pulverized rock represented in the filtered suspension.
5. Application of immersion oil between cover slip and slide. Just enough oil is applied to drive all air from under the cover slip. No excess oil can be removed.
6. Counting and measurement of fibers using 450X PLM and a micrometer stage. Traverses of measured width are made using step-wise advances in the micrometer stage in such a way as to cover the entire sample area without overlap. Only regulatory tremolitic amphibole fibers are counted. The fiber count is converted to fibers per gram by dividing the number of fibers counted by the weight of pulverized rock represented on each slide. Tremolitic amphibole is identified using index of refraction, birefringence, extinction angle, cleavage, and particle morphology. The index of refraction of the immersion liquid used ($n = 1.62$) falls within the range of tremolite samples from the quarries, providing an important criterion for identification.

In addition, for further analysis, aspect-ratio data were plotted as frequency within fixed ranges of value as outlined by Campbell and others (1977).

Measurement of Potentially Respirable Fiber Content Using PLM

Respirable mass sampling is the principal method used by the American Industrial Hygiene Association (AIHA) in gauging worker exposure to insoluble dusts (AIHA, 1970). The AIHA sampling method involves passing air samples through a fluid-dynamic size selector which excludes all particles of fluid dynamic diameter (fdd) greater than 10 microns and includes most particles of less than 5 microns fdd (AIHA, 1970). These criteria are based on observation of particle deposition in human lung tissues. Fluid dynamic diameter is defined as the diameter of a quartz sphere with the

same settling velocity as the particle (AIHA, 1970; Krumbein and Pettijohn, 1938). The particles being analyzed are not themselves considered to be spherical. Spheres are merely being used, according to convention, as a measure of settling velocity.

Potentially respirable particles are defined for the analyses presented here as particles with fdd less than 5 microns. Particles of less than 5 microns fdd were extracted from insoluble fractions of samples in the manner used by sedimentologists in size analyses of "fines" (Krumbein and Pettijohn, 1938). The procedure used here for measuring potentially respirable fibers per gram of product is as follows:

1. Splitting and weighing of a 30 gram sample.
2. Dissolution of carbonate in dilute HCl.
3. Dilution with distilled water in a 500 ml graduated cylinder.
4. Suspension of particles by inverting the graduated cylinder several times until a uniform cloud is produced.
5. Settling of particles under undisturbed conditions for a fixed time interval (1 hour in this case).
6. Pipette withdrawal of a measured volume of the suspension at a depth calculated on the basis of the theoretical settling velocity of a quartz sphere of 5 microns diameter (Krumbein and Pettijohn, 1938).
7. Neutralization of excess HCl in the withdrawn suspension using Na_2CO_3 .
8. Membrane filtration of the suspension and analysis of fiber concentration and aspect-ratio distribution as described in the section "Measurement of Regulatory Asbestos Fiber Content."

Characterization of Fibers and Measurement of Respirable Fiber Content by Electron Microscopy

Transmission electron microscopy (TEM) was used for investigation of structure, chemistry, and dimensional characteristics of randomly-chosen amphibole fibers. The same product samples were analyzed by TEM as were analyzed using PLM. In addition, a sample of weathered and worn marble gravel from a park road near the Great Falls, Paterson, N.J., was analyzed by TEM.

Samples were treated with dilute HCl and respirable fractions were extracted as described previously. The dried suspension, if uniform, was considered ready for analysis. Beryllium grids were used for the two pulverized marble samples, while a copper grid was used for the worn gravel sample. Unlike copper and nickel, beryllium does not emit x-rays in the range employed for chemical analysis of amphiboles. Cleaner, more easily interpreted

EDXS spectra can thus be obtained.

For measurement of quantity and mass of respirable amphibole fiber, a suspension of respirable particles was prepared from insoluble residue as previously described for PLM. This suspension was then analyzed as if it were a water sample, using a variation of the method of Anderson and Long (1980) described by Puffer and Germine (1982). Particles were deposited on 400-mesh nickel grids using the modified Jaffe-Wick method (Anderson and Long, 1980).

In both characterization of random fibers and measurement of respirable fibers, sample grids were analyzed using a Phillips 400 TEM. Systematic searches were conducted on grid squares at a magnification of 17,000X. Regulatory asbestos fibers were identified according to EPA interim guidelines for water samples (Anderson and Long, 1980). These guidelines differ from PLM guidelines in that all amphibole fibers, including hornblende, are counted. A fiber is defined as any particle having an aspect ratio greater than 3. Fibrous particles were first characterized by EDXS to determine if chemical composition was consistent with that of a regulated mineral. If so, structural data were gathered using selected area electron diffraction (SAED). Once positive identification was made, a bright field photograph was taken of the fiber. Fiber measurements were subsequently made from these photographs. EDXS and SAED data were recorded for most fibers and identification confirmed by comparison with standards.

SAED patterns were identified by direct comparison of negatives with a set of reference negatives prepared from the tremolite standard. Differentiation of amphiboles was done with EDXS data.

EDXS data were analyzed by measuring peak height from photographs using a ruler and measuring magnifier. The x-ray frequency of each peak serves to distinguish the element responsible. The peak intensity is an index of elemental abundance. Relative peak intensities for Fe, Mg, and Al were plotted on ternary diagrams, and mineral fields were delineated on the basis of standards in the manner described by Langer and others (1978). Mineral fields are delineated on the diagrams using International Mineralogical Association amphibole classification (Leake, 1978), with compositional boundaries expressed in terms of relative intensity of x-ray fluorescence maxima. Analyses used in construction of the diagrams have been previously presented along with similarly-constructed diagrams in Germine, 1981. The same procedure was used for both SEM and TEM analyses.

Measurement of Zinc and Cadmium Content

Zinc and cadmium content were measured using

atomic absorption spectroscopy on samples that had been dissolved in oxidizing acid.

One gram was split from each sample and immersed in aqua regia prepared by mixing 20 ml concentrated HNO₃ and 5 ml concentrated HCl. The solutions were heated in polypropylene bottles at about 60°C for 6 hours. The solutions were then allowed to cool, and 10 ml of 30 percent H₂O₂ was added to each sample. This solution was heated at 60°C for 3 days, allowed to cool, diluted to 100 ml using distilled water, then filtered to remove insoluble particles. This is the same procedure as used by the U.S. E.P.A. in preparation of sediment samples for metals analysis, and is identical to that described by Torlucci (1982). Two blanks were prepared using the same reagents and labware to determine background concentration.

Zinc content was determined using a Perkin-Elmer Model 290B acetylene flame atomic absorption spectrophotometer. This instrument was found to be inadequate for cadmium determination due to detection limitations. Flameless atomic absorption analysis was performed for cadmium using a Perkin-Elmer 503 spectrophotometer equipped with a graphite furnace and deuterium arc supply. Use of flameless atomic absorption in analysis of cadmium in carbonate rocks has been previously described and tested by Gong and others (1977). Standards were prepared using distilled

water and Fisher certified stock solutions containing 1000 ppm Cd and Zn. For zinc, solutions containing 0.25, 0.50, 1.00, 2.00, 5.00, and 10.00 ppm zinc were prepared. For Cd, a single 5 ppb solution was prepared and injected in aliquots of 5, 10, and 20 mg. Reference curves were prepared separately for cadmium and zinc on the basis of these standards. Distilled water samples were analyzed separately to determine background levels. Standards were run periodically to check for instrumental drift.

Repeat analyses for cadmium indicate a standard error (precision) of ±12 percent for determinations on the same solution. Separate grab samples from the same source and separate portions of split samples were also analyzed for some samples to provide an index of sampling and analytical error. Repeated runs conducted on the two blank solutions showed a background ranging from 0 to 0.2 ppb Cd and a relatively consistent background of about 0.02 ppm Zn. On the basis of these data, background levels of 0.2 ppb for Cd and 0.02 ppm for Zn were subtracted from determinations on solutions of unknowns. This corrected value was then multiplied by 100 in order to arrive at a value for Cd and Zn content in dry unknowns. The factor of 100 is based on the dissolution of 1 gram of sample in 100 ml of solution.

Table 1. Descriptions of selected samples.

Franklin Quarry:

- CH1 —Crushed rock, predominantly pebble-to granule-sized fragments, from a stockpile in the quarry.
- CH3 —“Pulverized limestone” from a freshly opened 50 pound bag.
- CH4 —“Pulverized limestone” from a freshly opened 50 pound bag. Not the same bag as CH1.
- CH9 —Surface sediment, Cork Hill Road, at quarry entrance.

Sparta Quarry:

- LC1 —“Barn calcite” from a freshly opened 50 pound bag.
- LC2 —“Pulverized limestone” from a freshly opened 50 pound bag.
- LC6 —“90-200 filler” from a freshly opened 50 pound bag.
- LC9 —“Granular limestone” from a freshly opened 50 pound bag.
- LC10 —“Pulverized limestone” from a freshly opened 50 pound bag. Not the same bag as LC2.

Table 2. Concentrations of insoluble mineral and amphibole in selected samples.

Sample	Percent insoluble	Percent amphibole in insoluble fraction	Percent amphibole in untreated sample
CH1	0.77	9.8	0.08
CH3	1.19	21.0	0.25
CH4 (#1)	0.93	8.1	0.08
CH9	1.68	1.5	0.03
LC1	12.70	7.0	0.86
LC2	9.02	1.7	0.15
LC6	7.85	2.5	0.20
LC9	9.44	1.7	0.16
LC10	9.76	2.9	0.28

RESULTS

Insoluble Mineral Content

The crushed stone samples examined in this study are described in Table 1. Table 2 shows data on insoluble residue content.

The insoluble fraction was greater in samples from the Sparta quarry. These had a median insoluble content of 9.0 weight percent. Those from the Franklin quarry had a median of 0.9 percent. Graphite and mica (mostly phlogopite) make up most of the insoluble mineral content at Franklin. These minerals are present in approximately the same abundance at Sparta as at Franklin, while quartz and feldspar are relatively much more abundant at Sparta, accounting for the much higher insoluble mineral content. XRD of the respirable fraction from Sparta pulverized marble (sample LC12) shows that quartz, mica, and chlorite are major constituents of the insoluble residue, with lesser amounts of talc and amphibole.

Amphibole Habit

At both the Franklin and Sparta quarries, a continuum exists between prismatic and acicular amphibole and between semiasbestiform and asbestiform amphibole. Particularly notable is the development at Sparta of asbestiform habit by "softening" of semiasbestiform fiber through weathering. This phenomenon has been previously described by Ladoo and Meyers (1951) in anthophyllite asbestos.

Prismatic to acicular amphibole makes up the overwhelming bulk of the amphibole in the quarries and in the crushed stone products. Semiasbestiform amphibole is, however, a persistent trace constituent. It is typically found as grains of less than 3mm that often have a euhedral crystalline form but possess a silky luster and break into fibrous aggregates under a needle probe. Asbestiform tremolite-actinolite occurs locally in faults and shear zones in the Sparta quarry as a light yellowish-brown, light green, or light blue flexible slip fiber (Germine, 1981; Germine and Puffer, 1981).

Coarsely crystalline, prismatic tremolite-actinolite minerals are a significant component of the insoluble fraction at both the Franklin and Sparta quarries. At Franklin, tremolite is typically gray and contains little iron, and actinolite is not in evidence. At Sparta, gray tremolite grades into greenish actinolite. Alteration of tremolite-actinolite minerals to talc occurs at both quarries. Alteration to talc is often associated with formation of semiasbestiform aggregates. In one instance, a prismatic crystal of tremolite about 3 cm long had a rind of semiasbestiform tremolite and talc. This rind, in turn, had a weathered surface of asbestiform tremolite.

Well developed fibril bundle structure was noted in asbestiform tremolite-actinolite mineral slip fiber from the Sparta quarry under the scanning electron microscope. Elongate graphite smears and fault grooves line up with slip-fiber orientations, indicating stress control of crystal growth. In some samples from the Sparta quarry, asbestiform tremolite-actinolite minerals occur in abundance in association with calcite, pyrrhotite, chlorite, and talc. The rock possesses a distinct schistosity. The tremolite-actinolite minerals are partly altered to talc and are found in planar or subplanar slip fiber zones. The extent of fiber-rich zones within the Sparta quarry was not determined.

At both quarries, a variety of hornblende known as edenite is found in granular form and as short, stout, euhedral crystals of light green color, as described by Palache (1935). Iron-rich hornblendes of the pargasite-hastingsite series were also noted in the pegmatites and calc-silicate rocks at Sparta. In general, hornblendes from both quarries were prismatic, and, less commonly, acicular. Semiasbestiform edenite was identified in SEM examinations of one crushed stone sample from Sparta.

Total Amphibole Content

XRD determinations of amphibole content in insoluble residues are in table 2. Figure 2 shows step-

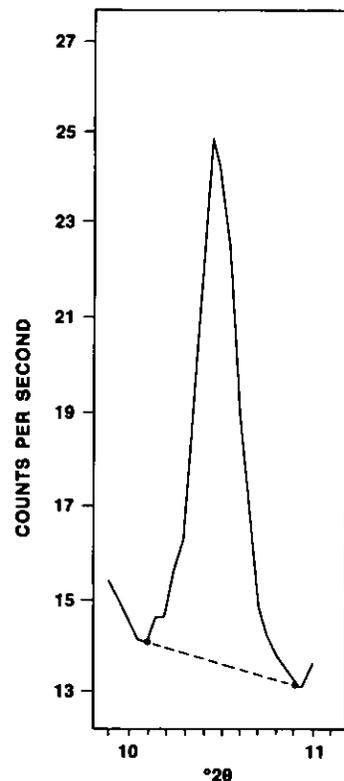


Figure 2. Amphibole peak from step-scanning XRD of insoluble residue of pulverized marble sample from Franklin (CH3).

scanning XRD results for sample CH3. These samples were also used for PLM and TEM fiber counts, presented in later sections. Reproducibility of XRD data was judged to be approximately 5 percent based on comparisons of results for sub-samples of the standard and unknowns. No interfering peaks were identified in continuous scans of unknowns.

Ranges of amphibole content in crushed stone samples measured by XRD were:

1. Franklin quarry: 0.08 to 0.25 percent
2. Sparta quarry: 0.15 to 0.86 percent

From EDXS, tremolite and hornblende are nearly equal in abundance in the Franklin crushed stone sample (CH3, figure 3). Actinolite is not in

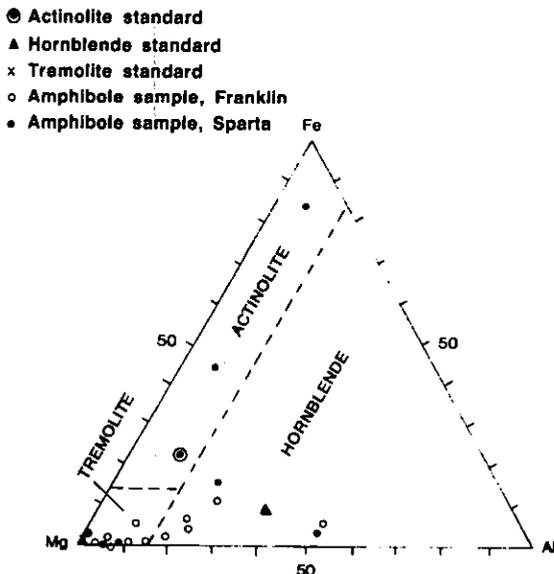


Figure 3. Ternary diagram for EDXS data showing relative intensities of elemental maxima from Mg, Fe, and Al.

evidence. At Sparta tremolite, actinolite, and hornblende were detected in approximately equal proportions (sample LC1, figure 3).

Origin of Fibers

Aspect-ratio distributions observed using PLM on grains selected to represent the major habit types, then ground to a gritty powder, are on figures 4 and 5. They are as follows: *Prismatic*—ground material from prismatic grains contains a relatively low content of fibers. Fibers rarely exceed an aspect ratio of 10. *Acicular*—contains abundant fibers. Fibers frequently exceed an aspect ratio of 10, and less commonly 20. *Semiasbestiform*—composed predominantly of fibers. Fibers commonly have aspect ratios in excess of 20, and less commonly 50. *Asbestiform*—similar to semiasbestiform. Distinguished by an abundance of high aspect-ratio fibers and the presence of fibers with aspect ratio greater than 100. As shown in figures 4 and 5, and as noted by Rohl and others (1976), fibers of low to moderate aspect ratio may be derived from any habit type of amphibole, and it is not possible in most cases to determine the origin of such fibers. However, the origins of high aspect-ratio fiber populations are generally identifiable in that: 1) prismatic amphibole produces no fibers of aspect ratio greater than 20, 2) acicular amphibole produces no fibers of aspect ratio greater than 50, and 3) semiasbestiform amphibole produces no fibers with aspect ratio greater than 100. It should be remembered that these habit-types are intergradational and frequently intergrown.

Results of fiber counts and measurements are summarized in tables 3 and 4. Differences between

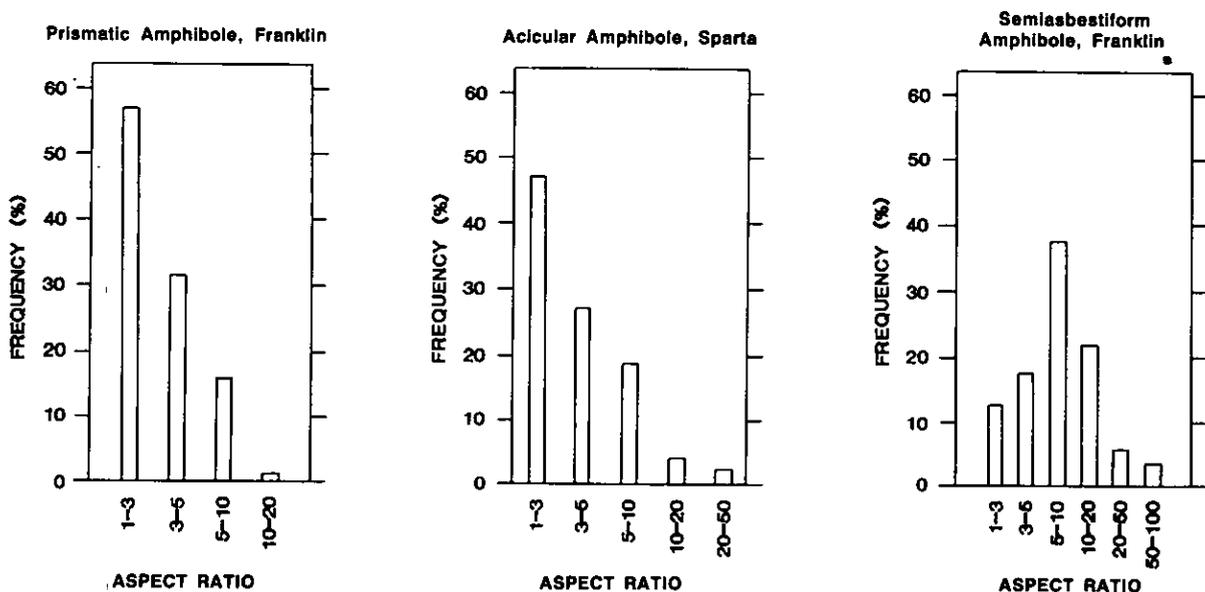
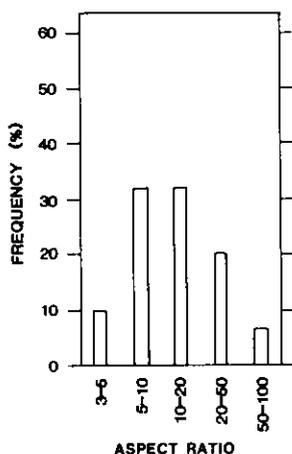


Figure 4. PLM aspect-ratio frequency data for crushed tremolite-actinolite grains from Franklin and Sparta.

Semiasbestiform Amphibole, Franklin



Acicular Amphibole, Sparta

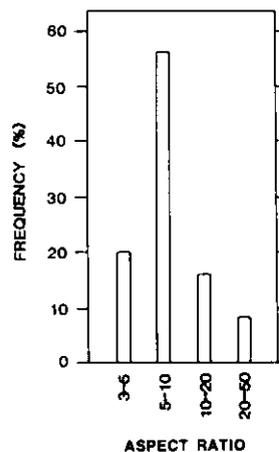


Figure 5. PLM aspect-ratio frequency of regulatory fibers from crushed tremolite-actinolite from Franklin and Sparta.

counts on sub-samples ranged from 2 to 32 percent. Results between sub-samples were similar for fiber concentration, size distribution, and aspect-ratio frequency distribution where counts of more than 30 fibers had been made. Regulatory fiber content was measured at 16.9 and 42.0 fibers per milligram in pulverized marble samples from Franklin and Sparta, respectively. All of the fibers counted were

tremolitic (having the optical properties of tremolite). Fibers having the optical properties of hornblende and actinolite were also observed, but were not counted. Hornblende was not counted as regulatory fiber because it is not included the minerals listed in OSHA regulations. Actinolite, although included in the OSHA list was not counted because: 1) its index of refraction differs

Table 3. Summary of PLM fiber counts.

Sample	Fibers counted	Regulatory fibers counted per mg
CH3	298	16.9
CH3*	224	8.6
LC2	210	42.0
LC2*	165	7.6

*Potentially respirable fraction.

Table 4. PLM length and aspect-ratio distribution data.

Sample	Length (microns)	Aspect ratio (percent frequency)				
		3-5	5-10	10-20	20-50	50-100
CH3	5-10	14	29	10	3	0
	10-20	1	18	13	4	0
	20-50	0	1	4	2	1
	total	15	48	27	9	1
CH3*	5-10	17	23	14	10	0
	10-20	2	11	7	7	3
	20-50	0	1	2	1	3
	total	19	35	23	18	6
LC2	5-10	24	30	12	2	0
	10-20	3	14	7	4	1
	20-50	0	1	0	0	0
	total	27	45	19	6	1
LC2*	5-10	19	34	15	5	0
	10-20	1	10	10	3	0
	20-50	0	1	1	1	0
	total	20	45	26	9	0

*Potentially respirable fraction.

significantly from that of tremolite and it therefore is not readily identified using the procedure outlined, and 2) it is not always distinguishable from hornblende in small particles. Highly elongate fibers (aspect ratio greater than 20) are most commonly tremolitic, while hornblende- and actinolite-like fibers are fairly abundant among the lower aspect-ratio particles, particularly in the Sparta sample. Other mineral fibers present in the samples include rutile, feldspar, and pyroxene.

Based on comparisons of aspect-ratio frequencies for pulverized marble samples (figure 6) and crushed samples of known habit (figure 5), it is concluded that most of the amphibole fibers present in the pulverized marble samples are the result of crushing of amphibole of prismatic to acicular habit. This conclusion is based on the preponderance of fibers of aspect ratio less than 20, and the high percentage of fibers of aspect ratio between 5 and 10. The amphibole fibers with aspect ratio greater than 20 indicate a contribution from amphibole of acicular or semiasbestiform habit.

Because acicular amphibole is far more abundant than fibrous amphibole in quarry samples, these fibers are attributed primarily to acicular amphibole. As might have been predicted from the presence of semiasbestiform amphibole in the quarry and crushed rock samples, a small percentage of the fibers are of aspect ratio greater than 50.

Respirable fiber content was measured at 8.6 and 7.6 regulatory fibers per milligram at Franklin and Sparta, respectively. Respirable mass sampling results indicate that a large portion of the regulatory asbestos fibers counted are not highly respirable, and that high aspect-ratio fibers are on the average more highly respirable than low aspect-ratio fibers (see figure 6).

Electron Microscopic Characterization of Amphibole Fiber

TEM examinations (figure 7) show that the preponderance of fibers in the crushed stone sample from Franklin is from tremolite. In the two samples from Sparta tremolite, actinolite, and hornblende are all major components (figure 7).

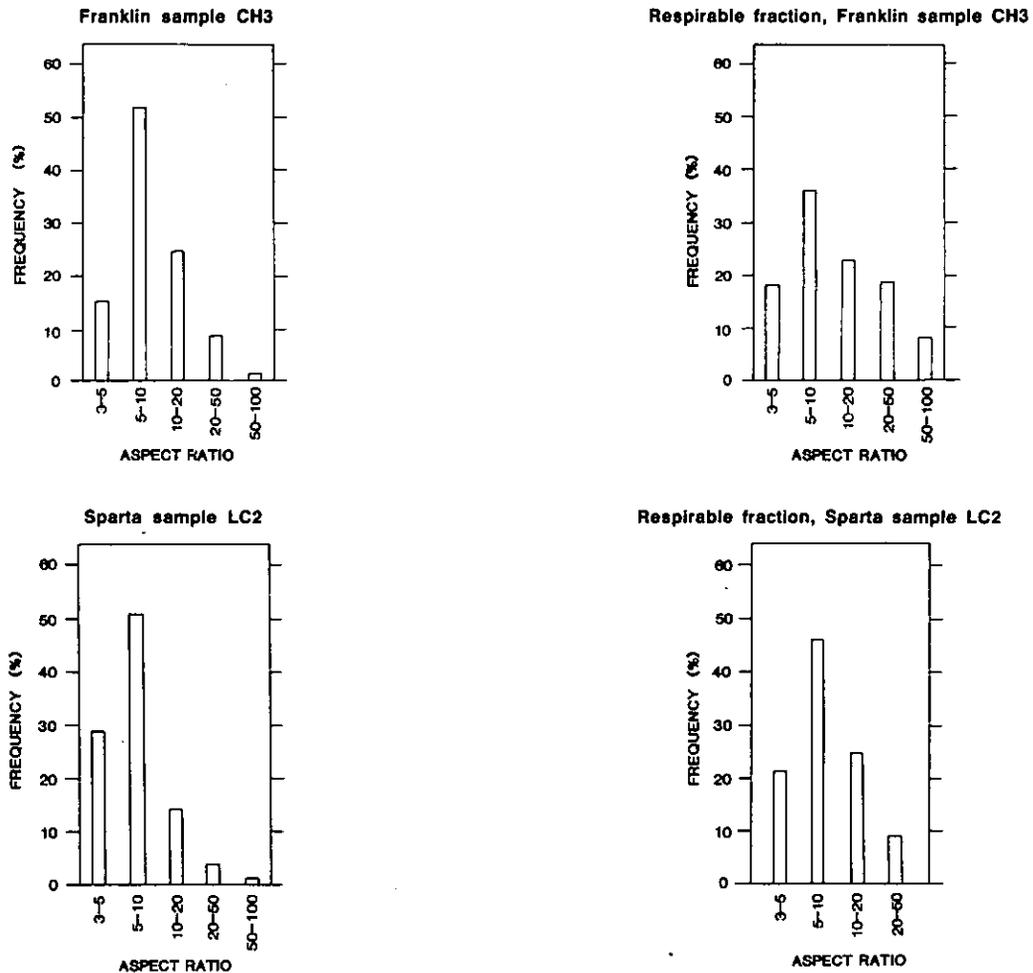


Figure 6. PLM aspect-ratio frequency data for regulatory amphibole fibers in pulverized marble samples.

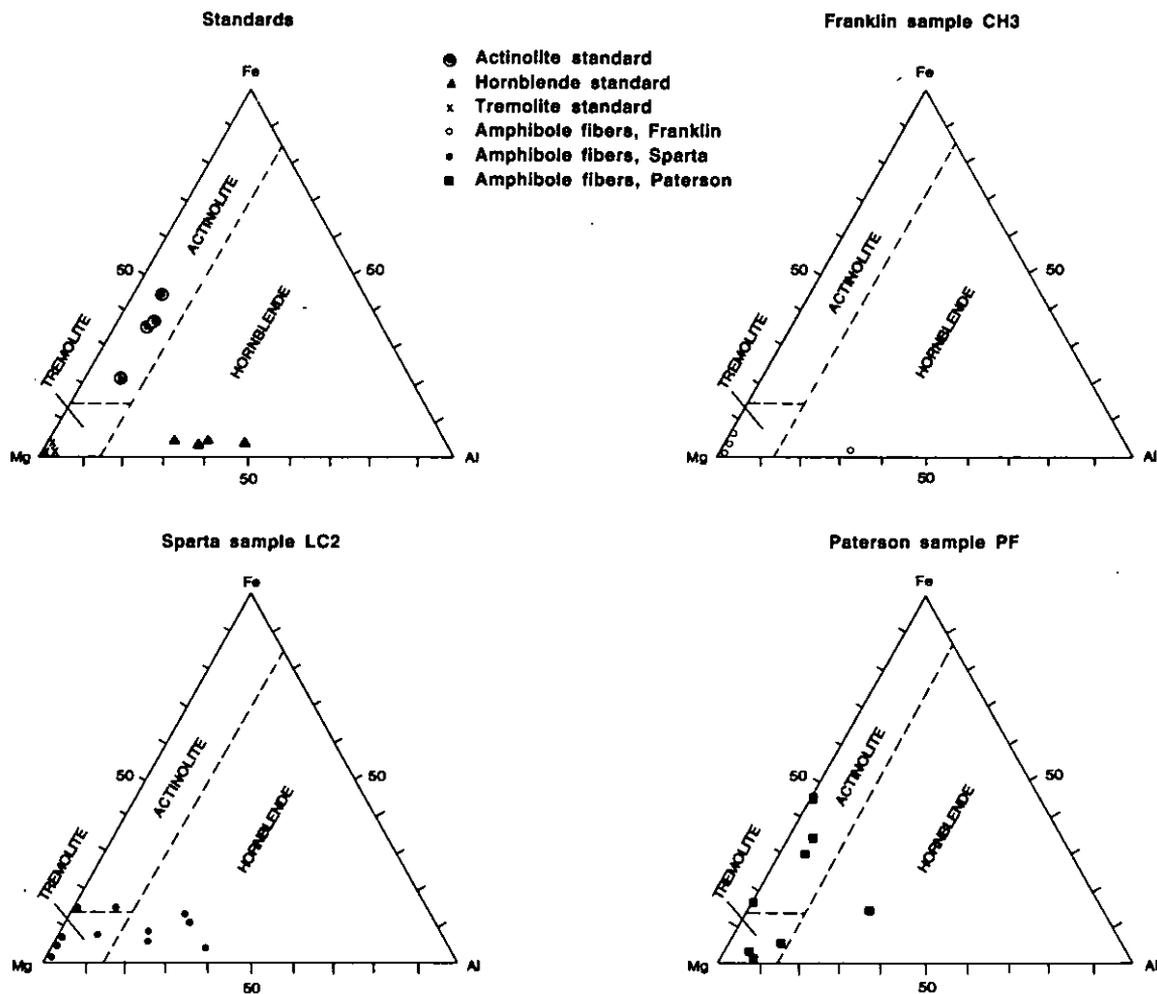


Figure 7. Ternary diagrams showing relative intensities (percent) of EDXS maxima from TEM examinations. Samples CH3 and LC2 are pulverized marble. Sample PF is worn marble chips.

Length and aspect-ratio distributions of fibers from both Franklin and Sparta are approximately log-normal. Cumulative frequency data for these appear as almost straight lines on log-probability plots (figures 8 and 9). Approximately log-normal distributions were also observed for aspect-ratio observations under PLM. As with the PLM observations, TEM aspect-ratio data are consistent with derivation of fiber from amphibole of predominantly prismatic to acicular habit; relatively long, high aspect-ratio fibers were occasionally observed in non-random searches of sample grids (figure 10). In sample PF long, high aspect-ratio fibers were relatively more abundant, as shown by cumulative frequency diagrams (figures 8 and 9). Fiber lengths from random TEM counts were between 0.6 and 2.8 microns in pulverized stone from Franklin and Sparta. Worn marble chips from Paterson showed a wider range, between 0.2 and 7.9 microns. This difference is probably the result of the method of comminution—crushing of the quarry samples as opposed to wear by traffic and weathering of the samples from the park road.

Fiber widths have an approximately log-normal

distribution for the Franklin sample, but are skewed towards narrower width ranges in the Sparta and Paterson samples (figure 11). Relationship between log-width and log-aspect ratio, particularly in the Sparta sample (figure 12), is consistent with the proposed origin of fine fibers from cleavage during abrasion. A similar effect could be the result of comminution of fibril bundles. This may be partly responsible for the observed trend.

High aspect-ratio fibers are thinner, on the average, than are low aspect-ratio fibers. Since fibers of less than about 0.3 micron are invisible to PLM, PLM counts will turn up a lower percentage of high aspect-ratio fibers than will TEM counts. With increasing development of cleavage, this difference in aspect-ratio frequency distribution can be expected to increase. This was observed. TEM aspect ratios tended to be somewhat higher than PLM ratios, particularly in the Sparta sample (LC2).

In the examples studied here, fibrillar structure is probably the result of the development of inhomogeneities in the chain structure of the amphiboles (see Veblen, 1980). Such inhomogeneities are

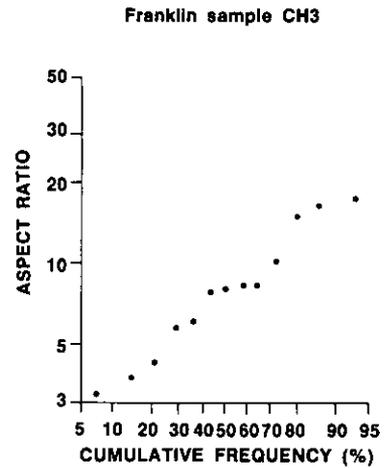
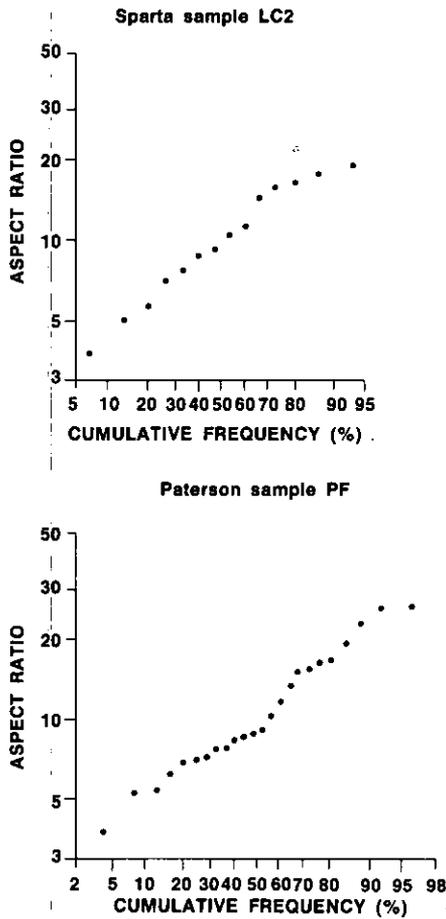


Figure 8. TEM aspect-ratio frequency data for amphibole fiber from two pulverized marble samples (LC2 and CH3) and worn marble chips (PF). Cumulative frequency on log-probability scale.

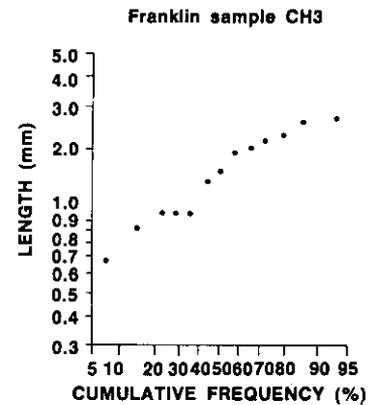
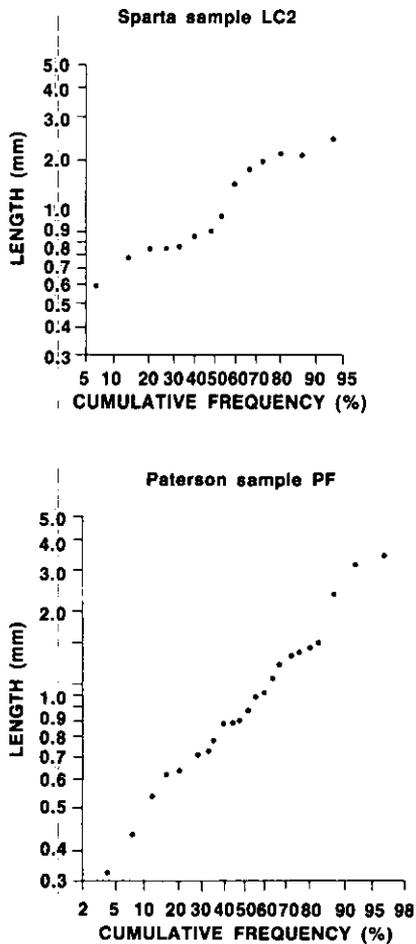


Figure 9. TEM length-frequency data for amphibole fibers from two pulverized marble samples (LC2 and CH3) and worn marble chips (PF). Cumulative frequency on log-probabilty scale.

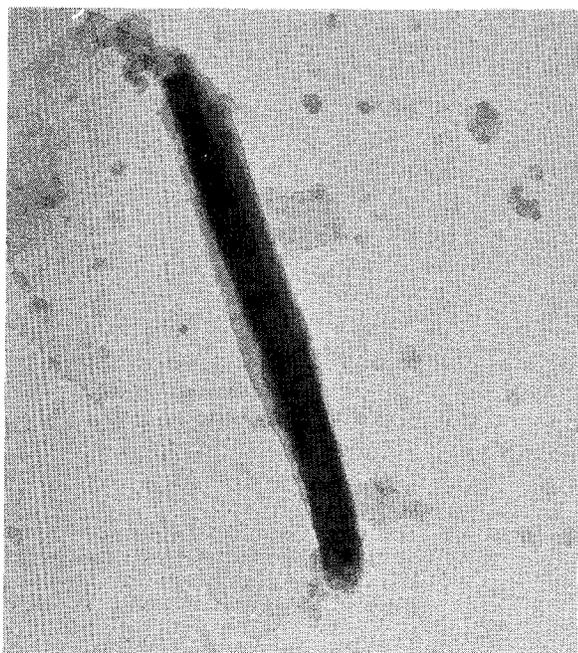


Figure 10. TEM images of amphibole fibers. a) Tremolite fiber showing irregular shape typical of cleavage of prismatic hornblende, 80,000X. b) Hornblende (edenite) fiber showing well developed cleavage typical of acicular amphibole, 39,000X. c) Actinolite fiber showing straight edges and fibrillar development characteristic of semiasbestiform amphibole, 22,000X. d) Tremolite fiber showing fibrillar structure and flexibility of thin fibrils distinctive of asbestiform amphibole 8,000X.

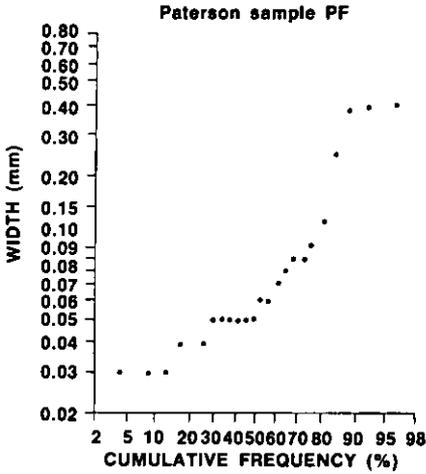
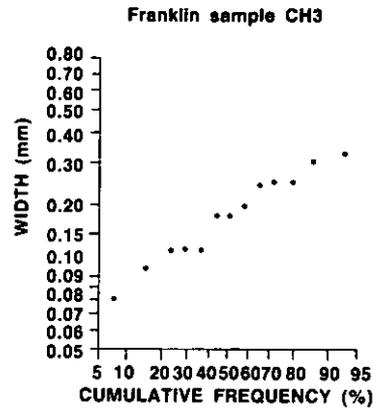
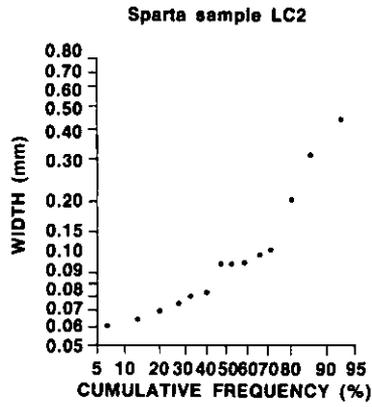


Figure 11. TEM width-frequency data for amphibole fibers from two pulverized marble samples (LC2 and CH3) and worn marble chips (PF). Cumulative frequency on log-probability scale.

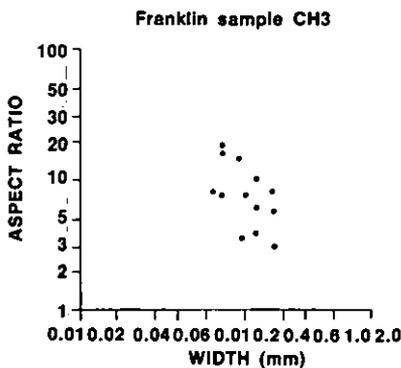
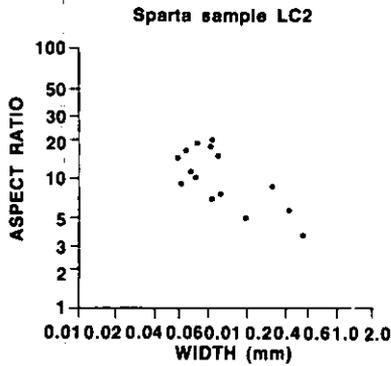


Figure 12. Plot showing relationship between width and aspect-ratio data for TEM measurements from two pulverized marble samples.

manifested as Wadsley defects—lengthwise diffraction contrasts produced under TEM as a result of structural differences in neighboring amphibole chains. Wadsley defects were observed in fibers which also showed signs of fibrillar development, but not in typical cleavage fragments (figure 10). This suggests that the inhomogeneities responsible for these defects are also the cause of fibrillar development.

On the basis of the foregoing, TEM observations support the conclusions reached in previous sections regarding the origin of amphibole fibers in crushed stone samples from the Franklin and Sparta quarries. Most fibers appear to originate from cleavage of amphibole of prismatic to acicular habit. There is evidence of fibrillar structure, and thus of the occurrence of amphibole of acicular-semiasbestiform habit, particularly at Sparta. Separability and flexibility of fibrils was noted in a small and undetermined percentage of fibers from Sparta crushed stone (figure 10), and particularly in the sample of marble chips from Paterson, subjected to weathering and pedestrian traffic. These characteristics indicate that a small portion of the fibers in the Sparta samples are derived from amphibole of semiasbestiform-asbestiform habit. As discussed previously, such fiber may be largely a product of weathering of semiasbestiform amphibole.

Table 5. Zinc and cadmium content of selected samples.

	Zinc	Cadmium	Zn: Cd ratio
Franklin samples			
CH4*	31 ppm	71 ppb	437
CH4*	36 ppm	126 ppb	286
CH6	19 ppm	47 ppb	404
CH8**	22 ppm	58 ppb	379
CH8**	20 ppm	34 ppb	588
Franklin average	26 ppm	67 ppb	419
Sparta samples			
LC1	85 ppm	671 ppb	127
LC4*	74 ppm	628 ppb	118
LC4*	85 ppm	514 ppb	165
LC5*	129 ppm	714 ppb	181
LC5*	140 ppm	757 ppb	185
LC10	200 ppm	1043 ppb	192
LC11	151 ppm	714 ppb	211
LC12**	64 ppm	414 ppb	155
LC12**	68 ppm	485 ppb	140
Sparta average	111 ppm	660 ppb	164
Mineral samples			
Sphalerite (Franklin)**	56.8 percent	0.14 percent	406
Aragonite (Sparta)	0.30 percent	14.9 ppm	201

*Separate grab samples

**Split samples

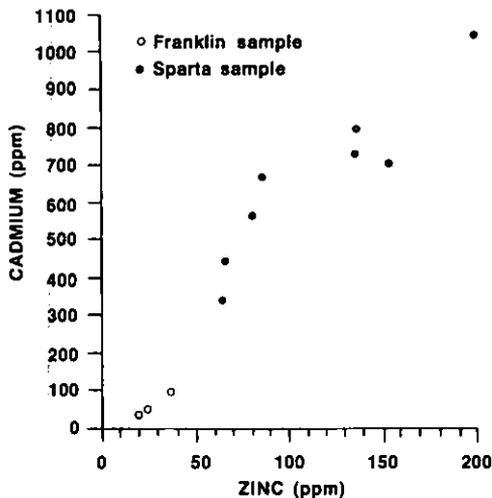


Figure 13. Plot showing relationship between cadmium and zinc concentrations in crushed marble samples.

Cadmium and Zinc Content

Cadmium and zinc determinations are presented in figure 13 and table 5. Cadmium content is of principal interest. Zinc data were obtained mostly for purposes of comparison and as an index of cadmium content. Cadmium averaged 660 ppb at Sparta, and 67 ppb at Franklin. Zinc averaged 111 ppm at Sparta and 26 ppm at Franklin. Zinc to cadmium ratios averaged 164 at Sparta and 419 at Franklin. Analyses of split samples and separate grab samples (table 5) indicate that error in Cd, Zn, and Zn: Cd increase at the relatively low concentrations of these metals found at Franklin.

Cadmium and zinc, being chalcophilic, tend to be associated with sulfur in carbonate rocks (Gong and others, 1977). Analysis of honey-colored sphalerite (ZnS) from a vein at Franklin shows a cadmium concentration of 0.14 percent, and a Zn to Cd ratio of about 406. In a previous analysis (Wedow and others, 1973), 0.15 percent Cd was measured in Franklin sphalerite.

Metalliferous aragonite (CaCO₃) was noted in one crushed stone sample from Sparta (LC1). The mineral occurs as tiny spheroidal grains and aggregates that have a yellowish-white color and fluoresce orange under short-wave ultraviolet light. A visual estimate under the ultraviolet light indicates that this mineral constitutes 1 to 2 percent of the sample. The mineral contains about 0.30 percent Zn and about 15 ppm Cd. This variety of aragonite has not been previously described in the area, although metalliferous aragonites have been described from oxidized zones of zinc ore deposits in other areas (Palache and others, 1951). Such aragonite is invariably of near-surface origin (Palache and others, 1951). Aragonite is deposited elsewhere in the marble of the Franklin area in the zone of oxidation (Frondele, 1972). It is thus probable that this mineral was precipitated at Sparta by either downward-percolating meteoritic water or by ground water.

The average Zn: Cd ratio worldwide in commercial zinc concentrates is about 230 (Page and Bingham, 1973). Zinc ores from the Appalachian region have an average ratio of about 200, from the Mississippi Valley region about 120, and from the entire United States about 150 (Wedow, 1973). The Sparta samples (Zn: Cd = 118-211) are thus in the

range found in typical zones of zinc mineralization. The higher ratio found at Franklin (Zn:Cd = 286-588) is more typical of relatively unmineralized zones.

Zinc mineralization has been described near the contact of marble and gneiss just east of the Sparta quarry and at a lead-zinc prospect known as the Indian Mine (Hague and others, 1956). Sphalerite (ZnS) was the ore mineral in both instances. The results presented here suggest that there is a broad area of low-grade mineralization, which extends into the Sparta quarry, associated with this "Indian Mine." Such broad mineralization is typical of zinc deposits in the region (Wedow and others, 1973).

Environmental Studies

TEM analyses of two water samples are available for asbestos fiber content (as defined by Anderson and Long, 1980) from a small stream that drains the Franklin quarry. These average 1.6 million fibers per liter (MFL) for tremolite-actinolite minerals, and 0.7 MFL hornblende (Puffer and others, 1983). Fiber lengths had an approximately log-normal distribution in the range of 0.3 to 6 microns. This distribution is approximately equivalent to that observed for worn marble chips, suggesting that the fibers may be derived principally from coarsely crushed stone stockpiles and from wear of surface materials on the quarry floor, rather than from erosion of the pulverized stone product.

An analysis of discharge water from the Sparta quarry shows a cadmium content of about 0.025 mg/l (Frenkel, 1982). This is considerably above the potable water limit of 0.01 mg/l (Tucker, 1981). Discharge water at the site is derived primarily from seepage of ground water from the walls of the quarry. The presence of relatively high Cd in the Sparta stone, together with apparent precipitation of Cd-rich aragonite at the site, suggest a natural source for cadmium in the ground water discharge.

DISCUSSION

Asbestos

The results of this study demonstrate the potential for release of regulatory amphibole asbestos fibers from crushed Precambrian marble in New Jersey. A similar potential probably exists in mineralogically similar marbles elsewhere. The extent and consequences of exposure to fibrous minerals that may be present in such products bears further investigation.

The term asbestos in the regulatory sense differs from its mineralogical and commercial meanings. Amphiboles ranging in habit from prismatic to acicular are capable of producing regulatory asbestos fibers and are abundant in igneous and

metamorphic rocks. On mineralogical grounds only material of semiasbestiform or asbestiform habit can be reasonably classified as asbestos. Commercial asbestos has a highly developed asbestiform habit. Distinctions between amphibole habits are very important when drawing parallels between the physical and biological properties of rock-forming amphiboles and commercial asbestos, for which the "regulatory fiber" designation was originally designed. It has been suggested (Wylie, 1979) that the minimum aspect ratio of 3:1 is too low to be applied to rock-forming minerals and that a cutoff of 20:1 would be more applicable. Such a cutoff should, based on the results here, eliminate fibers derived from cleavage of prismatic amphibole, which appear to be biologically inert (Palekar and others, 1979; Smith, 1974), while not failing to include a significant portion of the fiber from truly fibrous amphibole. By virtue of their greater production of high aspect-ratio fibers, semiasbestiform and asbestiform amphibole would be weighted more heavily than acicular amphibole using the 20:1 aspect-ratio cutoff, in keeping with what is known about the relationship between amphibole habit and toxicity (Palekar and others, 1979).

The results presented here need to be interpreted with caution. The total amphibole content values cited for crushed stone samples cited here, for example, should not be construed as amphibole asbestos values. By the same token, the semi-asbestiform and asbestiform amphiboles described should not be presumed to be any different from similar material that is used commercially.

There has been considerable discussion of the relative advantages and disadvantages of various methodologies in asbestos analysis. Phase contrast microscopy is typically the methodology of choice for regulatory work on air samples (Goodwin, 1978), while TEM is the methodology of choice for water samples (Anderson and Long, 1980). Among optical methods, phase contrast microscopy cannot be used to identify individual asbestos minerals, while polarized light microscopy (PLM) can. PLM has the disadvantage of requiring training in optical mineralogy. In addition, fibers are not as readily visualized under polarized light as by phase contrast.

From comparison of PLM with TEM data in this study, it appears that PLM analysis was quite successful in describing amphibole fiber content. The PLM method has advantages over TEM in that a much larger sample aliquot is analyzed (approximately 20,000 times larger in this study) and that fibers can be described in a shorter time interval.

Cadmium and Zinc

Cadmium content in Sparta crushed marble is elevated above normal levels. Since carbonate rocks are an important host for zinc deposits (Clark

and Neeley, 1983), it is probable that pulverized carbonates from elsewhere will have substantially elevated cadmium levels. The use of such limestones for agricultural purposes would constitute an addition of cadmium to soils. This addition would be cumulative, since cadmium is concentrated in soils (Gong and others, 1977). The level of cadmium introduction into food crops from the use of such limestones is unknown, and bears further investigation.

Average cadmium content in 6 sedimentary limestones from Pennsylvania is reported to be 28 ppb, with a median value of 14 ppb, and a range of 7 to 109 ppb. A marble sample from Pennsylvania was reported to contain 129 ppb Cd (Gong and others, 1977). Three commercial pulverized sedimentary limestones from Pennsylvania were analyzed. All contained below the measurement limit of about 25 ppb Cd. These were from the Kittatinny Supergroup, the predominant sedimentary limestone in New Jersey. Similar values for Cd are thus to be expected for most New Jersey sedimentary limestones.

The geochemical association between cadmium and zinc is borne out in this study, and it would appear plausible that zinc content may be used as a "flag parameter" to detect elevated cadmium in crushed stone material, as well as being an index for cadmium in stone from sources where the approximate cadmium to zinc ratio is known. It is interesting to note that the high zinc content of Sparta crushed stone is advertised as a desirable feature, since zinc is a basic nutrient to plants. As noted by Keller (1979), however, when natural sources of zinc are employed for plant nutrition, cadmium may be introduced in the process.

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