MINNESOTA POLLUTION CONTROL AGENCY

COMMENTS ON ASBESTIFORM AND FIBROUS MINERAL FRAGMENTS, RELATIVE TO RESERVE MINING COMPANY TACONITE DEPOSITS.

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ABSTRACT

Given our present state of scientific knowledge and analytical capability, there seems to be no conclusive means by which fibers of cummingtonite-grunerite cleavage fragments derived from the metamorphosed iron formation of the Peter Mitchell Mine and fibers of commercial "amosite" can be distinguished in micron size samples. The average crystal structure and chemical composition of these two types of fibers (cleavage fragments and asbestos) are essentially the same. Consequently, they cannot be distinguished by electron diffraction and x-ray microspectroscopy in air and water samples, although differences in their structural and chemical details may exist. There are no medical data available, to our knowledge, that demonstrate which of the specific properties of amphibole asbestos, or other fibers, are responsible for observed carcinogenic effects. We must therefore conclude that there is no evidence to indicate that any detectable or undetectable differences in the minor structural and chemical details of the two types of fibers has any influence on their harmful biological characteristics.

Our comparison of cummingtonite-grunerite minerals in the Homestake and the Peter Mitchell mines leads to conclusions similar to the above. The average crystal structure and chemical composition of the amphibole fibers produced from these two ores are equivalent. Minor differences in the growth habits of some of the amphiboles has been observed.

Although there are some questions concerning the application of the proposed conclusions of the Homestake study (NIOSH, 1975), its comparison with the Silver Bay area may be justified on the basis of mineralogical similarities. However, we cannot

evaluate the medical applicability of this study. We should emphasize that there are numerous variables that are potentially important in the evaluation of a study of this sort, and that many of these variables are still not understood by scientists. Consequently, all studies of this sort are open to valid criticism.

Although the conclusions of the Homestake report have some applications to the Reserve Mining operation, the difficulties involved in the detailed comparison of the specific properties, and especially, the possible biological effects of amphibole fibers derived from different occurrences of the same mineral should be eventually investigated. We believe that direct evidence concerning the biological effects of the Silver Bay fibers should be preferred over the physical comparison of the fibers with fibers at other localities.

As a result of our examination of analytical facilities at various laboratories involved in the analysis of airborne fiber concentrations in the Silver Bay and Duluth regions, we conclude that most, if not all, of their reported fiber concentrations are minimum values. The lack of exact agreement on duplicate air samples between laboratories results from: fiber loss due to differences in sample transportation and sample preparation; differences in counting procedures; differences between the acceptable levels of amphibole identification; and possible inhomogeneity of samples. Values of airborne fiber concentrations obtained by averaging the results from several laboratories appears to be a less satisfactory approximation to the true concentration then the highest values reported for a given sample.

Attention is called to the current misinterpretation and improper use of certain mineralogical terms in connection with pollution problems. This is apparently responsible for the undesirable confusion concerning the identification and the mineralogy of fibrous amphibole air pollutants. This trend of improper application of mineralogical terms was initiated, in part, in connection with the Reserve Mining Co. trial. Consequently, the Minnesota Pollution Control Agency is in a good position to reverse that trend, by adhering to the proper definition of mineralogical expressions, and thus influencing others to adopt proper usage.

PART A

DISTINCTION BETWEEN FIBERS OF NATURAL ASBESTOS AND OF CLEAVAGE FRAGMENTS

There is considerable confusion concerning the mineralogy of amphiboles and the use of mineralogical expressions in current literature dealing with the amphibole fibers found around Silver Bay and Homestake mines. This confusion originated in the early stages of the Reserve Mining trial and has since propagated to various reports including those of EPA, MPCA, NIOSH, Mt. Sinai School of Medicine, and court transcripts. As a consequence of these usages, an ambiguous terminology is beginning to show up in articles printed in national and international journals of environmental and public health sciences.

Unfortunately, the misuse of some relevant mineralogical concepts and terms are becoming so widespread that it may be extremely difficult to correct them. However, if that is not done, some mineralogical concepts and expressions will have double definitions: one for mineralogists and physical scientiests, and one for use in environmental public health sciences and practices. The continuing use of these double definitions would be most unfortunate as it will undoubtedly lead to additional misunderstanding and conflict between mineralogists and geologists, on one side, and environmental and public health personnel on the other. As the concepts and expressions are mineralogical, the logical solution to this problem would be for the personnel in the second category to restrict themselves to the proper use of mineralogical terms.

The problem of the modified definitions of mineralogical terminology was initiated, at least in part, in connection with the Reserve Mining Company trial. Consequently, we suggest that the Minnesota

Pollution Control Agency make an extensive effort to use the proper mineralogical terminology and influence all associated organizations and personnel to follow suit.

The most frequently misused mineralogical or pseudo-mineralogical terms and expressions include: Asbestiform, asbestos-like, asbestiform minerals, asbestos, asbestos minerals, asbestos fibers, asbestos-like fibers, amosite, amosite fibers, non-commercial asbestos, short-fiber asbestos, amphiboles in the grunerite-amosite-cummingtonite series, etc.

The current misuse of these expressions originated in part from the presumed identity of fibers produced by the Reserve Mining operation and of those produced by breakage of commercial amphibole asbestos. That is, by using an expression in reference to the fibers produced at Silver Bay which includes the word asbestos (or its modification) automatically implies that the fibers are identical to asbestos. For example, the term "asbestiform" in mineralogy refers to the crystallization habit of a mineral, say an amphibole, in a specific type of occurrence. The same amphibole, however, may crystallize in other habits elsewhere. The other habits may be, for example, radiating, acicular, prismatic, massive etc. The current use of "asbestiform" in reference to the cummingtonite-grunerite fibers of Reserve Mining changes the definition to something like: "any mineral which may crystallize as asbestos and/or has fibrous cleavage fragments, with length:width aspects of 3:1 or higher, is asbestiform." If we accept that definition, then we should call jade (the nephrite type) an asbestiform mineral in spite of the fact that it is the toughest known natural substance. Mineralogically, nephrite jade is actinolite-tremolite which frequently crystallizes as asbestos (in fact, the name asbestos was first applied to actinolite asbestos) and if jade is crushed to small enough fragments (micron sizes), it will consist of fibrous cleavage fragments, similar to those found at Silver Bay. The other recognized jade mineral, jadeite, is a pyroxene and would similarly break into fibrous cleavage fragments. Consequently, all jades would be called asbestiform according to that erroneous definition. This illustration is one of the reasons why mineralogists could not accept that definition of asbestiform. The appropriate mineralogical term for the fibers derived from the Peter Mitchell ore is: fibrous cleavage fragments of cummingtonite-grunerite.

The establishment of the exact equivalence of amphibole fibers derived from the breakage of commercial amosite (i.e. natural asbestos fibers)* asbestos and amphibole fibers derived from the crushing of ore materials at Silver Bay is a difficult problem. Two different occurrences of the same minerals, in spite of the identity of their chemical composition and crystal structure, may have differences at the molecular scale (structural defects, cation ordering, domain structures, etc.) which can effect their physical properties. Therefore the problem of establishing equivalence of amphibole fibers derived from natural asbestos and those derived from single crystals (Peter Mitchell pit) requires that we specify at what scale and in what respect that equivalence can be demonstrated, and the detail to which their physical and chemical properties are deemed equivalent.

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* Natural asbestos may be "commercial asbestos" if it is available in sufficient quality and quantity to warrant profitable exploitation.

There is no question that at the scale of a fist-sized specimen, natural asbestos and cummingtonites, in the rocks of the Peter Mitchell ore, are not the same. They differ in many of their physical properties, notably in tensile strength and elasticity for which natural asbestos is well known. These are porperties imparted to asbestos by virtue of its asbestiform habit; that is, a crystallization habit of amphibole (and other minerals) to grow in some situations as bundles of individual fibers (or in some other, yet unknown modified structural pattern) rather than as single crystals.

After both natural amphibole asbestos and ore from Silver Bay have been crushed into aggregates of fibers, the physical properties of the individual fibers are much more similar. The evidence that supports their equivalence at this scale is:

A-1. Very similar or identical chemistry.
A-2. Very similar or identical "average" crystal structures as demonstrated by comparable electron diffraction patterns.
A-3. Very similar or identical optical properties of some fibers in natural asbestos.
A-4. Very similar or identical external morphology.

Comments and discussion of this evidence (1-4) is as follows:

A-1) It seems well established from previous studies that the chemistry of the majority of amphibole fibers from the Reserve Mining operation are within the cummingtonite $(Fe,Mg)_7(OH)_2Si_8O_{22}$ - grunerite $Fe_7(OH)_2Si_8O_{22}$ series. Most commercial "amosite" asbestos from South Africa is in that same mineralogical series, although some commercial blends may contain other amphibole components (e.g. actinolite, anthophyllite). In a similar manner, the cummingtonite-grunerite at Silver Bay includes minor amounts of actinolite and hornblende. Some of the Reserve Mining fibers are even within the range of the iron-magnesium ratio of the grunerite-cummingtonite in the South African "amosite."

A-2) The average or basic crystal structure of a fiber is the fundamental structural pattern or the arrangement of atoms as inferred from x-ray or electron diffraction patterns. On the basis of very similar or identical electron diffraction patterns, all crystallographers who have studied them agree that the basic crystal structures of fibers derived from commercial "amosite" asbestos are identical to that of fibers found in the Reserve Mining operation.

A-3) Samples of natural amphibole asbestos, including "amosite" from Penge, South Africa, break up into individual fibers when ground on a glass slide. Our observations with the optical microscope show that the aggregate of fibers consist of both single crystal cleavage fragments and bundles of fibers (in some cases, it is questionable whether both were asbestos fibers or the former is derived from single crystal components mixed with asbestos fibers). These two types of fibers may be readily distinguished as the single crystal cleavage fragments give uniform inclined extinction angles varying from 0 to 20 degrees depending on crystallographic orientation. These fragments, insofar as we are presently able to determine, have optical properties that are identical to colorless, monoclinic amphiboles studied previously by the same methods from the Peter Mitchell Mine.

A-4) The comparison of amphibole cleavage fragments from the Reserve Mining operation to amphibole fibers derived from commercial "amosite" asbestos again depends on scale. Individual asbestos fibers from a fist-sized specimen are commonly elongated more than 100 to 1, whereas the elongation of fibers in the crushed equivalent is considerably less. Electron microscopy studies made at NIOSH and at Mount

Sinai show that amphibole fibers from crushed amphibole asbestos, from the diseased lung tissue of commercial asbestos workers, and from the Reserve Mining operation cannot be distinguished from one another on the basis of length to width ratio and prismatic cleavage. A possible exception is the apparently more frequent rectangular termination and the square cross section of some "amosite" asbestos fibers, as pointed out by Dr. A. Langer at Mt. Sinai School of Medicine (personal communication).

Upon closer examination of the finer details of the amphibole structure, there are some indications that differences may exist between amphibole fibers derived from asbestos and those which are from single crystals:

B-1. The mechanism responsible for the development of asbestiform habit may be related to unique surface structures and properties of the individual fibers that make up a bundle.

B-2. Electron microscopic studies of "amosite" asbestos fibers reveal the presence of narrow bands of polysynthetic twinning and of triple chains interlayered with the usual double chain structure of the amphiboles.

B-3. Most of the natural asbestos (amosite) fibers have apparent orthorhombic optical properties at a scale of several microns.

B-4. Some natural asbestos contains adsorbed metals and compounds.

Comments and discussion of this evidence (1-4) is as follows:

B-1. The basic problem here is that the fundamental reasons for the development of asbestiform habit are not known. The possibility exists that the individual asbestos fibers possess unique surface properties that enable them to develop as bundles (asbestiform habit) rather than as single crystals. Because of these properties, the individual fibers may energetically prefer the asbestiform habit. The possibility that the two types of fibers may have different surface properties is consistent with basic crystal chemical and crystal physical principles, and must be seriously considered. Unfortunately, there are no experimental studies, to our knowledge, that compare the specific surface structures and properties of these fibers. Such differences, if their existence can be demonstrated, could have an important effect on the relative biological activity of the fibers as suggested by the studies (Allison and Pooly; Langer, et.al., 1974) on the relationship between the biological character and the surface properties of free silica (quartz).

B-2. There is a growing body of evidence to indicate the presence of detailed structural variations, such as stacking faults and Wadsley defects, in individual asbestos fibers (Chisolm, 1971). More recently, Hutchinson, et.al. (1975) have demonstrated that some amosite asbestos fibers contain polysynthetic (100)-twinning on the scale of tens of Ångstroms, and consist in part of triple chain structural units. This twinning pattern can change the surface features (and possible the properties) of the crystals (Hartman, 1963). Unfortunately, a parallel study of the ultra-fine structure of individual cleavage fragments from a non-asbestos source has not yet been conducted, and therefore a direct comparison of the two fiber types on this basis cannot be made.

Simple, non-polysynthetic (100)-twinning of cummingtonite-grunerite is common in single crystals and cleavage fragments, and is easily observed with a petrographic microscope. It has been observed in fibers of the Silver Bay tailings (P. Cook, personal communication) by electron diffraction techniques. However, if it can be proven that all asbestos fibers are characterized by a cyclic repetition of narrow (tens of Ångstroms) twin bands, and that single cleavage fragments (e.g. at Silver Bay) are not, then this may be an important structural difference. Moreover, if it can be shown that the presence of triple chain structures is unique to amphibole asbestos fibers and is absent in single crystal (Silver Bay) fibers, then there will be additional structural evidence that the two fiber types are not exactly equivalent, and that they may have differences in physical properties. It would still remain to be established, however, that these differences have biological significance.

B-3. Although some of the micron sized fibers in "amosite" asbestos have inclined extinctions, the major portion of these fibers studied optically consist of bundles of fibers that still retain asbestiform habit. They are recognized by their "apparent" parallel extinction. These asbestos fibers consist of many individual fibers which have a common c-axis (long direction of the fiber). The a- and b-axes, however, are apparently randomly oriented about the c-axis such that the composite extinction angle becomes zero degrees. This imparts an "apparent" orthorhombic symmetry which is easily distinguished from the single cleavage fragments. The proportion of single crystal cleavage fragments to bundles of fibers seems to depend on the commercial quality of the asbestos, and how finely it is ground. Bundles of fibers recognized on this basis are very rarely, if ever, found at Reserve Mining's operation. It should be noted that a new mineral series, biopyriboles, containing triple chains in its crystal structure has been found recently (Veblen and Burnham, 1975). That mineral is an intermediate phase in the alteration of an amphibole (anthophyllite) to talc. Although this alteration process is not comparable with asbestiform crystallization, the information on the crystal chemistry and physical properties of this mineral may help research toward the understanding of the occasional asbestiform crystallization of amphiboles.

B-4. The different geological and industrial histories of the two types of fibers may result in different surface chemistry which could be important even at submicroscopic dimensions. Natural asbestos fibers may have acquired different metals and compounds, during geologic time which are now held by adsorption, and some of them may be carcenogenic. Various metals have been observed by Roy-Chawdhury (1973), iron oxides by Deer, Howie and Zussman (1963, II, p. 243), and organic compounds, like the well-known carcinogenic 3, 4-benzpyrens, by Harington (1962). No previously adsorbed substances are expected to be on the surfaces of freshly broken cleavage fragments. However, iron oxides, for example, could easily be adsorbed by cleavage fragments in an iron ore-beneficiation plant, such as Silver Bay.

Although the non-equivalence of the fine structural details of the two types of fibers may not be proven, the possibility of differences in the fine structure still remains and cannot be neglected. The recognition of possible differences at the submicroscopic scale between asbestos fibers and cleavage fragments does not necessarily imply that the latter type of fibers may not possess the same or similar harmful characteristics. That is, even if physical differences can be demonstrated, the biological significance of that still needs to be proven. The direct comparison of the Silver Bay and Duluth area with South African amosite asbestos mines, or with amosite asbestos plants, is less satisfactory than comparisons of the former area with other localities where the population is exposed to fibrous cleavage fragments of cummingtonite-grunerite.

PART B

MINERALOGICAL AND PETROLOGICAL RELATIONSHIPS BETWEEN THE HOMESTAKE MINE AND THE PETER MITCHELL MINE

The Homestake Mine is located in the northern part of the Black Hills in a series of steeply dipping Precambrian Metamorphic rocks. Gold was first discovered in this region in 1894 as placer deposits. Lode gold was first discovered in 1875 on the site of the present Homestake property. The Homestake Mine has operated continuously since its founding in 1877 and is now recognized as the largest gold producer in the United States (Connolly, 1974).

Petrologically, the Homestake Mine is uniquely situated for the following 2 reasons:

1. The original chemistry of the sedimentary parent was suitable for the later development of ore bodies and related silicate minerals. This chemistry is almost entirely restricted to the Homestake formation.
2. The temperature achieved during the later Precambrian metamorphism was sufficient to concentrate the gold-bearing ore and to stabilize amphiboles of the cummingtonite-grunerite series.

Regarding reason 1, the Homestake Formation is a relatively thin formation, originally consisting of primary carbonate sediments interlayered with chert or SiO_2-rich beds. According to recent fluid inclusion and stable isotope studies (Rye, 1972), the Homestake ore constituents were introduced during the original sedimentation and later concentrated during the metamorphism. There has been considerable debate over the age and origin of the Homestake deposit, including theories of either a tertiary age (Hosted and Wright, 1923; Noble, 1950) or a Precambrian age (Paige, 1924; Connolly, 1927; Gustafson, 1933).

Rye's (1972) study shows that the Homestake ore body has a metamorphic origin distinctly different than the known tertiary ore deposits. Lead isotope studies (Rye, 1972) establish an age for the Precambrian metamorphism at about 1800 million years.

Studies on the progressive metamorphism of Precambrian sediments in the Homestake area (Noble and Harder, 1948) demonstrate at least three well-defined metamorphic zones which correspond to an increase of temperature from west to east. The Homestake formation and mine are located in the garnet zone or intermediate temperature zone of the sequence. Cummingtonite first appears in this zone, occurring in crudely radial groups, with crystals up to 0.5 mm long. Locally, it makes up as much as 25 percent of the rock and is commonly associated with lesser amounts of green hornblende. The actual ore bodies within the Homestake Mine are found on the limbs and crests of the Homestake anticlinorium, and principally within beds of cummingtonite-chlorite schist. The principle gangue minerals are cummingtonite, chlorite, quartz, biotite, calcite and dolomite (Allsman, 1940, p. 12).

Specific studies of the Homestake cummingtonite have been made by Wayland (1936) who believed that the origin of the cummingtonite was closely related to the occurrence of ore minerals. His optical and chemical examination of 15 cummingtonite specimens from the Homestake Mine and immediate vicinity is summarized in Table 1. The total FeO content of these specimens varies from 21.54 weight percent to 34.45 weight percent. Wayland (1936) describes these cummingtonites as follows:

> *"The cummingtonite occurs as radiating blades or fibers averaging a half a centimeter in length, but occasionally extending several centimeters. It is brownish or greenish-gray, and sometimes shows a slightly silky luster. Its hardness is 5 to 6, and the cleavage is parallel to (110). Cummingtonite in the form of asbestos-like material around quartz has been found; here its fibers may attain several inches in length and are a translucent yellowish gray.*

> *The specific gravity varies from 3.19 to 3.40, increasing with ferrous iron (Table 1).........*
>
> *In thin section the mineral is colorless, or faintly grayish brown. No pleochroism was observed by the writer. The extinction angle Z∧c is from 17° to 24°"*

TABLE 1. PHYSICAL AND CHEMICAL DATA

Sample	Indices			Biref. $\gamma-\alpha$	Extinc. Angle Z∧c	Optic Angle (Thru X)	Optic Sign	Sp. Gr. (Obs.)	Per-cent FeO
	α	β	γ						
hf#1	1.662	1.687	1.702	0.040	18°	80°	−	—	34.45
hf#2	1.665	1.679	1.692	0.027	19	84	±	—	26.61
hf#3	1.662	1.680	1.693	0.031	19	98	±	3.19	27.93
hf#4	1.661	1.682	1.697	0.036	18	86	−	3.40	34.45
hf#5	1.661	1.680	1.692	0.031	19	84	−	—	—
hf#6	1.658	1.672	1.683	0.025	20	94	±	—	24.20
hf#7	1.660	1.679	1.689	0.029	24	70	−	—	29.92
hf#8	1.664	1.687	1.697	0.033	17	85?	−	—	33.05
hf#9	1.653	1.670	1.682	0.029	18	82	−	—	—
frf#1	1.657	1.672	1.683	0.026	20	88	±	—	29.65
frf#2	1.658	1.673	1.688	0.030	19	93	±	3.26	31.10
frf#3	1.669	1.684	1.697	0.028	20	92?	±	—	27.20
R.hf#1	1.663	1.679	1.692	0.029	20	87	±	3.02	21.54
R.hf#2	1.665	1.686	1.698	0.033	18	80	−	—	33.72
R.frf#1	1.672	1.694	1.704	0.032	18	80	−	—	30.40

Avg. $N\gamma$ = 1.693 Avg. % FeO = 29.55

Sherwood (1911) in his analysis of minerals from the Homestake Mine describes cummingtonite* occurrences as follows (p. 746):

> *"...Its composition as shown below (Analyses 44 and 45) agrees with either of the minerals anthophyllite or cummingtonite, and Professor G.D. Louderback, of the University of California, has identified it as cummingtonite by its optical properties, pointing out the very close agreement between the analysis of this and of the type mineral originally described from Cummington, Massachusetts.*
>
> *Owing to the large proportion of ferrous oxide this mineral absorbs oxygen and chlorine very rapidly, and in large proportions if finely crushed. This accounts largely for the consumption of oxygen in the cyaniding of the Homestake tailings,..................................*
>
> *Occasionally it is met in long soft fibers, forming true asbestos. Most of the asbestos examined has been contaminated with quartz, but one specimen from the 1100-foot level contained portions which appeared quite pure, the fibers being fine and silky and varying in color from white to light ash gray, some of them eight inches long (see analysis 45)"*

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* The terms cummingtonite and hornblende are used interchangeably in this article.

Sample :..... oxide wgt. percent	44a	44b	45	46	47	Cummingtonite
SiO_2	52.36	52.77	50.36	45.66	46.8	54.67
Al_2O_3	1.54	1.55	1.86	6.87	5.02	0.27
FeO	33.76	34.02	34.62	31.40	33.0	27.81
MnO	0.45	0.45	0.62	---	0.31	0.80
MgO	8.10	8.16	9.86	9.20	9.50	13.66
CaO	0.94	0.95	---	1.04	1.16	0.99
Na_2O	---	0.40	0.74	0.50	---	0.05
K_2O	---	---	---	0.73	---	0.06
H_2O	1.68	1.70	---	0.14	---	1.27

Sample descriptions:

44a: 800 ft. level. Light brownish white, in masses of small radial aggregates, containing a little pyrrhotite.

44b: same as 44a but without pyrrhotite

45: 1100 foot level. Long-fibered white asbestos, silky, free from quartz.

46 and 47: Dark impure masses of radiating "hornblende". Greenish black. Appears to contain both chlorite and biotite with iron oxide.

cum: cummingtonite from Peter Mitchell Mine (submember L) (Gunderson and Schwartz, 1962, p. 76)

Gustafson (1933) in his study of the metamorphism of the Homestake gold-bearing formation (his Harvard Ph.D. thesis, 1930), describes the formation as (p. 128):

> *"...a laminated aggregate of beds of quartz-cummingtonite-biotite schist, containing locally subordinate garnet, chlorite, and carbonate; of quartz-carbonate schist with subordinate biotite and chlorite; and of chlorite-quartz schist which is commonly garnetiferous.*
>
> *The dull greenish or brownish amphibole, cummingtonite, with characteristic fibrous, radiating texture is a useful diagnostic mineral for identifying the formation in the mine.*
>
> *...cummingtonite is plentiful in most occurrences in the mine and along the limb of the Homestake Formation extending Northeast from the mine; carbonate is correspondingly less abundant, and quartz pods are less conspicuous."*

Gustafson also describes the cummingtonite that occurs within the Homestake Mine as (p. 137):

> *"Cummingtonite occurs as brownish to greenish tufts of radiating fibers that may measure several centimeters in lenth, although the majority do not exceed 5 mm."*

and later on pages 138 and 139,

> *"The fresh Homestake mineral is colorless to faint brown and non-pleochroic in thin section......the fibers of cummingtonite are repeatedly twinned on (100). Twin individuals average 0.2 mm in thickness.*
>
> *Cummingtonite was recrystallized for a few inches around some quartz masses into a silky asbestiform substance. Fibers of this material in some cases are four to six inches long. Chemical analysis and optical data prove this to be cummingtonite. In one instance, however, slightly lower indices were measured, and the mineral was too finely fibrous to tell whether it was orthorhombic or monoclinic."*

Gustafson, like other writers who have studied the relationships between the actual ore and presence of cummingtonite, concludes that where one is found, so will the other. In particular, locations where cummingtonite schist is in contact with quartz masses and where chlorite is locally developed are commonly enriched in sulfides and gold. In contrast, gold and metallic minerals are rare in areas where the cummingtonite-quartz association is not found.

Studies on the mineralogy and petrology of the Biwabik Iron Formation and the Peter Mitchell Mine have been reviewed extensively in previous court proceedings (1973) and will not be repeated here. The primary references, however, may be found in French (1972), Gunderson and Schwartz (1968), and Bonnichson (1974).

French (1972) outlines the general aspects of the metamorphism. He defines four zones, labelled Zone 1 (greater than 10 miles from the Duluth Complex), Zone 2 (2.5 to 10 miles from the contact), Zone 3 (1.5 to 2.5 miles from the contact) and Zone 4 (within 1.5 miles from the contact). Minerals of the cummingtonite-grunerite series are restricted to Zones 3 and 4, and to Iron Formation with the appropriate bulk chemistry. It follows that cummingtonite and grunerite should not generally be found within the Gunflint Iron Formation west of the Erie and Babbitt operations because the temperatures attained during rock metamorphism were not sufficiently high.

Gunderson and Schwartz (1962, p. 83) state that with the exception of quartz, cummingtonite is the most abundant silicate in the metamorphosed iron formation. The optical properties of cummingtonite, all of which are considered identical by Gunderson and Schwartz, are as follows:

> *"Positive elongation (length slow) to amphibole cleavage*
> *maximum extinction angle $c \Lambda z$ = 16°*
> *Strong birefringence (Ca. .037)*
> *Weak dispersion (r v, rhombic and inclined)*
> *Polysynthetic twinning parallel to (100) is common"*

"Average" refractive indices are given by the above authors as:

$\eta^{1}_{\beta} = 1.658$ and $\eta^{1}_{\gamma} = 1.677$

French's (1968) study of the progressive metamorphism of the Biwabik Iron Formation estimated the compositions of 25 grunerites and cummingtonites from his zones 3 and 4 (p. 65) from measured refractive indices. The range of Fe/(Fe + Mg) values for zone 4 (closest to the Duluth Complex contact) is from 0.53 to 0.89 with an average of 0.73. The range of values from Zone 3 (1.7 to 2 miles from the contact) is from 0.63 to 0.85 with an average of 0.77. These data are given in Table 8 of French (1968).

Briefly, the overall petrologic settings of the Peter Mitchell Mine and the Homestake Mine are similar. The Precambrian sedimentary rocks in the Mesabi Range have been progressively metamorphosed from west to east with temperature increasing to the east toward the contact with the Duluth complex of igneous rock. The latter was intruded approximately 1,100 million years ago and supplied the thermal energy for rock metamorphism.

French, 1968:

Table 8. Refractive Indices and Estimated Compositions of Cummingtonite-Grunerite Amphiboles from the Metamorphosed Biwabik Iron-formation (Zones 3 and 4) *

No.	D†	n_γ	$\frac{Fe^{2+}}{Fe^{2+}+Fe^{3+}+Mg+Mn}$	Associated Minerals
		Zone 3		
125	2.01	1.707	0.79	M,Q, (St?)
70	1.94	1.701	0.73	M,Q,C,A
138	1.93	1.713	0.85	M,Q
72	1.92	1.702	0.74	M,Q,C,A
95A	1.90	1.704	0.76	M,C,A, (Q?)
95B	1.90	1.704	0.76	same as 95A
96A	1.90	1.704	0.76	M,C,A, (Q?), (Mi?)
96B	1.90	1.702	0.74	same as 96A
74	1.78	1.713	0.85	M,C, (Q)
124	1.75	1.690	0.63	M,Q,A, (Mi), (St)
140	1.71	1.712	0.84	M
141	1.71	1.702	0.74	Fay?
Average		1.705	0.77	
		Zone 4		
75	1.57	1.718	0.89	M,Q, (St?)
76	1.57	1.717	0.89	M,Q,C
77	1.57	1.715	0.87	Q,C
131	1.53	1.696	0.69	M,Q,H, (A?)
136	1.47	1.707	0.79	none
133	1.38	1.700	0.73	M,Q,Hd,Fe-Hbd
150	1.36	1.679	0.53	M,Q
135A	1.28	1.712	0.84	none
80	1.24	1.696	0.69	Q,Fe-Hbd
99	1.15	1.712	0.84	M,Q,Fe-Hyp, (C?)
82	0.73	1.682	0.56	M,Q, (Bio?)
83	0.73	1.680	0.54	M,Q,Fe-Hbd
88	0.39	1.691	0.64	M,Q,Fe-Hyp
Average		1.700	0.73	

* A key to abbreviations for minerals in the Biwabik Iron-formation is given in Table 3.
† Distance in miles from the Duluth Gabbro contact.

PART C

EVALUATION AND COMMENTS ON THE NIOSH HOMESTAKE REPORTS

The following discussion makes no attempt to cover all aspects and implications of the two NIOSH reports referenced on the cover page. Our comments here are restricted to mineralogical questions, matters of sample handling and analysis, and to the scientific logic and reasoning on which conclusions are based. Our comments are based on a critical reading of appropriate documents, and on personal communication (oral) with John Dement, R.A. Lemen and J.K. Wagoner, all of NIOSH and authors of the reports discussed here.

Before proceeding, we must comment that a purely scientific evaluation of this and similar reports is not an easy task. The complexity of the crystal structures and the chemical and physical properties of extremely small mineral fragments is enhanced by an even more complex human physiology. Mineralogical research has been limited, until recently, to much larger-sized minerals, and to the consideration of average crystal structures and average chemistry. Our knowledge of submicroscopic variations in the structures and properties of mineral fragments from a purely mineralogical point of view is very limited. The medical sciences seem to have corresponding difficulties in explaining the nature of the undesirable biolgical processes related to fibrous air polluting substances (see the summary of hypotheses given by Reeves, et al., 1974). Ultimately, science will be faced with answering precisely how a submicroscopic mineral fiber interfaces on an atomic scale to complex biological systems. It is unfortunate that at this time there is very little information on the relationship between minor chemical and structural variations and degrees of health effects.

Some of the major problems and sources of error we have detected in the course of this study apply not only to the NIOSH Homestake studies but to any other study that atttempts to correlate observed fiber concentrations to occurrence of disease. These are: (1) obtaining truly representative air or water samples of fiber pollutants is difficult. The samples are usually collected over a short period of time relative to the duration of human exposure; (2) analysis of the samples is time consuming, expensive, and calls for highly qualified expertise. Because of the time constraints often imposed by the health issue itself, analytical shortcuts are commonly employed that normally would not be; (3) present methods of fiber analysis require that only a small portion of a given filter paper be used to extrapolate to total fibers in the filter paper and from that to ambient air concentrations; (4) present methods of fiber analysis lead to substantial losses of fibers, particularly in the smaller range sizes; (5) because of the many variables, either considered or not recognized by the researcher, an even more difficult problem is determining which pollutant is responsible for the observed excess of disease (judging from our readings and discussions, the list of known carcinogens is growing rapidly); (6) once a carcinogenic mineral is identified, it is still questionable whether the same mineral is carcinogenic at other localities as well, until we know the ranges of major and minor chemical and structural variations of its carcinogenic character; (7) the assessment of the health effects caused by a combination of environmental faactors, or the differences in the biological role of a particular pollutant depending on its chemical and physical millieux is an extremely difficult problem and one for which no conclusive answer may be given.

The principal conclusion reached by the authors in the two Homestate reports is that an excess risk of respiratory-tract cancer exists among workers of the Homestake Mine due to inhalation of airborne amphibole fibers, and because of this, the measured levels of exposure should be considered unsafe. The following discussion will first consider those factors that support the validity of these conclusions, and secondly those that argue against them.

Factors that Support the Conclusions:

1. Section B of the present report demonstrates that the principal amphibole found in the Homestake ore is in the cummingtonite-grunerite series, and that the major proportion of it consists of individual cleavage fragments rather than asbestiform material. Available chemical analyses show that the average chemistry is similar both to commercial "amosite" asbestos and to cleavage fragments found in the Peter Mitchell pit. We must conclude on the basis of the fundamental mineralogical equivalence of the fibers that the comparison of the Homestake Mine and the Peter Mitchell Pit is valid.

2. Given the available body of raw data, there does appear to exist an excess risk of respiratory tract cancer among Homestake workers. This appears to be true regardless of whether the white male population of South Dakota or the U.S. white male population is used as the control group.

3. Given the above conclusion (2), the authors seem to give adequate consideration to alternative explanations insofar as the available data allows. Radon daughter levels, trace metal concen-

trations, silaca dust content, cigarette smoking, and amphibole fiber inhalation were among these. Although none of these parameters may be singled out as the sole cause of the observed excess of the disease, the conclusion that exposure to small ($<5\mu$) amphibole fibers represents a prominent variable appears to be valid.

4. The analytical procedures employed by the NIOSH group based on our own evaluation of their laboratory procedures are among the best available. Considerable care was taken to count all fibers in the airborne dust samples, and to record both electron diffraction patterns and energy dispersive x-ray spectra on at least 20% of the fibers counted. The U.I.C.C. amosite and a Smithsonian grunerite were employed as standards for comparison. Because of the probable loss of some fraction of the smallest fibers ($<1\mu$ length) during the acetone vapor dissolution process, the airborne fiber concentrations in the two NIOSH reports must be considered minimum values.

5. In spite of the loss of small fibers, the NIOSH authors convincingly show that 90-95% of the observed fibers are less than 5μ long. Their conclusion that the OSHA "1972" standard of 2 fibers/cc longer than 5μ may be inadequate is well documented.

6. A major point of emphasis in the NIOSH reports is that safe levels of amphibole fiber concentrations have not been established. Only unsafe levels can be determined from careful morbidity and mortality studies of exposed populations. The authors clearly recognize this fact in their attempt to establish an unsafe level. Even if their attempt is deemed inconclusive, there is no basis to conclude that observed levels of exposure in the Homestake Mine should be considered safe.

7. There are several additional supportive arguments made by the NIOSH authors for which we are not qualified to evaluate. It should be noted that the main report (I) was presented at an international conference that was apparently well-attended by industrial representatives. Plans for the formal publication in the Proceedings of the New York Academy of Sciences along with discussion and reply have been made. The NIOSH authors seem quite confident that their study will stand up to any professional criticism.

Factors that Argue Against the Conclusions

1. The ideal choice of the "control group" should be such that it is comparable with the study cohort in all respects except for the absence of the factor(s) concluded to be responsible for the excess disease. Such a control group may not be always available, however. The NIOSH comparison of a mining population with a primarily agricultural population is far removed from the ideal. The first control group, used in the preliminary version of the report, was the U.S. white, male population, in the appropriate age group. The excess rate of malignant respiratory diseases was 2.5 in that comparison. That was then raised to 3.7 when the South Dakota white, male population was used for control. If we assume that the U.S. white male population is a better control, because it contains a higher percentage of industrial workers then the change in the rate of excess disease (2.5 to 3.7) indicates that the closer we get to the ideal control group the smaller that rate becomes. The NIOSH reports do not demonstrate what that rate would be if the Homestake miners were compared with

other miners working in comparable environment except for the absence of fibrous cummingtonite-grunerite cleavage fragments.

2. The author's improper use of the mineralogical terminology causes some confusion. In fact, provides a good illustration of the problems caused by the improper use of accepted terminology. They identify observed grunerite (but not cummingtonite and other amphiboles) as an asbestiform mineral and equate it with "amosite." As noted earlier, asbestiform cummingtonite-grunerite is known to be present in the Homestake Mine (Sharwood, 1911; Gustafson, 1933; Wayland, 1936; Roberts and Rapp, 1975, etc.), consequently, their report could be interpreted in either of the following ways:

(a) The authors used the proper mineralogical terms and were referring to truely asbestiform grunerite as the material responsible for the excess rate of disease. In that case, their conclusion is not transferable to the Peter Mitchell ore where asbestiform cummingtonite-grunerite is present only in negligible quantity (if at all).

(b) The authors did not use the proper mineralogical terms and have substituted the definition of a "fiber" for asbestiform, and further restricted that to fibers of a certain range of composition. In that case they did not distinguish between natural asbestos and fibrous cleavage fragments. (Such distinction between the two types of fibers should be made during the macroscopic and optical microscopic examination of the ore as it cannot be easily done with the electron microscope.) Consequently, we cannot conclude from their reports which one of the two types of fibers is responsible for the excess rate of disease. We can only assume that they consider the two types of fibers equivalent.

3. There are several other minerals in the ore which are not yet considered to be carcinogenic but may soon become suspects. Some of these are micas and chlorites, iron oxides and carbonates, and sulfides of arsenic and other metals. Micas and chlorites are layer silicates and as such they are similar to talc. The known carcinogenic character of talc was attributed to asbestos, usually present in talc ore and talc products. Recently, it has been shown that talc itself may be carcinogenic (Henderson, et al., 1974, 1975). Iron oxides are also known to be carcinogenic (Faulds, 1957, Roussel, et al., 1964, Boyd et al., 1970) and may be even more so when associated with silica (Campbell, 1940, Faulds and Stewart, 1960). There is, however, no similar information available for iron carbonates. Arsenic metal and certain arsenic compounds are considered carcinogenic but there is no direct information on arsenopyrite. Dr. Dement may be correct that the high 5-6µg/cm^3 arsenic readings given in the preliminary version of the NIOSH report are misleading as they "did not represent exposure to individual miners and should not be considered pertinent" (December 15, 1975 review, Rockville, Maryland), and that "arsenopyrite is a very stable compound" (deposition, November 24, 1975, p. 47), compared to known carcinogenic compound such as arsenic trioxide.

4. There are a large number of factors which comprise the total environment of an underground mine. The biological affects of many of these factors are as yet unknown. Examples include: the less than ideal ventilation in underground drifts, and especially in cross cuts; the composition and reaction products of blasting fumes and other exhausts; the character and composition of mine

waters; the effect of occasional mechanical failures in the ventilation systems; consequent changes in the underground environment as mining operations move to mineralogically different sections; and changes in the mining operations and conditions (that is, during the period when some members of the study cohort were employed in underground mining). The importance of changes in mining operations and conditions may not be fully unknown. For example, up till 1970 mercury was used in the amalgamation of the ore which caused some concerns. The company made improvements in contolling dust levels and a major improvement in the ventilation system was initiated in 1970 (Connolly, 1974).

SUMMARY AND DISCUSSIONS

(1) Although there is no conclusive evidence available today for the demonstration of differences in the physical properties of micron-sized fibers of natural asbestos and cleavage fragments of the same mineral of identical composition, there is no conclusive evidence to prove the contrary either. Even though differences may exist, there is no evidence to indicate that one type is less harmful than the other, nor that they are equally harmful. Current studies on free silica grains imply that minute variations of surface properties may be coupled with changes in biological response (Langer and Rohl, 1974).

(2) There is an extensive range of observed chemical variations in the cummingtonite-grunerite series of amphiboles. The most obvious of these is the variation in the ratio of iron to magnesium. In spite of the varying Fe/Mg ratios, the basic crystal structure of the mineral is constant. However, there are minor changes in the crystal structure associated with different Fe/Mg ratios, such as variable rotation of the SiO_4 tetrahedra, and different degrees of distortion of the M IV cation sites. These minor structural features can affect the stability of the crystal structure and the consequent physical properties to some degree. Many cummingtonite-grunerites contain other cations (e.g., Ca, Mn) in Fe, Mg octahedral sites and some may contain small quantities of other cations in Si tetrahedral sites (e.g., Al, Fe). Even minor substitutions of that nature can affect the chemical-physical properties of the mineral.

(3) The geological history of amphiboles can also modify the small-scale chemical and physical properties of individual

fibers. Amphiboles that exhibit exsolution phenomena or replacement relationships with other primary minerals (like fayalite, for example, at Peter Mitchell Mine) have differences in physical and physico-chemical properties (e.g., Brady, 1974; Klein, 1964; Ross, et al., 1969). Another example is the fibrous cummingtonite described by Bonnichsen (1969) and the asbestiform cummingtonite from the Peter Mitchell property presented in court (November 14, 1975) by Dr. Colin Harwood. This material has unique characteristics. The fibrous cummingtonite is apparently a late crystallization product in the Mesabi Range and occurs in narrow veins. We have examined the samples collected by Dr. Harwood near and outside the edge of the Peter Mitchell pit. These fibers are reasonably flexible and may be called asbestiform. However, they have low tensile strength, are unstable and lack the characteristic orthorhombic optical properties of asbestiform fibers (some fall apart and break into tiny fibrous fragments just by a slight touch of the needle). Another demonstration of the importance of geological history on the properties of minerals can be taken from the South African "amosite." Fresh amosite fibers are ash gray. Some fibers, however, have a reddish color due to the presence of iron oxides on the fiber's surface (Deer, Howie, Zussman, 1963, p. 243; Roy-Chowdhury, et al., 1973)

(4) Minor variations in the physical and physico-chemical properties of amphibole fibers due to differences in crystallization habit (e.g., asbestiform); to differences in chemistry (Fe/Mg ratio, minor substitutions); and to unique geological history (replacement, alterations, etc.) can either be demonstrated or anticipated. The questions of: (1) whether these differences are associated with any change in biological effects, and (2)

what are the nature and extent of these changes, and (3) what are the ranges of physical and chemical properties of the dangerous varieties, are questions which cannot be answered today.

(5) Throughout this report, we have attempted to objectively represent the scientific facts that bear on the overall problem. At present, it does not seem possible to identify which of the many properties, singly or collectively, are responsible for fiber-related disease. If the fibrous morphology and average crystal structure and chemistry of cummingtonite-grunerite prove to be the sole responsible properties, then the details of the crystal structure and minor variations in chemistry may be neglected. On the other hand, if it can be shown that the gross morphology and average crystal structure and chemistry alone are not the responsible properties, then the effects of minor variations summarized in points (1), (2) and (3) must be examined more carefully.

(6) The disparity of the fiber concentrations reported by different laboratories (e.g., Illinois Institute of Technology Research Center in Chicago, NIOSH in Cincinnati, Mount Sinai School of Medicine in New York, McMaster University in Hamilton, and National Water Quality Laboratory in Duluth) for the same air quality samples (i.e., split samples) is due in part to preparatory and counting procedures. It seems clear that all these laboratories are reporting conservative figures, that is, minimum fiber concentrations, and that the minimum values vary between laboratories. It appears safe to say that, in general, the average value of the data reported by several laboratories is probably not the best approximation of true

fiber concentration. The maximum value reported by any one of these laboratories is probably closer to the truth.

(7) It is recommended that the mineralogical nomenclature recently introduced and currently used in connection with fibrous air and water pollutants be changed to conform with the appropriate mineralogical definitions. As the misuse of these expressions was, in part, initiated in connection with the Reserve Mining trials, the Minnesota Pollution Control Agency, as a Minnesota agency, is in an excellent position to assume a leading role in correcting this situation by using the proper nomenclature.

RECOMMENDATIONS FOR ADDITIONAL STUDIES

These recommendations are proposed for future and long range studies to develop a more fundamental and broader understanding of the problem. Consequently, they should not be considered as suggested conditions for any decision to be made in the near future concerning the Reserve Mining Co. operations.

1. It has become apparent during the compilation of this report that several scientific questions must remain unanswered because of insufficient knowledge concerning the formation of minerals with asbestiform habit. A thorough study should be made, not only for amphiboles but for other minerals like minnesotaite and talc which are known to crystallize occasionally in asbestiform habit.

2. Additional studies are needed on the surface structures and properties of amphibole fibers both as a function of natural growth and of forceful fracturing. This is a necessary first step if science is ever going to understand how amphibole and other fibers interface on an atomic scale with biological systems.

3. Theoretical selected area electron diffraction patterns for all common orientations of single and twinned crystals of amphiboles and other minerals of concern should be determined and tabulated. Due to the complexity of interpretations, this is necessary if unambiguous routine interpretations of diffraction patterns are going to be made. These should be available to all laboratories engaged in fiber counting and analysis.

4. Additional direct comparative studies of Silver Bay amphiboles and standard amosite should be made. Fundamental and

systematic x-ray and electron diffraction, and optical microscopic studies can and should be conducted.

5. The known and feasible variations in the chemical and physical properties of cummingtonite-grunerite with variations in: (1) Fe/Mg ratios, (2) substitutions in the octahedral and tetrahedral sites, (3) detailed crystal structures, and (4) crystallization habit and geological history, should be studied. As soon as more reliable data are available, limits of permissible variations in the above four categories could be established, within which the consequent risks in chemical and physical properties are negligible. With the availability of such data, a simple and quick method could be designed to express the degree of comparability of cummingtonite-gruneritesat different locations. Similar schemes could,of course,be designed for other minerals as well.

6. Lastly, it must be recognized that the fundamental question of whether or not there exists an imminent health hazard in the Silver Bay region cannot be fully answered on the basis of scientific arguments andat mineralogical comparisons. It seems that a more dependable answer to the health issue would be: (1) a thorough mortality and morbidity study of Reserve Mining workers and general population at Silver Bay and Babbitt; and (2) animal studies using non-asbestiform cummingtonite-grunerite fibers, preferably that obtained from the Reserve Mining Co. tailings at Silver Bay. These seem to be the best ways, at present, to demonstrate the biological characteristics of cummingtonite-grunerite cleavage fragments in the Duluth-Silver Bay area. It should be kept in mind, however, that possible negative results of such studies may not be conclusive because of the long incubation period of some asbestos related diseases and of other inherent difficulties.

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APPENDIX I

DEFINITIONS AND DESCRIPTIONS OF RELEVANT MINERALOGICAL TERMS AND EXPRESSIONS

DEFINITIONS

After: Glossary of Geology. American Geological Institute, 1972 (2nd print, 1973)

in pages:

41 ASBESTOS: *(a) A commercial term applied to a group of highly fibrous sillicate minerals that readily separate into long, thin, strong fibers of sufficient flexibility to be woven, are heat resistant and chemically inert, and possess a high electric insulation, and therefore are suitable for uses (as in yarn, cloth, paper, paint, brake linings, tiles, insulation, cement, fillers, and filters) where incombustible, nonconducting, or chemically resistant material is required. (b) A mineral of the asbestos group, principally chrysotile (best adapted for spinning) and certain fibrous varieties of amphibole (ex. tremolite, actinolite, and crocidolite). (c) A term strictly applied to the fibrous variety of actinolite.---Syn: asbestus; amianthus; earth flax; mountain flax.*

321 HABIT [CRYST]: *The characteristic crystal form or combination of forms, including characteristic irregularities of a mineral.*

41 ASBESTIFORM: *Said of a mineral that is fibrous, i.e. that is like asbestos.*

41 ASBESTINE adj.: *Pertaining to or having the characteristics of asbestos.--n. A variety of talc; specif. agalite.*

5 ACICULAR [CRYST]: *Said of a crystal that is needlelike in form. Cf: fascicular; sagenitic.*

258 FIBROUS: *Said of the habit of a mineral, and of the mineral itself (e.g. asbestos), that crystallizes in elongated thin, needle-like grains, or fibers.*

265 FLEXIBLE: *Said of a mineral, the tenacity of which allows it to be bent without breaking but without returning to its original form; e.g. talc.*

22 AMPHIBOLE: *(a) A group of dark, rock-forming, ferromagnesian silicate minerals closely related in crystal form and composition and having the general formula:* $A_{2-3}B_5(Si,Al)_8O_{22}(OH)_2$, where A = Mg, Fe^{+2}, Ca, or Na, and B = Mg, Fe^{+2}, Fe^{+3}, or Al. *It is characterized by a cross-linked double chain of tetrahedra with a silicon:oxygen ratio of 4:11, by columnar or fibrous prismatic crystals, and by good prismatic cleavage in two directions parallel to the crystal faces and intersecting at angles of about 56° and 124°; colors vary from white to black. Most amphiboles crystallize in the monoclinic system, some in the orthorhombic or triclinic systems; they constitute an abundant and widely distributed constituent in igneous and metamorphic rocks (some are wholly metamorphic or secondary), and they are analogous in chemical composition to the pyroxenes. (b) A mineral of the amphibole group, such as hornblende, anthophyllite, cummingtonite, tremolite, actinolite, reibeckite, glaucophane, and arfvedsonite. (c) A term sometimes used as a syn. of hornblende.--Etymol: Greek amphibolos, "ambiguous, doubtful," in reference to its many varieties.*

27 AMOSITE: *A commercial term for an iron-rich, asbestiform variety of amphibole occurring in long fibers. It may consist of an orthorhombic amphibole (anthophyllite or gedrite) or of a monoclinic amphibole (cummingtonite or grunerite).*

126 CHRYSOTILE: *A white, gray, or greenish mineral of the serpentine group:* $Mg_3Si_2O_5(OH)_4$. *It is a highly fibrous, silky variety of serpentine, and constitutes an important type of asbestos. Not to be confused with chrysolite. Cf: antigorite. Syn: serpentine asbestos; clinochrysotile.*

166 CROCIDOLITE: *A lavender-blue, indigo-blue, or leak-green asbestiform variety of riebeckite, occurring in silky fibers and in massive and earthy forms. Syn: blue asbestos; krokidolite.*

276 FRACTURE [MINERAL]: *The breaking of a mineral other than along planes of cleavage. A mineral can be described in part by its characteristic fracture, e.g. uneven, fibrous, conchoidal.*

131 CLEAVAGE [MINERAL]: *The breaking of a mineral along its crystallographic planes, thus reflecting crystal structure. The types of cleavage are named according to the structure, e.g. prismatic cleavage. Cf: fracture [mineral]; parting [mineral].*

132 CLEAVAGE FACE: *In a crystal, a smooth surface produced by cleavage.*

132 CLEAVAGE FRAGMENT: *A fragment of a crystal that is bounded by cleavage faces.*

567 PRISMATIC CLEAVAGE: *A type of crystal cleavage that occurs parallel to the faces of a prism, e.g. the* [110] *cleavage of amphibole.*

567 PRISM [CRYST]: *A crystal form having three, four, six, eight, or twelve faces, with parallel intersection edges, and which is open only at the two ends of the axis parallel to the face intersection edges.*

518 PARTING [CRYSTAL]: *The breaking of a mineral along planes of weakness caused by deformation or twinning: e.g. garnet. Cf: cleavage* [*mineral*].

DESCRIPTIONS OF SOME IMPORTANT MINERALOGICAL TERMS AND EXPRESSIONS

CRYSTAL HABITS

Most minerals are known to occur in a number of different crystal habits. That is, the same mineral may crystallize: (1) in relatively large distinct crystals of various characteristic shapes and forms; (2) in certain types of aggregates or groups of crystals; or (3) in fine-grained, polycrystalline masses. There are several terms used by mineralogists to describe these different crystal habits. For example, single crystals may be: equidimensional, tabular, platy, acicular, fibrous, etc.; groups of crystals may be: columnar, reticulated, radiating, etc.; and fine-grained massive minerals may be described as granular, compact, banded, botryoidal, etc.

Minerals crystallizing in the habits of radiating or columnar groups of acicular or fibrous crystals may be said to have asbestiform habit, provided that they possess some of the unique physical properties of asbestos (e.g. tensile strength, flexibility). Several common silicates, when occurring in asbestiform habit, may be utilized in industry as asbestos, and may have a special variety or commercial name (amosite, crocidolite, prieskaite, montasite, bedenite, byssolite, etc). There is only one asbestiform mineral which is considered to be a distinct mineral and not just a variety of another mineral. That is chrysotile. Although it has the same chemical composition and basic crystal structure as antigorite or lizardite, in chrysotile the layered structure is not planar but it is curled up as the sheet in a scroll. That variation of the structure is considered to be sufficiently unique to warrant its recognition as a distinct species.

Although the basic physical and chemical properties of the single crystals of minerals are constant, some of their specific properties may be strikingly different when they occur in different habits. This point can be well demonstrated with minerals in the actinolite-tremolite series. All minerals in these series may occur in asbestiform habit. The same minerals may also crystallize in small, sturdy, prismatic crystals. They may also crystallize in a massive habit, in which the individual crystals are of microscopic size. In this massive habit the actinolite-tremolite minerals may constitute the toughest natural substance known to man. Its variety name is nephrite, and is one of the two accepted jade minerals. That is, the same mineral(same crystal structure and chemical composition) may occur in contrastingly different forms such as asbestos and jade.

AMOSITE

An ash-gray, asbestiform mineral occurring in the Lydenburg and Petersburg Belt in Transvaal, South Africa (Penge, Amos mines), named "amosite" by A.L. Hall in 1918:

On the mode of occurrence and distribution of asbestos in the Transvaal. Trans. Geol. Soc. So. Africa. XXI, 1-36.

M.A. Peacock analyzed two specimens of that South African asbestiform mineral:

The nature and origin of the amphibole-asbestos of South Africa. Amer. Mineral. 13 (1928) 241 - 285.

and concluded that this mineral is not a distinct species but is probably ferroanthophyllite:

p. 262

> Considering firstly TABLE IX, it will be seen that there is a strong general similarity in the optical properties of anthophyllite, ferroanthophyllite, amosite and gedrite; and that therefore, as far as optics go, amosite belongs properly to the orthorhombic amphiboles In each case crystallographic *c* is the direction of highest refraction, and where data are given, of strongest absorption. The refractive indices and birefringence of the members of the series vary somewhat evidently in sympathy with chemical composition. Ferroanthophyllite and amosite, which have high iron-contents with correspondingly low magnesia, have systematically higher indices than anthophyllite and gedrite in which iron is very subordinate. From the optical data alone the validity of amosite as a distinct species cannot be judged as even such distinct species as anthophyllite and gedrite would be hardly distinguishable in small fragments.

p. 281

> (f) The long-fibred, ash-gray asbestos, amosite, typically developed in ironstones within the contact aureole of the Bushveld Intrusion, proves to be an orthorhombic amphibole with ferrous oxide as the dominant base. Carrying sesquioxides intermediate in amount between the ideally sesquioxide-free anthophyllites and the highly aluminous gedrite, amosite is sustained as a mineral species. The composition of amosite is expressed in the same general manner devised for crocidolite (d). A greenish, short-fibred form of amosite carries about 11 per cent of lime.

In 1948 J. C. Rabbitt studied various specimens of anthophyllite, with the use of x-ray diffraction techniques.
A new study of the anthophyllite series. Amer. Mineral. 33 (1949) 263-323.

In this study he concludes that the two samples of amosite he has examined are actinolite and cummingtonite:

p. 287

> *Numbers 86 and 87.*—These analyses are of two amosites from South Africa described by Peacock (1928). It will be shown by *x*-ray evidence that both are monoclinic. As they are monoclinic, their composition shows that number 86 is probably actinolite (10.84% CaO, 29.34% FeO, 4.96% MgO) and number 87 is probably cummingtonite (36.60% FeO, 5.80% MgO, 0.77% CaO). Both of these specimens are asbestiform and their identification cannot be determined by optical methods.

J.C. Rabbitt's study was considered to constitute sufficient evidence to discredit the mineral name "amosite," and the Mineralogical Society of America officially discredited amosite:

Amer. Mineral. 34 (1949) page 339:

DISCREDITED MINERALS

Hagemannite (=Ralstonite + Thomsenolite)

Clifford Frondel, Am. Mineral., 33, 84-87 (1948).

Amosite (=Actinolite)

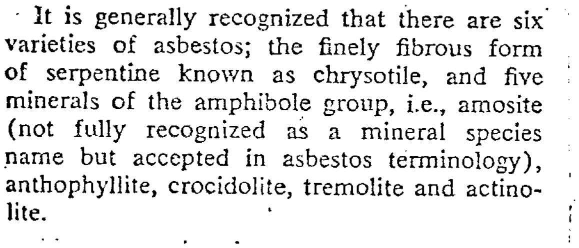
John C. Rabbit, Am. Mineral., 33, 263-323 (1948).

Following this announcement of the Mineralogical Society of America the name amosite has been omitted from all major mineralogy text and reference books as the name of mineral species. That was done, not only in the U.S., but in all major countries.

However, asbestiform cummingtonite-grunerite (and actinolite-tremolite) mined in South Africa, continued to be marketed under the commercial name of "amosite." For the same reason in many books, especially those in mineral deposits and economic or industrial mineralogy, the term amosite is still used. In some books the authors make it clear that "amosite" is not a proper mineral name.

for example: Industrial Minerals and Rocks, Editor J.L. Gillson. Am. Inst. of Min. and Metall., and Petrol. Eng. New York, 1960.

page 23:



It is generally recognized that there are six varieties of asbestos; the finely fibrous form of serpentine known as chrysotile, and five minerals of the amphibole group, i.e., amosite (not fully recognized as a mineral species name but accepted in asbestos terminology), anthophyllite, crocidolite, tremolite and actinolite.

Others, on the other hand, are less careful and imply that "amosite" is a mineral.

for example: A.M. Bateman: Economic Mineral Deposits.
2nd Ed. 1950, J. Wiley & Sons.

pages 750-751:

> **Asbestos Minerals.** Asbestos is a commercial term applied to a group of minerals that separate readily into fibers. The minerals differ in chemical composition and in the strength, flexibility, and usefulness of their fibers. Broadly, they fall into two groups — serpentine and amphibole; the former includes the mineral chrysotile and the noncommercial picrolite, and the latter includes anthophyllite, crocidolite, amosite, tremolite, and actinolite. Mountain leather, mountain wood, and mountain cork are varieties of amphibole.

Consequently, any company mining and marketing an asbestiform amphibole may choose to call that an "amosite asbestos." The known amosite asbestos, mined in South Africa, is mineralogically cummingtonite-grunerite and actinolite-tremolite, while that of the Idaho deposit is ferro-anthophylite [Shannon, Proc. U.S. Nat'l. Museum, (1921) 397-401).

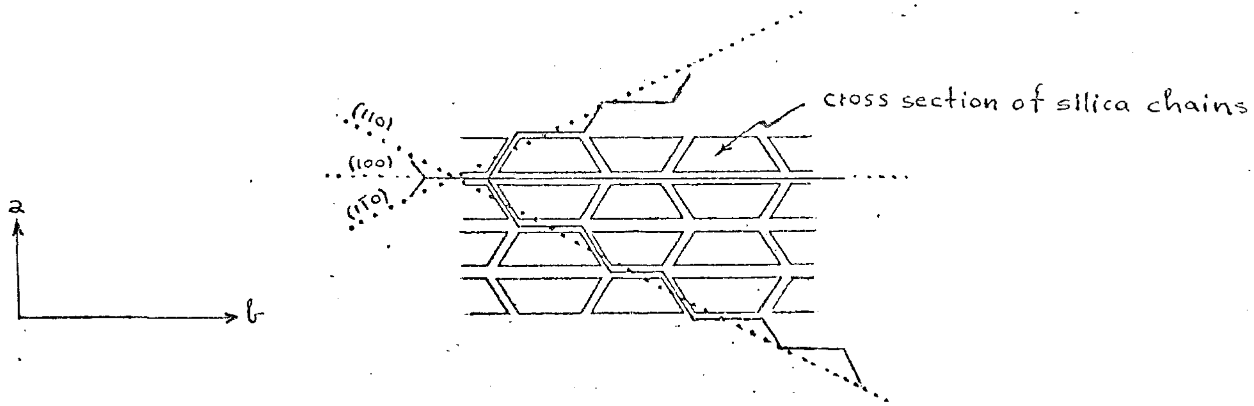
FIBERS OF ASBESTOS AND OF CLEAVAGE FRAGMENTS

Minerals, when crystallized in asbestiform habit, will contain thin and long fibers. The length over width ratios of these fibers are very high; in general, they will be over 100 to 1 for any commercial and over 1,000 to 1 for good quality asbestos. In contrast to these fibers, similar fibers (with shorter length/width ratios) can be created by breaking up minerals which have prismatic cleavages. Amphiboles have prismatic cleavages. Consequently, amphiboles can be fractured into fibrous cleavage fragments which will resemble naturally grown asbestos fibers.

The crystal structures of some minerals are characterized by weak atomic bonds across one certain plane. That plane may be so weak that the mineral can easily be peeled into sheets, like in the micas. In other minerals the weak plane may be stronger (yet weaker than the bonds in other directions) and, although, the mineral could not be peeled into sheets when an attempt is made to break the mineral, it will first break along that weakness plane, that is, along the cleavage plane. The fragment of this mineral will be platy or tabular.

If a mineral has two cleavage planes it is said to have prismatic cleavage as the mineral will first break along these planes, and the resulting fragments will have prismatic shapes. If the two cleavage planes are well pronounced the cleavage fragments may be fibrous.

The crystal structure of the amphiboles are characterized by the double chains of strong silicon-oxygen tetrahedra and the weak iron-magnesium (etc.)-oxygen octahedral chains. When the mineral is subjected to stress it will break easily along planes which are parallel to the silica tetrahedral planes, and will break with difficulties across these silica chains. There are two perfect cleavage planes, ((110)) and (($1\bar{1}0$)), and one less perfect, ((100)), cleavage planes in amphiboles.



As these three cleavage planes are all parallel with the silica chains and the c-axis of amphiboles, all cleavage fragments will be prismatic, and frequently fibrous.

APPENDIX II

LIST OF THE MAJOR POTENTIALLY FIBROUS MINERAL POLLUTANTS

The complete list of minerals which are known to occur in asbestiform habit and/or can produce fibrous cleavage fragments would be very extensive. The following list is restricted to those common rock-forming silicates which are known to occur in asbestiform habit and/or have a better than accidental chance to produce fibrous cleavage fragments. Many of these minerals may be found in association with chrysotile and amphibole asbestos. The following list may provide first order information for their identification.

NOTE: At present, only a few fibrous minerals are known to pose serious health hazards to human populations when small fibers of such are inhaled or consumed in water or food. That small number, however, may be due to limited information on the biological effects of most fibrous minerals rather than on the absence of their toxic properties. Many of the other fibrous minerals have physical and chemical properties comparable to known hazardous species and it is conceivable that some may be proven harmful in the future.

(1) The minerals which are known to occur in asbestiform habit are capitalized and have the variety or commercial name(s) of their asbestos form given in parenthesis below their mineral names.

(2) All chain silicates have prismatic cleavages and, consequently, may produce fibrous cleavage fragments.

(3) Only a few layer silicates have been found to crystallize in asbestiform habit, e.g.serpentines and talcs. There is only one good cleavage plane in the non-asbestiform layer silicates, ((001)), which yields platy cleavage fragments. However, small fragments can be broken along secondary, weaker planes, and consequently,

may produce prismatic, or even fibrous cleavage fragments. (Especially, if fibers are defined as particles with 3/1 or higher length/width aspect.)

(4) In most cases only one polytype of a mineral is given. Either the most common polytype or the 1M or 1-layer structure. In chlorites the old species-type mineral names are used rather than the recently proposed structural names.

CHAIN SILICATES

MINERAL GROUP	MINERAL (asbestos variety names)	CRYSTALLOGRAPHY: a,b,c,(Å), α,β,γ,(°) Space group	CHEMICAL COMPOSITION (SIMPLIFIED)
PYROXENES	Enstatite	18.23,8.81,8.19 Pbca	$MgSiO_3$
	Hyperstene	18.24,8.88,5.21 Pbca	$(Fe,Mg)SiO_3$
	Diopside	9.73,8.91,5.25,β=105.83 C2/c	$CaMgSi_2O_6$
	Hedenbergite	9.85,9.02,5.26,β=104.33 C2/c	$CaFeSi_2O_6$
	Johannsenite	9.83,9.04,5.27,β=105 C2/c	$CaMnSi_2O_6$
	Augite	9.8,9.0,5.25,β∿105 C2/c	$Ca(Mg,Fe,Al)(Al,Si)_2O_6$
	Spodumene	9.50,8.30,5.25,β=110.23 C2/c	$LiAlSi_2O_6$
	Jadeite	9.50,8.61,5.24,β=107.43 C2/c	$NaAlSi_2O_6$
	Pigeonite	9.73,8.95,5.26,β=108.55 $P2_1/c$	$(Mg,Fe,Ca)(Mg,Fe)Si_2O_6$
PYROXINOIDS	Wollastonite	7.94,7.32,7.07,α=90.05 $P\bar{1}$, β=95.29,γ=102.46	$CaSiO_3$
	Pectolite	7.99,7.04,7.02,α=90.05 $P\bar{1}$, β=95.29,γ=102.46	$Ca_2NaHSi_3O_9$
	Rhodonite	7.66,12.27,6.68,α=86.0, $P\bar{1}$, β=93.2,γ=111.1	$MnSiO_3$
AMPHIBOLES	ANTHOPHYLLITE (Amosite, Prieskaite)	18.56,18.08,5.26 Pnma	$(Mg,Fe)_7(OH,F)_2Si_8O_{22}$
	Gedrite	18.59,17.89,5.30 Pnma	$(Mg,Fe,Al)_7(OH,F)_2Si_8O_{22}$
	Ferrogedrite	18.51,17.95,5.32 Pnma	$Fe_5Al_2(OH,F)_2(Si,Al)_8O_{22}$

AMPHIBOLES	HOLMQUISTITE	18.36,17.75,5.29 Pnma	$Li_2(Mg,Fe)_3(Al,Fe)_2(OH,F)_2Si_8O_{22}$
	CUMMINGTONITE (Amosite, Montasite)	9.51,18.19,5.33,β=101.92 C2/m	$(Mg,Fe)_7(OH)_2Si_8O_{22}$
	GRUNERITE (Amosite, Montasite)	9.56,18.30,5.35,β=101.87 C2/m	$(Fe,Mg)_7(OH)_2Si_8O_{22}$
	ACTINOLITE (Asbestos, Amosite)	9.86,8.11,5.34,β=105.00 C2/m	$Ca_2(Mg,Fe)_5(OH,F)_2Si_8O_{22}$
	TREMOLITE (Asbestos, Amosite)	9.84,18.05,5.28,β=104.70 C2/m	$Ca_2Mg_5(OH,F)_2Si_8)_{22}$
	HORNBLENDE (Byssolite)	9.87,18.01,5.33,β=105.73 C2/m	$(Ca,Na,K)_{2-3}(Mg,Fe,Al)_5(OH,F)_2(Si,Al)_8O_{22}$
	Edenite	9.9,18.0,5.3,β∿105 C2/m	$NaCa_2Mg_5(OH,F)_2(Si,Al)_8O_{22}$
	TSCHERMAKITE (Bedenite)	9.9,18.0,5.3,β∿105 C2/m	$Ca_2(Mg,Al,Fe)_5(OH,F)_2(Si,Al)_8O_{22}$
	Pargasite	9.9,18.0,5.3,β∿105.5 C2/m	$NaCa_2(Mg,Al,Fe)_5(OH,F)_2(Si,Al)_8O_{22}$
	Hastingsite	9.94,18.01,5.34,β=104.92 C2/m	$NaCa_2(Fe,Al)_5(OH,F)_2(Si,Al)_8O_{22}$
	Kaersutite	9.9,18.21,5.4,β∿106 C2/m	$(Ca,Na,K)_3(Mg,Fe,Ti)_5(OH,O,F)_2(Si,Al)_8O_{22}$
	Barkevikite	9.9,18.34,5.34,β∿106 C2/m	$(Ca,Na,K)_3(Fe,Mg,Mn)_5(OH,F)_2(Si,Al)_2O_{22}$
	Glaucophane	9.7,17.7,5.3,β∿104 C2/m	$Na_2Mg_3Al_2(OH,F)_2Si_8O_{22}$
	RIEBECKITE (Crocidolite)	9.75,18.0,5.3,β∿103 C2/m	$Na_2Fe_5(OH,F)_2Si_8O_{22}$
	RICHTERITE	9.82,17.96,5.27,β=104.33 C2/m	$Na_2Ca(Mg,Fe,Mn,Al)_5(OH,F)_2Si_8O_{22}$
	Katophorite		$Na_2Ca(Fe,Al)_5(OH,F)_2(Si,Al)_8O_{22}$
	Eckermanite	9.7,17.7,5.3,β∿104 C2/m	$(Na,Ca)(Fe,Mg,Al)_5(OH,F)_2(Si,Al)_8O_{22}$
	Arfvedsonite	9.9,18.0,5.3,β∿104 C2/m	$(Na,Ca)(Fe,Mg,Al)_5(OH,F)_2(Si,Al)_8O_{22}$

LAYER SILICATES

SERPENTINES	Antiqorite	5.30,9.20,7.46,β=91.40 Cm	$Mg_6(OH)_8Si_4O_{10}$
	Lizardite	5.31,9.20,7.31,β=90.00 Cm	$(Mg,Fe)_6(OH)_8Si_4O_{10}$
	CHRYSOTILE	5.34,9.25,14.65,β=93.27	$Mg_6(OH)_8Si_4O_6$
	Chamosite	5.40,9.36,14.03,β=90.00	$(Fe,Mg)_6(OH)_8Si_3AlO_{10}$
	Amesite	5.31,14.01(n) $P6_3cm$	$(Mg,Al,Fe)_6(OH)_8(Si,Al)_4O_{10}$
	Greenalite	5.55,9.61,7.20,β=90.00	$Fe_{<6}(OH)_8Si_4O_{10}$
	Cronstedtite	5.49,9.52,7.08(n),β=104.50 Cm	$Fe_6(OH)_8(Si,Fe)_4O_{10}$
	Berthierite	5.41,9.33,6.82,β-104.50 Cm	$(Fe,Al,Mg)_6(OH)_8(Si,Al)_4O_{10}$
KAOLINS	Kaolinite	5.15,8.95,7.39,α=91.8 β=104.5,γ90	$Al_4(OH)_8Si_4O_{10}$
	Dickite	5.15,8.95,14.42,β=96.8	$Al_4(OH)_8Si_4O_{10}$
	Nacrite	5.15,8.96,43.0,β=90.0	$Al_4(OH)_8Si_4O_{10}$
	HALLOYSITE	5.2,8.9,10.1	$Al_4(OH)_8\ Si_4O_{10}\cdot 4H_2O$
	Donbassite		$(Na,Ca,Mg)Al_4(OH)_8Si_3AlO_{10}$
TALCS	TALC (Agalite)	5.27,9.12,18.85,β=100.25 C2/c	$Mg_6(OH)_4Si_8O_{20}$
	Pyrophyllite	5.15,8.92,18.59,β=99.9 C2/c	$Al_4(OH)_4Si_8O_{20}$
	MINNESOTAITE	5.4,9.42,d_{001}=19.14	$(Fe,Mg)_6(OH)_4(Si,Al,Fe)_8O_{20}$

MICAS	Muscovite	5.19,9.04,20.08,β=95.5 C2/c	$K_2Al_4(OH,F)_4Si_6Al_2O_{22}$
	Paragonite	5.13,8.89,18.92,β=95 C2/c	$Na_2Al_4(OH)FSi_6Al_2O_{20}$
	Glauconite	5.25,9.09,10.03,β∿100 Cm or C2/m	$(K,Na,Ca)_{<2}(Fe,Al,Mg)_4(OH)_4(Si,Al)_8O_{20}\cdot nH_2O$
	Phlogopite	5.3,9.2,10.3,β=100.0 Cm	$K_2(Mg,Fe)_6(OH,F)_4Si_6Al_2O_{20}$
	Biotite	5.3,9.2,10.2,β=100.0 Cm	$K_2(Mg,Fe,Al,Ti)_6(OH,F,O)_4(Si,Al)_8O_{20}$
	Lepidolite	5.3,9.2,10.2,β=100.0 Cm or C2/m	$K_2(Li,Al)_{<6}(OH,F)_4(Si,Al)_8O_{20}$
	Zinnwaldite	5.27,9.09,10.07,β=100.0 Cm	$K_2(Fe,Li,Al)_6(F,OH)_4(Si,Al)_8O_{20}$
	Margarite	5.13,8.92,19.50,β=95.0 C2/c	$Ca_2Al_4(OH)_4Si_4Al_4O_{20}$
	Clintonite	5.21,9.02,19.24,β∿95 C2/c	$Ca_2(Mg,Fe,Al)_6(OH)_4(Si,Al)_8O_{20}$
	Xanthophyllite	5.24,9.02,9.98,β=100.01 Cm or C2/m	$Ca_2(Mg,Fe,Al)_6(OH)_4(Si,Al)_8O_{20}$
	Stilpnomelane	5.40,8.42,12.12,β∿93	$(K,Na,Ca)(Fe,Mg,Mn)_{6-8}(O,OH,H_2O)_{4-8}Si_8O_{20}$
CHLORITES	Talc-chlorite	5.3,9.2,14.3,β∿97 C2/m	$Mg_3(OH)_6Mg_3(OH)_2Si_4O_{;0}$
	Penninite	5.2,9.2,28.6,β=96.9 C2/m	$Mg_3(OH)_6(Mg,Al)_3(OH)_2(Si,Al)_4O_{14}$
	Clinochlore	5.2,9.2,28.6,β=96.9 C2/m	$Mg_3(OH)_6(Mg,Al)_3(OH)_2Si_3AlO_{10}$
	Prochlorite	5.36,9.28,28.4,β=97.15 C2/m	$Mg_3(OH)_6(Mg,Fe,Al)_3(OH)_2(Si,Al)_4O_{10}$

CLAYS	Illite	5.2,9.0,d_{ool}=9.95	$K_{<1\frac{1}{2}}Al_4(OH)_4(Si,Al)_8O_{20}$
	Montmorillonite	5.23,9.06,vrbl	$(Ca,Na)_{<1}(Al,Mg,Fe)_4(OH)_4(Si,Al)_8O_{20}nH_2O$
	Vermiculite	5.3,9.2,28.9,β=97.0 Cc	$(Mg,Ca)_{<1}(Mg,Fe,Al)_6(OH)_4(Si,Al)_8O_{20}\cdot 8H_2O$
	Prehnite	4.61,5.47,18.48 P2cm	$Ca_2Al(OH)_2Si_3AlO_{10}$
	Apophyllite	9.00,15.84 P4/mnc	$KFCa_4Si_8O_{20}\cdot 8H_2O$

APPENDIX III

COMMENTS ON SELECTED AREA ELECTRON DIFFRACTION

Electron diffraction patterns, combined with chemical analysis (electron microprobe or energy dispersive x-ray spectrum) can be considered the most powerful identification technique for micron-sized particles. Unfortunately, a thorough evaluation of electron diffraction patterns is time-consuming and requires crystallographic expertise. For conclusive identification: selected area electron diffraction patterns should be taken in two or more different and well-oriented lattice planes, and from these patterns, the lattice parameters and the systematic extinction patterns should be calculated and determined. The former point requires that the electron microscope be equipped with a goniometer stage, allowing for the reorientation of crystals. The electron diffraction patterns taken from the selected lattice planes should be photographed to order to facilitate the measurements and the interpretations of the patterns. This is extremely time-consuming and requires a high level of crystallographic training.

There is another problem in selected-area electron diffraction techniques which enhances the difficulties in the interpretation of the patterns. Because of the short wave length of radiation and long focal distance the spheres of limit and reflection are very large. This in turn allows the diffraction of reciprocal lattice points which are near to but not exactly in the diffracting reciprocal lattice plane. These diffractions will appear as extra spots in the pattern, which can destroy the characteristic extinction pattern of the mineral, may lead to measurements which are fractions of true reciprocal translations, and can pose other confusing problems. These patterns are further complicated if the crystals are completely horizontal or are not perfectly oriented, as a minor degree of inclination can cause a different pattern of extra reciprocal lattice points.

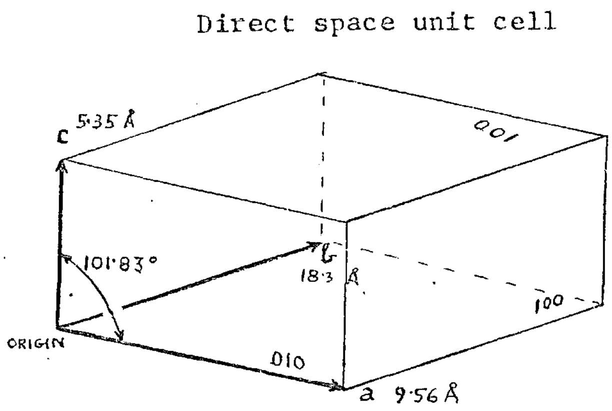
Due to the complexity of the patterns and to time and special training involved in proper electron diffraction techniques, most analytical laboratories (in fact, all of those we have visited) take shortcuts. They look at the diffraction patterns of crystals and conclude its identity on the basis of apparent similarity with standards. That similarity is usually limited, in the case of the amphiboles, to the presence of rows of reciprocal lattice prints separated by an interplanar distance equivalent to d_{001} =5.2 to 5.3 Å. Unfortunately, minerals may be misidentified using this method. For example, there are many minerals, some containing the same chemical elements as amphiboles, which have similar interplanar distances in corresponding orientation (e.g., cummingtonite d_{001} = 5.3, hyperstene d_{001} =5.2, olivine d_{100} = 4.8, humites d_{010} = 4.8, minnesotaite d_{100} = 5.4 Å). Careful measurements are needed to resolve a few tenths of Ångstrom differences in these interplanar distances. That is further complicated by the fact that not only different minerals can give similar patterns but that the same mineral may give strikingly different patterns in various orientations.

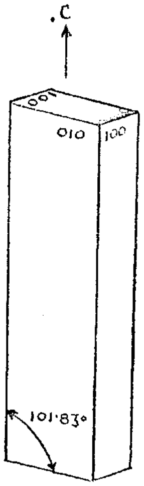
In the following pages, the electron diffraction patterns of grunerite-cummingtonite are given for various orientations (laying on crystal or cleavage faces) for electron microscope equipped with goniometer or have only a stationary stage. A certain arbitrarely chosen level of interference of additional reciprocal lattice points is included in these patterns. Although they have been checked against actual patterns obtained from natural cummingtonite, additional confirmation, and calculations of other orientations twins is necessary to insure their usefulness.

ELECTRON DIFFRACTION PATTERNS

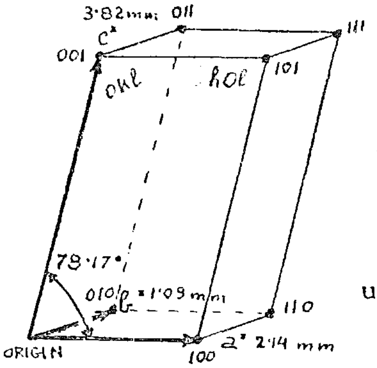
(Subject to revision)

Grunerite $(Fe,Mg)_7(OH)_2Si_8O_{22}$
Assume camera constant 20
Scale of drawings x50
Lengths given in millimeters





Acicular crystal



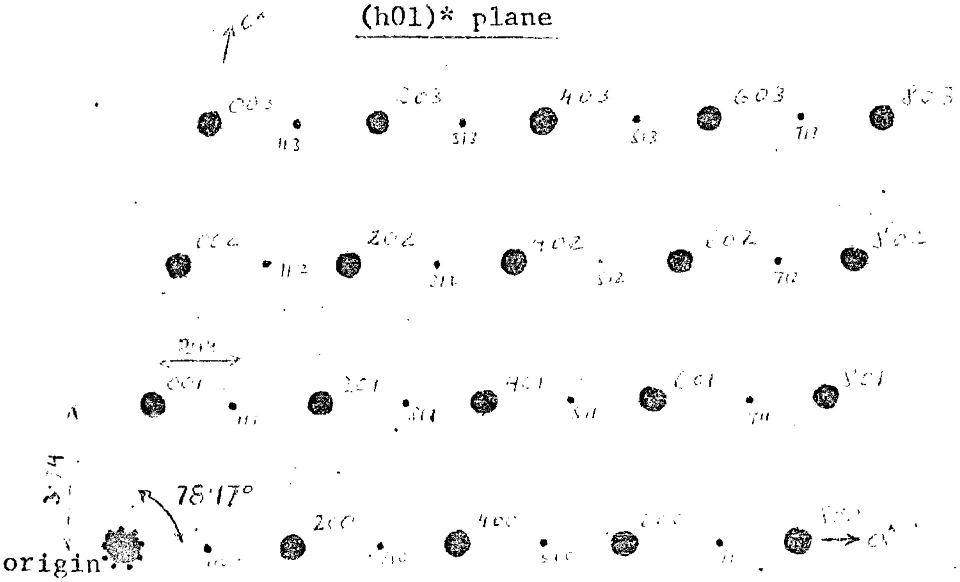
Space group: C/2m The c-side centered space group requires the systematic extinction of all those reciprocal lattice points where:

h + k ≠ 2n that is (h00) h ≠ 2n (0k0) ≠ 2n
(hk0) and (hkl) h + k ≠ 2n

If the electron microscope is equipped with a goniometer the crystal can be rotated into reciprocal lattice planes (left column of diagrams). If the crystal cannot be rotated and the beam is perpendicular to a crystal face, but not to a reciprocal lattice plane, nearby lattice points will "screen" through giving a more complex pattern (right column of diagrams).

SINGLE CRYSTALS

(h01)* plane

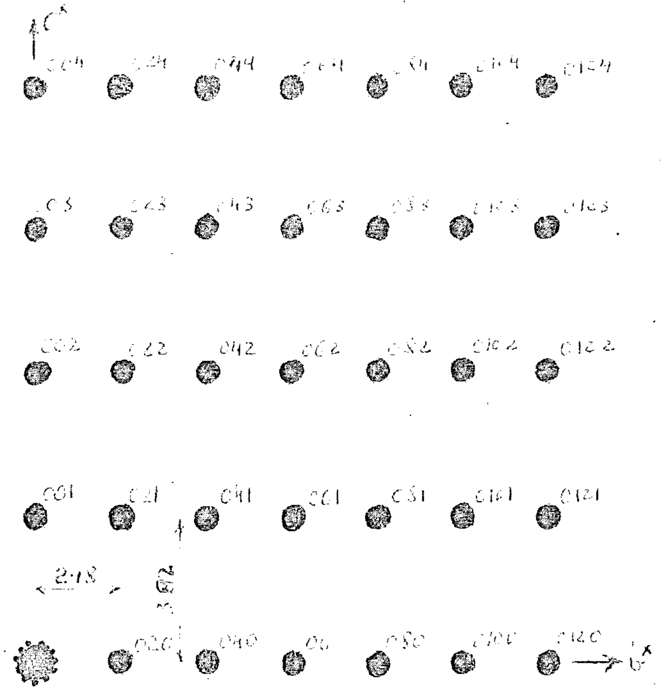


Crystal laying on the (010) face

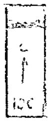
[010] projection

The (010) face is parallel with the (h01)* plane and perpendicular to [010]* direction. Consequently the pattern is the same in a stationary stage microscope

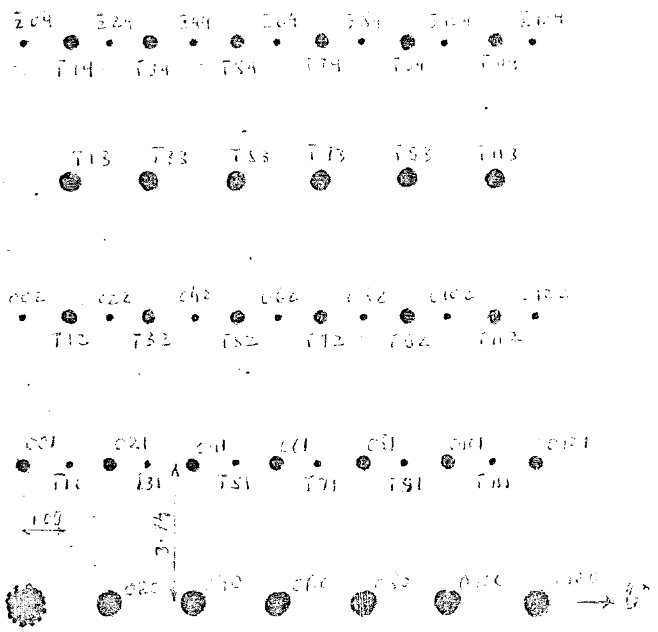
(0kl)* plane



crystal tilted 11.83°

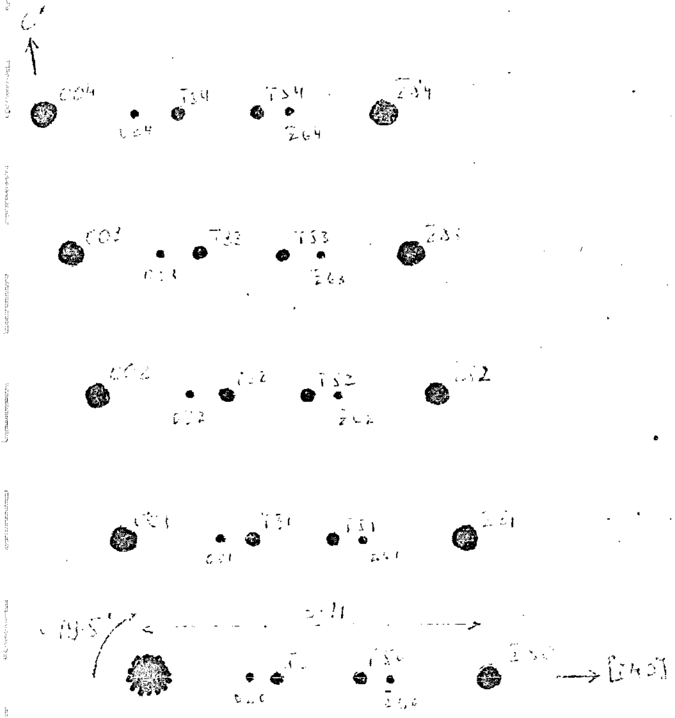


[100] projection

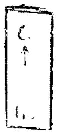


crystal laying on (100) face

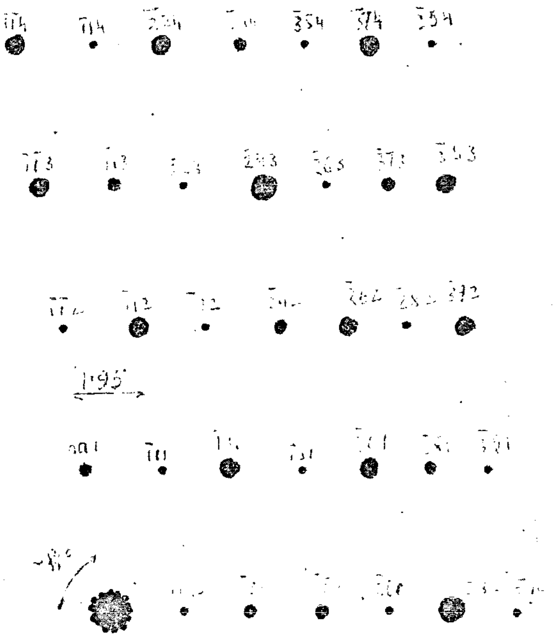
(h̄ 4h 1)* plane



crystal tilted by -11.0°



[110] projection

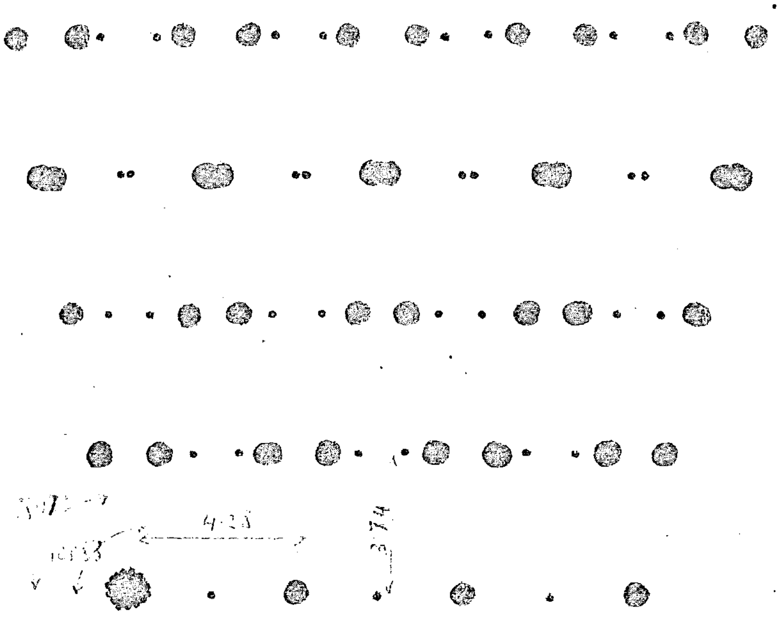


crystal laying on (110) cleavage face

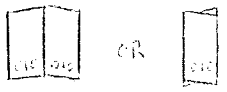
(100) TWINS

(or [010] rotation twin)

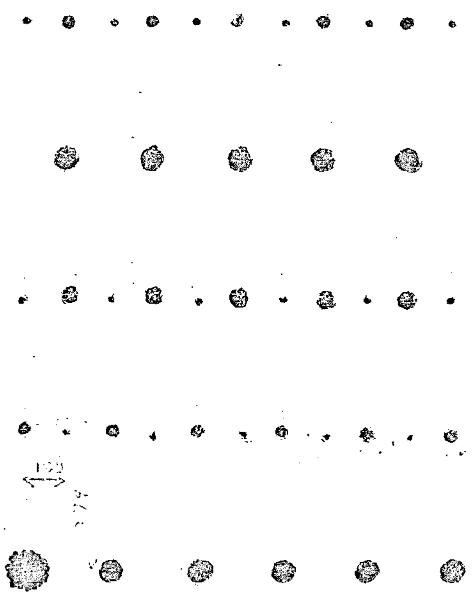
(hol)* plane or [010] projection



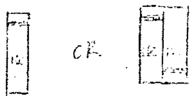
crystal laying on (010) face



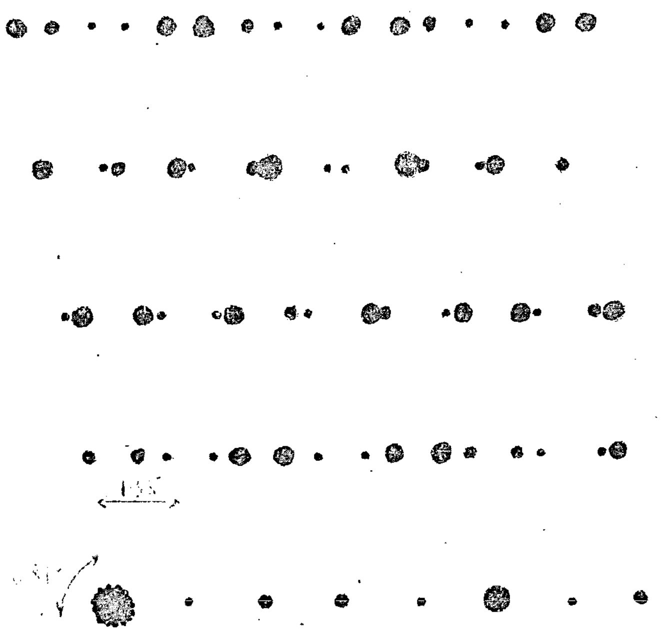
[100] projection



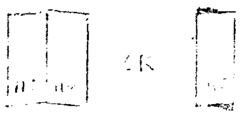
crystal laying on (100) face



[100] projection



crystal laying on
(110) cleavage
face



Decreasing size of dots represent decreasing probability for diffraction spots to be present. Dots do not represent relative relative intensities of diffraction.

Calculations based on preliminary data and assumptions which need to be checked.

MN 1000

STATE OF MINNESOTA

Office Memorandum

DEPARTMENT Division of Air Quality

TO : Peter L. Gove
Executive Director
MPCA

DATE: 2/20/76

FROM : Tibor Zoltai, P.Eng., Ph.D., Professor of Mineralogy and Crystallography
James H. Stout, Ph.D., Associate Professor of Petrology and Mineralogy
Department of Geology and Geophysics
University of Minnesota

SUBJECT: TRIP REPORTS ON:

I. Visit at Illinois Institute of Technology Record Center, Chicago, Illinois
December 17, 1975

II. National Institute for Occupational Safety and Health Cincinnati, Ohio
December 18, 1975

III. Mount Sinai School of Medicine, New York, N.Y.
December 18, 1975

IV. McMaster University, Hamilton, Ontario
December 22, 1975

V. National Water Quality Laboratory, Duluth, Minnesota
January 6, 1976

NOTE: These minutes were written on the basis of our recollections of the discussions. Consequently, there may be some statements which are misunderstood or misquoted. Consequently, no quotations should be taken from these minutes without the confirmation of the appropriate personnel.

I

ILLINOIS INSTITUTE OF TECHNOLOGY

SUBJECT: Abbreviated Minutes of MPCA Trip, December 17-19, 1975.

At 2:30 p.m. on December 17 we met with Dr. Colin Harwood of the Illinois Institute of Technology (IIT) in Chicago. Also present were Tibor Kosa and Edward Pryzina of the MPCA, John Stockham and Paul Siebert of IIT, and R.C. Woodland from the Chicago Field Museum. Tibor Kosa began the meeting with a summary of MPCA's objectives and a statement of our purpose.

Dr. Harwood then proceeded with a summary of their handling of Air Quality samples. Specifically, we discussed the relative merits of Millipore and Nucleopore filters. IIT, under the direction of Harwood, is now beginning a study to provide a rigorous evaluation of sampling procedures. At this time, they prefer to work with Millipore filters, apparently because they have devoted substantial time and effort to refining their use. It seemed generally accepted, but not with adequate proof in Harwood's opinion, that there is greater loss of the finer size distribution of fibers with Millipore filters compared to Nucleopore. This is because the greater thickness of Millipore (~150μ) allows a substantial portion of very fine fibers to become imbedded within the filter and therefore not be available for direct surface analysis. During the dissolution of the filter with acetone, the 150μ filter collapses to a thinner gelatinous layer which contains the previously embedded fibers. Dr. Harwood expressed concern that finer particles may be washed out at this stage, and that the concentration of the final residue is lessened. In contrast, the Nucleopore filter is only 10µ in thickness and most if not all size fractions of fibers are captured at the filter surface.

When questioned about the possible loss of fine fibers during handling and storage between the time of sample collection and time of C-coating and analysis, Dr. Harwood was of the opinion that it was minimal. He cited some informal experiments they did with grossly mishandled Millipore filters that were not heavily loaded. He said that even by shaking the filter, it was difficult to liberate fine fibers. This would not apply to Nucleopore filters, however. He felt that additions from settling of dust particles, etc. from the ambient air may be more of a problem. He had no reservations concerning the representative nature of the 20 ERC samples that were collected 18 months ago but which had not been received by IIT until December 15, 1975.

The problem of overloaded filters was discussed. Optimal loading of approximately 5% of the filter surface area results in the best counting statistics. Most air quality samples have greater loading densities.

Harwood then summarized the criteria by which they identify fibers. These are:

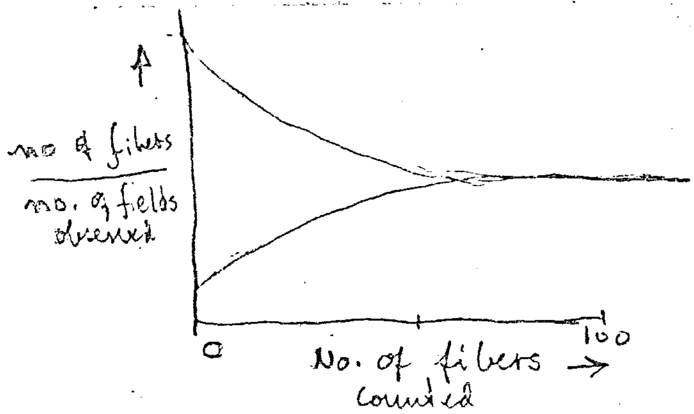
1. Morphology (3/1 length-width ratio)
2. Morphology and electron diffraction
3. Morphology and energy dispersive chemistry
4. Morphology, electron diffraction, and chemistry

For a filter for which there is no additional information (source of fibers, etc.), these criteria are listed in order of increasing reliability and certainty of identification. The point was made that if one knows that the source region limits amphibole fibers, then criterion 1 alone may have the same reliability as the other criteria. The suggestion was made with regard to some 500 EPA samples collected in 1973 but for which no analytical work has been done, that considerable savings in cost could be obtained by relaxing criterion 4 (~$500.00/sample). This suggestion came after considerable discussion on the interpretation of electron diffraction patterns. The principle information derived from them at this time is the identity of the 5.3 Ångstrom cell dimension parallel to the long axis of an amphibole fiber. This is sufficient to positively identify a member of the amphibole mineral group with the exception of accidental, random orientations of other minerals. It is extremely unlikely that the combination of an elongate fiber orientation and a 5.3 Å C-axis repeat could be a mineral other than amphibole. The problem with electron diffraction for amphibole identification is its sensitivity to fiber orientation, thickness, etc. As a result, Dr. Harwood pointed out that given a control sample known to be 100% amphibole, application of the above 4 criteria would give the following identifications:

Criterion 1..........	15%
Criterion 2..........	25%
Criterion 3..........	45%
Criterion 4..........	less than 100%

As far as the Reserve air quality samples are concerned, we know that a large fraction of total fibers are amphibole. Therefore, perhaps the detailed electron diffraction aspect of fiber count analysis could be dispensed with at a savings of approximately $150/sample. In this manner, a great deal of machine time would be saved as large scale photographs could be taken and fiber concentrations determined from them directly.

The question came up concerning the validity of counting only 100 fibers per sample. Harwood replied to this with the following graph:



Where the number of fields observed are each at 20,000 magnification. What this graph means is that the number of fibers in the first field of view may vary according to where you are on the filter. But as more and more fields are observed, we get a better average which converges around 60 fibers counted. By the time 100 fibers are counted, the average has leveled off. Of these 100 fibers, 20 are routinely examined by both electron diffraction and energy-dispersive chemistry. The choice of those 20 is made as best as possible over the entire size range. Magnification and counting at 20,000 times was given as optimal because fibers whose diameters are 200 Å may be counted. These fibers have a length of at least 600 Å (0.06µ) and represent the lower limit of dimensions counted. When the counting is done, each fiber is measured separately and recorded over the range 0.02µ to greater than 5µ so we can get any statistical breakdown we like.

Another interesting and important development was the fact that the standard U.I.C.C. amosite from South Africa gives apparently single crystal electron diffraction patterns. Dr. Harwood showed photos of a single fiber, elongated perhaps 30:1, from the standard and the electron diffraction pattern from it. This appeared to be the pattern of a single crystal. The 5.3 Å repeat was obvious. They believed this to be a single crystal rather than a bundle of smaller fibrils, although it was pointed out that a bundle of fibrils would collectively yield a discrete 5.3 Å repeat providing all fibrils shared a common C crystallographic axis. Dr. Harwood stated that with long exposure and collection times, electron diffraction patterns could be obtained on even 200 Å diameter fibers. He also stated that "many" of the smaller (less than 1μ diameter) fibers gave good single crystal diffraction patterns.

There are some important implications to these observations. It appears that perhaps a significant fraction of commercial amosite asbestos may be broken down or disaggregated to individual, single crystal fibers. That is, at diameters below 1μ, some of the U.I.C.C. amosite no longer consists of bundles of fibers (and therefore asbestiform material) but rather single crystal fibers to which no apparent form of growth habit remains. This means that they may be then identical in physical properties to liberated amphibole cleavage fragments in the same size range found at both Homestake and Reserve. However, the surface properties of the natural single fibers may still be different from that of the fracture fragments and that distinction may be significant.

At this point in the discussion Paul Siebert brought in some hand specimens of material collected mainly at the east end of the Peter Mitchell Pit. They had photographs of the collecting site which admittedly was above the ore zone currently being mined. This material consisted of a monomineralic aggregate of fibers which from their outward appearance looked like a brownish amphibole. In detail, the most notable feature was the presence of bundles of flexible fibers ranging from about 1 to 3 mm in length. These bundles could be bent over with the tip of a pencil and they would spring back elastically. They did not display the brittle behavior one would anticipate if these were the normal single crystals more commonly found in the Peter Mitchell Pit. This is clearly the most asbestiform material we have observed to date from the Reserve Mining operation.

This specific sample was taken from a vein that, according to Dr. Woodland, was crosscutting the compositional layering of the surrounding rocks. The vein was described as extending "a few hundred meters" along the vertical wall. As a vein, we can anticipate the possibility that it may now, or may have previously, extended across the region of mined ore. It was agreed that a field trip to the Peter Mitchell Pit as early as possible in the spring would be worthwhile in order to determine whether this material may be present in the ore.

Some attempt was made by the IIT group to positively identify this material by comparing its chemistry, as determined by the energy dispersive method, to standard U.I.I.C amosite and crysotile whose chemistries are well known. Their preliminary data was difficult to evaluate because the analytical data was normalized to constant Si and they had instrumental problems with Al. The unknown sample did have high Ca, suggesting actinolite or hornblende. A small sample was obtained for an electron microprobe analysis at the University of Minnesota.

The x-ray powder diffraction pattern of these asbestiform fibers, taken by Paul Siebert, was found to be significantly different from both actinolite-tremolite and cummingtonite-grunerite. The x-ray study will be checked at the U of M on the material brought home.

IIT personnel were planning to feed this asbestiform mineral to animals to detect its cancerogenic effect. They were advised, however, to be cautious as this material is different from the cummingtonite-grunerite found in the ore and could be labelled non-representative.

A final note of interest was a report IIT prepared for Reserve Mining in the fall of 1973. "Several hundred" air quality samples were submitted by Reserve for fiber counting. These analyses were performed and the results submitted to Reserve. Dr. Harwood's recollection was that "there were lots of fibers present". What has happened to this report and was it ever submitted to the court as scientific data?

The meeting adjourned at approximately 6:30 pm.

II

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

At 11:15 am of the following day we met with the NIOSH group in Cincinnati. Present from NIOSH were Dr. Joseph Wagoner, John Dement and Dick Lemen. The MPCA contingent from the previous day was also present.

Tibor Kosa and Ed Pryzina led off with a brief summary of our intentions and an assurance that this was to be an open scientific discussion. Tibor Kosa summarized 2 principle problems of the Reserve issue, namely 1) the air pollution and 2), the water pollution. Dr. Wagoner quickly added a third major problem of occupational hazards at Reserve.

Dr. Wagoner then summarized the history of his involvement in the case. In 1973, he testified in court about some epidemiological aspects of:

1. multiplicity of organ systems
2. fiber carcinogeniety
3. minimal levels of dose responses.

His conclusion based on the evidence at that time was that an excess risk of lung cancer existed for workers exposed to asbestos fibers, but that no minimum (presumably safe) levels of exposure could be established at that time.

Dr. Wagoner then summarized the lack of cooperation on the part of Homestake with regard to the recent NIOSH study. A similar study had been suggested by Reserve in 1973 and apparently Dr. D. MacDonald of McGill University was planning to do the study of mortality patterns among Homestake Mine workers. But apparently MacDonald would only do the study, and would only testify to the results if it were at the Court's request. Reserve apparently felt that this request was unreasonable, and the study was never completed.

After the NIOSH study was completed, the results were presented on March 17, 1975 at a 4-day conference on Occupational Carcinogenesis. One of the sessions was devoted to fiber carcinogenesis. The population of miners studied at Homestake was restricted to those which:

1. had at least 5 years of underground exposure at Homestake, and
2. had no previous mining exposure.

The details of this study were not generally reviewed, but Dr. Wagoner concludes that because of the inhalation of airborne cummingtonite-grunerite cleavage fragments, there exists an excess of risk of respiratory tract cancer among these workers. The conference at which the paper was presented was international in scope, and was well-attended by industrial representatives. When this paper is formally published in the Proceedings of the New York Academy of Sciences, there is space planned for critical comments by Kotin, et. al. onthe condition that Wagoner be able to comment on these criticisms. This is apparently unresolved as yet but Wagoner seemed quite confident that the NIOSH study will stand up to any criticisms.

Several specific questions were raised concerning the criticisms of the NIOSH paper. The most notable of these were:

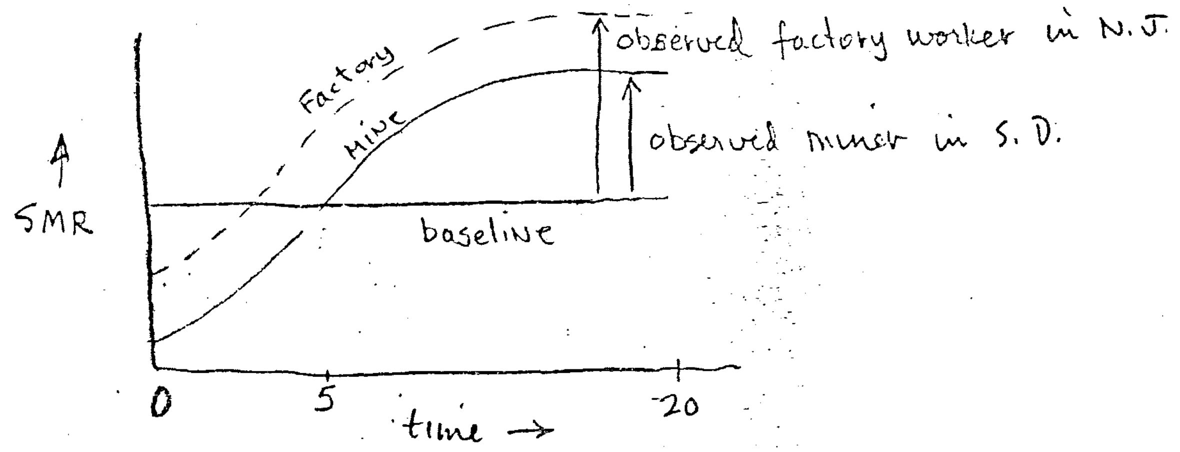
1. Q: Why was the identity of the control group for the Homestake

A: The reason given was that although the general white make population rates for the country were used first, there still exited an excess risk of respiratory tract cancer. The control group was later changed to the South Dakota white male population because this was thought to be more representative. With the new control group, the risk was greater.

2. Q: If the inhaled amphibole fibers (derived from amosite) at commercial amosite factories are identical to those at either Reserve or Homestake, then why are the mortality patterns so different?

A. Two reasons were given. The first is that the study groups differed in the total length of exposure. At Homestake, the 20 year fraction of the study consisted only of those workers for which 20 years had elapsed since first exposure. At Patterson, N. J., however, the 20 year fraction consisted only of those workers for which 20 years of continuous exposure had elapsed. So the risk factor in commercial factories was maximized.

The second reason given was that the standard mortality rate (SMR) for Patterson, N. J. factory workers and Homestake miners may differ significantly. This was illustrated by Dr. Wagoner with the following graph:



The point of this was to show qualitatively that because of poor living conditions, polluted air, etc., a typical amosite factory worker in N.J. is not as healthy at time = 0 as a similar worker in South Dakota. Both populations require a certain lead time before possible carcinogenic effects can be observed. In the case of the Homestake study, it was taken as 5 years.

3. Q: Where is the excess gastro-intestinal (GI) tract cancer and mesothelioma at Homestake" None are reported out of 70 deaths studied, yet several are reported from amosite factory workers.

A: Dr. Wagoner's answer to this was that the risk factor for GI cancer is much less than for respiratory tract cancer and the study population at Homestake just is not large enough. Mesothelioma, on the other hand, has a much longer incubation period and it may still be coming.

4. Q: How does one know for certain that Arsenic does not cause the excess risk of respiratory tract cancer at Homestake?

A: the answer given by Drs. Wagoner and Lemen was that the cancer rate in a mining population at Butte, Montana (previous NIOSH study) was about the same,or somewhat less than that at Homestake, S.D., yet the Arsenic content of the ore is 3-5% compared to Homestake. Therefore, Arsenic alone cannot be the cause of the excess cancers at Homestake.

5. Q: How does one know for certain that airborne silica dust at Homestake could not cause the excess risk of respiratory cancer?

A. The answer given by Dr. Wagoner was that there is no existing study that shows excess risk of respiratory tract cancer to silica dust at any concentration. Besides, silicon concentrations at Homestake are low.

6. Q: Are there statistics available on miners working in underground operations where the conditions are identical (or very similar) to Homestake, except for the absence of fibrous amphiboles?

A. Dr. Wagoner responded that, unfortunately, there is no such record available. However, two mines that may be compared with Homestake are: a potash mine and Butte. At the potash mine the cancer rate was significantly lower than at Homestake. At Butte, the cancer rate was similar to that of Homestake. It is believed, however, that the excess cancer at Butte can be contributed to arsenic.

7. Q: Dr. Selikoff said, when analyzing some statistical data of amosite workers based on the study of about 900 persons, that statistics based on such small numbers is unstable and unreliable (Trans. Proc., Sept. 18, 1973, p 4,661-). The number of people studied at Homestake is less than half of that. Would the instability of small number statistics apply to Homestake?

A: Dr. Wagoner responded that he has confidence in the validity of the Homestake statistics, in spite of the "small numbers", and does not agree with that statement of Dr. Selikoff.

8. Q: Another question at this point was asked concerning the chest x-ray study of the Homestake workers that NIOSH is doing.

A: Apparently the x-rays are of poor quality, many taken under field conditions and therefore ambiguous to interpret. Dr. Wagoner did make the comment that there is no proven relationship between asbestosis and lung cancer. That is, an individual need not develop asbestosis before he can develop lung cancer.

A discussion developed around how good the control group was for the

Homestake study. Dr. Wagoner stated that ideally you want a control group that is exposed to the same confounding parameters as the mine workers. That is, if the concept of excess risk is to have full meaning, then if 1/2 of the miners smoke, then 1/2 of the general public should smoke for comparisons to be best made. In general, a laboratory control group is undesirable because the general public to whom these comparisons are made are not subject to laboratory controls.

Lastly, Dr. Wagoner concluded that we have no scientific data available as yet to state what safe exposure levels of airborne amphibole fibers are. We do have data, however, that show what <u>unsafe</u> levels are. And in Dr. Wagoner's opinion, the airborne concentrations at Homestake are unsafe. Perhaps much lower concentrations are also unsafe, but we do not know as yet.

Following these discussions, our session with the NIOSH group centered around Dr. Dement who is responsible for the electron microscopy. He has carefully examined the international amosite standards (U.I.C.C. standards) and samples of amosite asbestos from Patterson, N.J., and Tyler, Texas. He stated that the minimum fiber diameter they have seen is 500 Å (0.05µ) and that none of their fiber counts extend below that limit. He also stated that certainly in this size range and perhaps up to 1µ diameter amosite fibers, the fibers give single crystal diffraction patterns. That is, they no longer consist of a bundle of fibers but rather of single crystals. This seems to substantiate the suspicion discussed at IIT, on the previous day, that at the size level of fiber inhalation (commonly less than 1u diameter), the physical properties that distinguish amosite from amphibole cleavage fragments are, on the basis of current observations, non-existent. The entire NIOSH group present agreed that there exists no detectable differences between inhaled fibers at amosite asbestos factories and those inhaled at either Homestake or Reserve. However, they accepted the possibility that the natural asbestos fibers may have different surface properties, even in small ($<1\mu$ dia.) sizes, or may even have unique (cyclic twined) detailed structures which may result in differences of some properties when compared to fibrous cleavage fragments.

The misuse of mineralogical terminology was also discussed. It was pointed out that the term "asbestiform" is a description of crystal habit, and refers to minerals if and when they crystallize as asbestos. The fibrous fracture fragments at Homestake (and at Reserve) did not crystallize in asbestiform habit, the fibers were created by crushing and grinding. They should be referred to as "fibrous amphibole fragments" rather than as "asbestiform amphiboles". Drs. Wagoner and Dement have conceded that the term is misused and it would be appropriate to get the terminology straightened out.

It was suggested that it would be advantageous to emphasize that the fibers at Homestake are fracture fragments, instead of insisting on that they are asbestos and amosite. Besides the fact that amosite is not a mineral (it has been discredited. Am. Mineral. 34, 1949, p. 339) and the asbestos marketed under the name amosite may be mineralogically actinolite-tremolite and/or ferroanthophyllite as well as cummingtonite-grunerite. It would be unwise to tie all of the arguments of the Homestake study to "identicity" with amosite asbestos and risk the consequent destruction of the validity of all arguments where and if somebody comes forth with a proof that significant differences exist between asbestos and fracture fragment fibers. Instead of just "asbestos" we should extend our category of carcinogenic fibers to "asbestos and fibrous fragments of minerals which may crystallize in asbestiform", that is if the latter category of fiber is proven to be carcinogenic. The NIOSH people agreed that that may be very advantageous. The meeting was adjourned at 3:15 p.m.

III

MOUNT SINAI SCHOOL OF MEDICINE

At 9:30 a.m. on December 19, 1975, we met with the Mt. Sinai Group in Environmental Medicine. Present were Tibor Kosa, Ed Pryzina from the MPCA and Dave Gray and Kyle Bishop from the Dept. of Health. The Mt. Sinai group was represented by Wm. Nicholson, Art Langer, Art Rohl and Steve Shirey.

Tibor Kosa began with a summary of our objectives and a statement that in the absence of lawyers and judges, we hoped for a purely scientific discussion of important problems.

Dr. Nicholson began by summarizing their sample preparation procedures. He noted that serious fiber loss problems exist with all techniques presently used in labs across the country. His own previous analyses have had losses up to 90% due to resuspension problems. His present "rub-out" technique loses 50% of total fibers during handling. He stated that many previous court samples have fiber concentrations so low due to analytical loss to be "essentially meaningless". The criteria used by the Mt. Sinai group to identify amphibole fibers are the same as other labs, but they are applied more rigorously. Specifically, a fiber is not counted as an amphibole unless it has the correct morphology (i.e., 3 to 1 length to width) and electron diffraction pattern with its characteristic 5.3 Å repeat. Rigorous application of these criteria automatically excludes a large number of amphiboles from the final fiber concentration. The reason for this is that electron diffraction cannot be rapidly obtained for fibers whose diameter is less than 1,000 Å (0.1μ). This is because the electron density is too weak and a photographic plate must be used to collect intensities. In principle, this procedure can produce electron diffraction for smaller fibers, it is not routinely done because of the time involved. Therefore, the Mt. Sinai total fiber concentrations do not include fibers whose diameters are less than 0.1μ, or whose length is less than 0.3μ. In many air quality samples, this procedure ignores at least 50% of the fibers present. This means that all Mt. Sinai fiber counts are at least a factor of 2 too low on this basis alone. This procedure also excludes larger amphibole fibers that are too thick for analysis. The electron beam must be able to fully penetrate the fiber for selected area diffraction mode. As this limit is approximately 0.2μ, all fibers whose diameters exceed this limit are also excluded from the fiber count unless a thin edge of the fiber can be found.

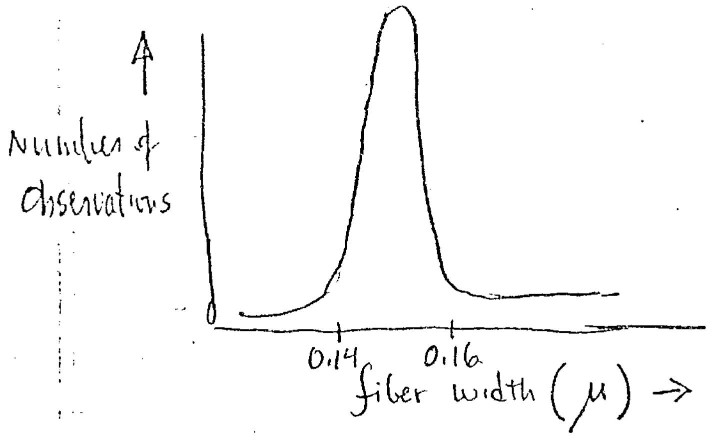
Contrary to previous written statements, this procedure for fiber counting differs from other groups. For example, both NIOSH and IIT count 100 total fibers per sample in all size ranges and the dimensions of each of these are recorded. Of these, 20 fibers or 5% are examined for electron diffraction and/or energy dispersive chemistry. If, for example, 50% of these 20 fibers give amphibole diffraction and/or chemistry, then 50% of the total number of fibers is counted as definite amphibole.

This difference of counting procedures between laboratories is reflected in the comparative median fiber dimensions reported for identical filter analyses. In samples with a significant small size fraction, the Mt. Sinai median values (as many fibers above that value as below) are higher than NIOSH or IIT. It is for this reason that the essentially identical fiber concentrations for the Homestake Mine and Silver Bay reported in the Homestake NIOSH study must be fortuitous. For reasons to be summarized later, each lab reports a different minimum concentration. The "real" fiber concentrations must be factors higher, and the appropriate factor varies from lab to lab.

Dr. Nicholson further indicated that his current counting procedures are low by an additional factor of 2 because of loss due to resuspension in the rub-out technique. He corrects for this in his final concentrations but does not correct for the exclusion of small fibers mentionedearlier. Nicholson also estimates that the loss of fibers by the acetone dissolution procedure used by NIOSH and IIT could be as high as 75% to 90%. Colin Harwood at IIT did say there was "substantial" loss of small fibers in his technique but would not estimate the percent until they had done further studies.

A discussion then extended around the dependence of carcinogenic effects of amphibole fibers on dimensions of the fibers. Dr. Langer alluded to one of his own studies in which it had been shown that amosite workers in S. African mines exposed to smaller (less than 0.2µ diameter) fiber dust have higher incidence of mesothelioma. Dr. Langer drew a graph of the size distribution of fibers actually observed and counted in diseased lung tissue of Patterson, N.J. amosite workers.

20



Dr. Langer further stated that in all amosite factories in which lung tissue has been examined, 95% of the amphibole fibers are less than 5μ in length, and therefore the present MESA Standard of so many fibers greater than 5μ in length is rather ridiculous.

Dr. Langer speculated at this point on why the smaller size fraction may be biologically more active. Certain cleavage planes in minerals have higher surface energies than others. Those with highest surface energy occur infrequently in nature because they are highly reactive and therefore are eliminated by surface adsorption, development of asbestiform habit, etc. But fine crushing of these fibers by man produces large numbers of cleavage fragments having high surface energies and these are more abundant in the smallest size fraction. These also are biologically most active and therefore are likely to do more damage to tissue.

The discussion moved on to the specific comparison of fibers found in commercial amosite factories with fibers found at Silver Bay and vicinity. Dr. Langer pointed out that the abundance of small fibers (previous graph) found in diseased tissue from Patterson are essentially 100% single crystal fragments as determined by electron diffraction. (Later in the afternoon we actually observed some diseased tissue by electron microscopy and there remained no doubt that the fibers were indeed amphibole and that many of them gave very good single crystal diffraction patterns. This discussion was further highlighted by some photographs of diseased lung tissue of a nun from Duluth, Minnesota. It contained many amphibole fibers, and an electron diffraction photograph of one fiber showed a good single crystal pattern.)

Considerable discussion centered on this topic because of alleged (court testimony by Reserve) differences between the fibers of "amosite" found in commercial factory workers and the single cleavage fragments found in both air and water samples from the Duluth-Silver Bay area and at Homestake. These differences were based on the macroscopic properties of commercial amosite asbestos which includes tests for flexibility, tensile strength, etc. These properties, however, are imparted to amosite asbestos by the asbestiform habit.

That is, asbestiform refers to parallel bundles of apparently single crystals, and in the case of amosite, bundles consisting of a large number of individual single crystals whose diameters average about 0.10-0.2μ. The possible differences between the apparently single crystals of asbestos fibers and the single crystals of fibrous cleavage fragments were discussed. Although there is no evidence available it is possible that the small apparently single crystal fibers of natural asbestos may have different surface structure and thus different surface properties. Dr. Langer pointed out that the biological effects of quartz grains are known to depend on their surface properties and their electrostatic balance, and that the difference may be significant. Dr. Langer also accepted the possibility that these apparently single crystals may be composed of cyclic (cylinder like) twines. Dr. Langer mentioned at this point that the amosite single crystals have an unexpected square cross-section which may support this possibility. Unfortunately the surface properties and structures of fibers of that size are either very difficult, if not impossilbe to determine. The possiblilty of twining, however, can and should be checked by available crystallographic methods.

At this point, the subject changed over to the Homestake study and the problem of the absence of GI tract cancer and mesothelioma. It was pointed out that medical experiments with rat populations has failed to produce GI tract cancer by lab ingestion of amphibole fibers. The same is apparently true of arsenic in controlled laboratory experiments. Mesothelioma, on the other hand, has a long incubation period and for that reason it may not yet have occurred at Homestake. The question was raised whether the general conditions in an underground mine (had air fumes, exhaust, etc.) could by themselves be responsible for a slight increase in respiratory cancer. Dr. Nicholson responded by stating that there is some evidence that that may be as high as 2-fold.

The question of the improper use of mineralogical terms, such as "asbestiform", was discussed in a fashion similar to that discussion in Cincinnati. There was an agreement between Dr. Langer and us that we shall make all attempts to clarify that and work out the details of proper terminology, in close cooperation. Dr. Nicholson also acknowledged that the term "asbestiform" has been misused.

Lastly, Tibor Kosa posed the specific question to Dr. Nicholson concerning the change in identity of fibers observed in stack samples from Hanna Mining operations. We looked at photographs of the material and there is no doubt that many fibers are present. Most are stubby, however, with the average having perhaps just 3 to 1 elongation. There were few that were elongated as much as 5 to 1 in contrast to a typical amphibole fiber sample. More convincing were the electron diffraction patterns. None of these gave the characteristic 5.3 Å repeat and monoclinic symmetry. Instead, a close examination showed an apparent hexagonal symmetry and a predominant spacing that was close to 9.5 Å.

It seems clear that retraction of his earlier identification of the fibers at Hanna was appropriate. It looks like a case of an honest scientific mistake. A technician does most if not all of the fiber counting and electron diffraction and Dr. Nicholson checks over the data once it is collected. It must have been checked over in a great hurry for such an obvious error of fact to occur. It seems fair to say that this unfortunate incident should not reflect poorly on the quality of operations in the Mt. Sinai laboratory. The entire MPCA group was left very favorably impressed with the scientific quality of the actual work that is being done. More care should be taken in preparing accurate, documented and well-written reports, however.

Finally, the proposed 2-week sampling program was discussed. Dr. Nicholson made the comment that rather than obtain the maximum number of new fiber analyses by several labs, time and money would be well spent on a series of duplicate samples by several collecting methods to enable more valid comparisons to be made between existing data. For example, run simultaneous nuclepore and millipore at the same locality, and perhaps change filters more frequently to lessen the fiber overload problem.

The visit at Mt. Sinai School of Medicine was formally concluded at 3:30 p.m. However, informal discussions were carried out between individuals till about 5:00 p.m.

IV

McMASTER UNIVERSITY

Tibor Zoltai visited, independently, with Dr. James Kramer and Otto Murdoch on December 22, 1975, from 9:00 a.m. to 2:00 p.m., at McMaster University.

The electron microscope laboratory of McMaster University is among the best equipped and organized I have seen recently. The sample preparation and preliminary examination equipment are located in the Geology Department and the microscopes in the Medical School.

Mr. Otto Murdoch is in charge of the fiber analysis section, including sample preparation and microscope analysis. He is undoubtedly a well qualified and competent analyst. Apparently, he is, in part, responsible for the development of the McMaster technique.

(1) Sample preparation:

The sample is removed from the filter paper and is suspended in water by ultrasonic vibration (frequency: up to 36,000 pulses per minute).

Water: They had difficulties to obtain clean water. The local public water supplies (Toronto, Hamilton, Dundas) all contain 2-3 million fibers per liter. They experienced similar problems with distilled water, before they found some clean spring water.

Fiber fractures: They feel confident that the ultrasonic vibration does not break up natural asbestos fibers. However, they admit that some fibrous cleavage fragments, if previously cracked, may break up. They have no quantitative data to estimate the magnitude of fiber breakage.

(2) Fiber loss:

Mr. Murdoch has conducted experiments to compare his technique with the "cold finger" procedure of I.I.T. and the "rubout" technique of Mt. Sinai. He claims that both the "cold finger" process has about 40-60% fiber losses, and the "rubout" process can have losses between 30-80%. In addition to that the latter is unreproduceable. The fiber loss at McMaster is estimated to be less than 10%.

Control: They check the fiber loss in the sample preparation by taking an x-ray fluorescence spectrum (for Si, Al, Mg, Fe, Ca, Na etc.) of the filter both before and after the ultrasonic process.

(3) Fiber mounting:

Two microscope screens are mounted for each sample by placing a 1 µl drop of the fiber-containing water on each microscopic screen with an automatic pipette, using a clean funnel tip each time - there is no information available concerning the loss of fibers in the pipette tips.

Distribution of fibers on the screen: The drop of water dries in a few hours. If the screen is kept right-side up the fibers will be concentrated around the edge. If the screen is dried in an upside down position the fiber distribution will be reasonably even.

(4) Electron microscope:

McMaster has three Phillips 300 transmission and a scanning electron microscope. The transmission microscopes are equipped with electron diffraction modes and by energy-dispersive x-ray analyzers. The latter is connected to a computer for evaluation.

(5) Fiber counts:

In each microscope screen they take a diagonal (or radial) row of grids and count all fibers found. Their minimum size of fibers determined is in order of 250 Å (=˙02.5 μ). They take both electron diffraction and energy-dispersive x-ray spectra on a certain portion of fibers. Their counting procedures are similar to those used by others. However, they may be less discriminatory than Mount Sinai. That is, their amphibole fiber counts include both amphiboles and possible amphiboles.

The personnel at McMaster have expressed concern about the difficulties associated with the conclusive identification of electron diffraction patterns.

In conclusion, I believe that the McMaster electron microscope laboratory is among the best and most dependable. Their usually high fiber counts seem to be, primarily due to less fiber loss in sample preparation, secondarily to a less discriminatory acceptance of amphiboles in the count, and tertiary to possible breakage of fibers in the ultrasonic treatment.

V

NATIONAL WATER QUALITY LABORATORIES

On January 6, 1975, between 11:00 a.m. and 3:00 p.m. we visited the National Water Quality Laboratory in Duluth. Present at the meetings were Gary Eckhardt, of MPCA, Tibor Zoltai and James Stout, consultants to MPCA, and Dave Gray, Kyle Bishop and Steven Ring representing the Minnesota Department of Public Health. This group met at 12 noon with Phil Cook, of EPA, to discuss analytical procedures and problems concerning fiber counts.

Phil Cook proceeded to run through their routine for gathering and handling samples. EPA prefers nuclepore filters because with proper loading the transfer problems are minimized. When they find it necessary to transfer and refilter, they use a low temperature asher in a clean lab. When asked what the probable percentage loss of fibers was with this procedure, Phil was reluctant to report a figure. He believed the number would be less than the factor of four reported by the Mt. Sinai group. Dave Gray and Kyle Bishop, from their own experience, were concerned that there could be significant losses in the ashing process.

As far as actual fiber counting is concerned, Phil Cook and his staff count all fibers, whether inorganic or organic. They need only have at least a 3 to 1 length-width aspect ratio. The only fibers counted as amphibole are those that meet the following criteria:

1. Have 3 to 1 length-width ratio,
2. Display an electron diffraction pattern that either matches or is very similar to the pattern of standard cummingtonite.

With regard to criterion 2, recognition of the cummingtonite pattern is based on the presence of a 5.3 Angstrom repeat in the reciprocal lattice parallel to the c-crystallographic axis, or the direction of fiber elongation, and the usual appearance in the perpendicular direction of more closely spaced diffraction spots corresponding to the a* and b* reciprocal lattice points. These patterns are not measured because of the time required for each fiber. According to Phil Cook, the time presently required to obtain a statistical fiber count is approximately 16 hours per sample.

When asked how he interprets the electron diffraction patterns, Phil maintained that it was unnecessary to measure each diffraction pattern because experience has shown that in every case, the energy dispersive analysis revealed the fiber to be amphibole. He admitted that if the sample were completely foreign, he would be very careful to interpret both the electron diffraction pattern and energy dispersive spectra.

It was also made clear at this meeting that there is no lower cut-off limit on fiber counting. All fibers are counted down to the resolution of the electron microscope. Phil distributed copies of an outline of their handling and fiber counting procedures.

Phil Cook then guided us through the electron microscope lab. It seemed very clean and orderly. In the instrument was a tailings overflow sample from Silver Bay. There were obvious fibers present, many of them showing recognizable amphibole form and cleavage. In particular, some fibers displayed a "dovetail" morphology due to intersecting (001) cleavage faces where the (100) twinning was apparently present. Electron diffraction patterns were obtained for several single crystals and twinned crystals were obtained. A preliminary examination of the diffraction photographs sent to us by Phil Cook confirmed this interpretation.