

*Please Circulate
Return to LFW*

10/10/77

RECEIVED
OCT 13 1977

MOV	_____	☒
ROP	_____	☒
LDW	_____	☒
SGC	_____	☒
SDS	_____	☒
RCM	_____	☒
CAR	_____	☒
WCF	_____	☒

The "Asbestos" Minerals: Definitions, Description, Modes of Formation,
Physical and Chemical Properties, and Health Risk to the
Mining Community

Malcolm Ross
U.S. Geological Survey
National Center, 959
Reston, VA 22092

*RTJ
pls copy
for the
"Asbestos"
file.
New 12/16
also me
copy for
KWN
mm*

PLAINTIFF'S EXHIBIT
ASA-847

To be published in: Workshop on Asbestos: Definitions and Measurement Methods,
National Bureau of Standards Special Publication (1977).

Abstract

The mineralogical description of "asbestos" given here is based on a very special feature common to all forms of commercial "asbestos" -- the property that permits the minerals to separate into long tubes or fibrils only a few tens of nanometers thick. This separation can be accomplished by very light grinding or agitation; the common nonfibrous amphiboles do not separate into such fibrils even after intense grinding. The ease of such fibril separation may be caused by the special nature of the crystal structures of the commercial "asbestos" minerals. Repeated twinning on (100) in amosite and crocidolite, the curling of layers of chrysotile to form tubes, and the presence of triple, quadruple, and n -tuple chains ("Wadsley" defects) in amosite, crocidolite, anthophyllite, and tremolite are the structural features that probably promote the formation of thin fibrils. Stability diagrams in the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ indicate possible geochemical processes by which commercial "asbestos" can form.

The relative health risk posed by exposure to the "asbestos" minerals may be related to the fibril composition, crystal structure, size, shape, and total surface area. The relative chemical reactivity of the fibril surface is predicted to be

chrysotile < anthophyllite < amosite < crocidolite

on the basis of the types of oxidation-reduction and exchange reactions that may occur. According to epidemiological studies relative health risk appears to be anthophyllite < chrysotile < amosite < crocidolite.

"Asbestos" health risks in the mining and milling industry and environs is reviewed. Health studies done in the chrysotile mining district of Québec, Canada, have presented good evidence that realistic "asbestos" dust standards can be set that not only protect the worker and resident of the mining areas from undue health risk but also allow the industry to operate economically.

Key Words

Asbestos, amphibole, chrysotile, talcbole, tremolite, actinolite, anthophyllite, amosite, cummingtonite, hornblende, amphibolite, serpentinite, grunerite, crocidolite, mesothelioma, lung cancer, health risk, Wadsley defects, asbestos stability, ambient air, dust levels, surface chemistry, chrysotile mining, chrysotile emissions, Thetford Mines, Quebec, Canada, Urals, U.S.S.R., Homestake Mines, S.D., Hunting Hill Quarry, Rockville, Md.

Introduction

It is generally a rather straightforward, though often time-consuming mineralogical task to describe the physical and chemical properties of amphiboles and serpentines, including those varieties referred to as "asbestos". Exceptions are minerals such as fibrous tremolite and fibrous talc that to date do not have adequate mineralogical descriptions. Defining minerals that constitute an "asbestos" health hazard is an entirely different and a much more complex problem, for it involves many factors not included within the science of mineralogy.

This commentary is concerned with the various definitions of "asbestos" as they relate to: (1) the medical profession, which must determine which types of mineral particles constitute an "asbestos" health hazard; (2) the legal and regulatory professions, which must enact and enforce the laws relating to "asbestos" use, (3) the mineralogical profession, which must describe the chemical, structural, and physical properties of such minerals, and (4) the mining ^{and} quarrying industries, which may be affected by these definitions.

What is "Asbestos"?

Three definitions of "asbestos" found in the Glossary of Geology [9, p. 41] are quoted as follows: "asbestos (a) A commercial term applied to a group of highly fibrous silicate 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 (esp. tremolite, actinolite, and crocidolite). (c) A term strictly applied to the fibrous variety of actinolite.

The term "asbestos," from a geoscientist's point of view, applies only to the minerals chrysotile (one of the serpentine polymorphs), "amosite" (a variety of grunerite), "crocidolite" (a variety of riebeckite), anthophyllite, tremolite, and actinolite when they are present in sufficient quantity to be commercially valuable for their special physical and chemical properties, which include fibrous habit, insulation qualities, low electrical conductivity, fire resistance, and suitability for weaving. Many other minerals sometimes possess habits described variously as acicular, asbestiform, elongate, fibrous, bladed, lamellar, filiform, prismatic, or columnar; for example, minerals of the zeolite group having acicular habit, fibrous calcite and quartz, acicular wollastonite, prismatic pyroxenes, elongate crystallites of attapulgite, and filiform sepiolite. Since these minerals are not exploited for the commercially valuable properties listed above, they are not called "asbestos" by geoscientists.

At present, the most widely used definition of "asbestos" by various groups concerned with environmental health problems, including the U. S. Environmental Protection Agency (EPA) and the U. S. Mining Enforcement and Safety Administration (MESA), is from the notice of proposed rulemaking for "Occupational Exposure to Asbestos" published in the Federal Register (Oct. 9, 1973: p. 47652, 47660) by the U. S. Occupational Safety and Health Administration (OSHA). In this notice, the naturally occurring minerals chrysotile, amosite, crocidolite, tremolite, anthophyllite, and actinolite are classified as "asbestos" if the individual crystallites or crystal fragments have the following dimensions: length - greater than 5 micrometers, maximum diameter - less than 5 micrometers and a length to diameter ratio of 3 or greater. Any product containing any of these minerals in this size range are also defined as "asbestos."

The crushing and milling of any rock usually produces some mineral particles that are within the size range specified in the OSHA rules. Thus, these regulations present a formidable problem to those analyzing for "asbestos"

1

minerals in the multitude of materials and products in which they may be found in some amount, for not only must the size and shape of the "asbestos" particles be determined, but also an exact mineral identification must be made.

A wide variety of amphiboles is found in many types of common rocks; many of these amphiboles might be considered "asbestos" depending upon the professional training of the person involved in their study and the methods used in mineral characterization. Campbell et al. [3] have carefully described the differences between the relatively rare fibrous varieties of the amphiboles and the common nonfibrous forms.

If the definition of "asbestos" from the point of view of a health hazard does include the common nonfibrous forms of amphibole, particularly the hornblende and cummingtonite varieties, then we must recognize that "asbestos" is present in significant amounts in many types of igneous and metamorphic rocks covering perhaps 30 to 40 percent of the United States. Rocks within the serpentinite belts; rocks within the metamorphic belts higher in grade than the greenschist facies, including amphibolites and many gneissic rocks; and amphibole-bearing igneous rocks such as diabase, basalt, trap rock, and granite would be considered "asbestos" bearing. Many iron formations and copper deposits would be "asbestos" bearing, including deposits in the largest open-pit mine in the world at Bingham, Utah. "Asbestos" regulations would thus pertain to many of our country's mining operations, including much of the construction industry and its quarrying operations for concrete aggregate, dimension stone, road metal, railroad ballast, riprap, and the like. The "asbestos" regulations would also pertain to the ceramic, paint, and cement industries and to many other areas of endeavor where silicate minerals are used.

We do not know whether health investigators will consider other minerals that commonly possess a fibrous or acicular habit to be health hazards; minerals such as wollastonite, the fibrous forms of calcite and quartz, acicular minerals of the zeolite mineral group, the pyroxenes, the sepiolite

1

minerals including attapulgite, and the calcium silicates found in Portland cement. Certainly if the common amphiboles such as hornblende, tremolite, actinolite, gedrite, and cummingtonite with their typical prismatic cleavage are considered health hazards, the common pyroxenes having similar habits should also be considered health hazards.

A Mineralogical Description of Commercial "Asbestos"

The commercial deposits of "asbestos" contain one of the following minerals: chrysotile, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$; amosite, $(\text{Fe}^{2+}, \text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ (a variety of grunerite); crocidolite, $\text{Na}_2(\text{Fe}^{2+}, \text{Mg})_3\text{Fe}_2^{3+}\text{Si}_8\text{O}_{22}(\text{OH})_2$ (a variety of riebeckite); "fibrous" anthophyllite, $(\text{Mg}, \text{Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$; and "fibrous" tremolite and actinolite, $\text{Ca}_2(\text{Mg}, \text{Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$. Tremolite and actinolite are now, as they were in the past, of little economic importance; anthophyllite is of little economic importance now. About 95 percent of the commercial asbestos now used in the United States is chrysotile; of which about 90 percent is imported from Canada. No commercial amosite or crocidolite has ever been mined in the United States.

In addition to being compositionally different, the five amphibole forms of commercial "asbestos" have completely different crystal structures from that of chrysotile. The structure of chrysotile consists of double layers, each consisting of a layer of linked SiO_4 tetrahedra that is coordinated to a second layer of linked $\text{MgO}_2(\text{OH})_4$ octahedra through the sharing of oxygen atoms; the composite double layer rolls up, like a window shade, to form long hollow tubes. The diameters of the individual tubes are on the order of 25 nm; the length-to-diameter ratio can vary from 5 or 10 to well over 10,000.

The structures of the amphibole minerals, on the other hand, are composed of strips or ribbons of linked polyhedra, which join together to form the three-dimensional crystal. The individual strips are composed of three elements--two

double chains of linked $(\text{Si,Al})\text{O}_4$ tetrahedra that form a "sandwich" with a strip of linked MgO_6 , FeO_6 , or AlO_6 octahedra. The structural relationship of the upper double tetrahedral chain to the octahedral part of the strip is shown in figure 1. The three-dimensional arrangements of these strips or "I-beams" [26] in orthoamphibole (anthophyllite) and in clinoamphibole (tremolite, amosite, actinolite, and crocidolite) are shown in figure 2.

One feature is common to the six "asbestos" minerals: their ready separation into long fibrils or tubes only a few tens of nanometers in diameter. This separation can be accomplished by very light grinding or by agitation in water by means of an ultrasonic separator. The common nonfibrous amphiboles do not separate into such fibrils even after intense grinding; instead, they break up along cleavage planes into rather short stubby prisms--th^{ough} the length-to-diameter ratio may still be greater than 3:1.

What causes the special type of fibril separation found in commercial forms of "asbestos" but generally not in the nonfibrous amphiboles? Three observations are pertinent:

(1) Chrysotile, which forms individual hollow tubes, can separate into fibrils as thin as the diameter of the individual tube. The chemical bonding between tubes is very weak and perhaps is due only to van der Waals forces; thus, the tubes are easily separated from one another.

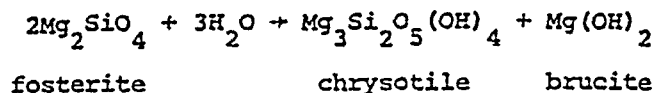
(2) Amosite and crocidolite "asbestos" from South Africa is repeatedly twinned on (100) as has been observed in electron microscope studies [4, 15, 25, 34]. This "polysynthetic" twinning, which produces repeated planar faults parallel to (100), is extremely rare in the nonfibrous calcium-rich amphiboles (temolite, hornblende) and uncommon in nonfibrous amphiboles of the cumming-tonite-grunerite series [30, 31, 32].

(3) Amosite, crocidolite, fibrous anthophyllite, and fibrous tremolite have been shown to possess chain defects, also called "Wadsley" defects [8, 15, 36, 37, 38]. These defects are caused by the formation of expanded "I-beams" that are composed of triple, quadruple ...etc. chains of linked $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra rather than the double chains found in all amphibole crystal structures. If these "I-beams" are expanded indefinitely, the resulting strip becomes identical with the single talc layer of composition $\text{Mg}_6\text{Si}_8\text{O}_{20}(\text{OH})_4$; recall that the composition of anthophyllite is $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. These expanded "I-beams" units can intermix with the regular amphibole "I-beams" to form a variety of minerals that I refer to as "talcholes" in allusion to their hybrid character--between talc and amphibole. Veblen [38] has described the detailed structures of four of these "talcholes" obtained from specimens originally described as "fibrous anthophyllite." In these crystal structures, "I-beams" of one or two types form an ordered three-dimensional structure. Veblen [38] showed evidence, as did Hutchison et al. [15], that disordered arrangements of these structural units also occur. Hutchison et al. [15] reported the presence of expanded "I-beams" structures in fibrous tremolite, and Franco et al. [8] reported the apparent presence of triple-chain lamellae, seen as planar faults on (010), in crocidolite from Western Australia.

Formation of "Asbestos"

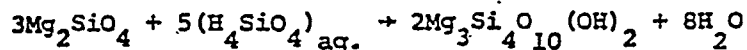
How do chrysotile and the "talcholes" form? Modes of origin can be inferred from the stability relationships among talc, anthophyllite, enstatite, forsterite, antigorite, and chrysotile given by Hemley et al. [13]. Their mineral stability fields at 1 kbar H_2O , in terms of crystallization temperature and molality of aqueous silica, are given in figure 3. This figure shows a number of relationships pertinent to the problem of ^{formation of} "asbestiform" minerals. As the temperature decreases, forsterite (Mg-rich olivine) can react

to form antigorite or chrysotile depending on the silica concentration in the aqueous solutions to which the olivine-bearing rock is exposed. One chemical reaction that may lead to the formation of brucite-bearing serpentinite is:

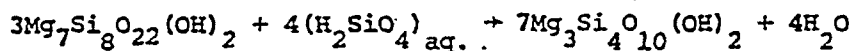


This reaction may explain the origin of the very long brucite needles, referred to as "nemalite," that are found in various serpentinites. Thirty-centimeter-long needles of this mineral were collected by C. E. Brown (U.S. Geol. Survey) from a Quebec serpentinite locality and were examined by single-crystal X-ray methods (Malcolm Ross, unpub. data). The brucite needles show hexagonal symmetry, $a = 0.315 \text{ nm}$, $c = 0.474 \text{ nm}$, and the long direction of the needles are parallel to the brucite a -direction. The rather marked line broadening that appears in the X-ray pattern suggests that the brucite needles are composed of many small crystallites oriented so that their a -axes are parallel to the fiber direction. The brucite needles are intergrown with chrysotile, for chrysotile X-ray reflections are superimposed on the diffraction pattern of brucite, and extremely long chrysotile fibrils remain when the brucite needles are dissolved by dilute HNO_3 .

At higher concentrations of aqueous silica forsterite may alter to talc by the reaction:



At silica concentrations near the quartz saturation curve, anthophyllite can alter directly to talc by the reaction:



This reaction may be of importance for the formation of fibrous anthophyllite and talc. As the temperature decreases and the H_2O , Mg^{2+} , and silica

activities remain within geologically reasonable limits one probable reaction sequence is: .



If the alteration of a chain silicate to talc proceeds by an intragranular reaction, "talcboles-type" phases may form as intermediates between anthophyllite and talc during low-temperature alteration. Figure 4 shows the stability fields of forsterite, enstatite, anthophyllite, and talc in terms of temperature and molality of aqueous silica [13]. A stability (or metastability) field for the "talcboles" (labeled "asbestos") is superimposed on this diagram, overlapping the fields of talc and anthophyllite. The fibrous nature of the "talcboles" can be explained if the alteration process of a chain silicate (anthophyllite) to a sheet silicate (talc) proceeds by reforming the double chains at the unit-cell level. In figure 4, the phase boundary between enstatite (a pyroxene having the formula $\text{Mg}_2\text{Si}_2\text{O}_6$) and anthophyllite suggests the possibility of having mixed single chain (pyroxene) and double chain (amphibole) structures.

The fibrous nature of commercial amosite and crocidolite appears to be related to the crystal growth mechanism; perhaps the crystallites nucleate at many centers and grow as individual fibers only a few tens of nanometers thick (see Franco et al. [8, figures 1, 2]). The presence of (100) twinning and "Wadsley" defects may be the result of rapid growth and, in addition, may hinder growth in a direction perpendicular to the fiber axis.

Properties of "Asbestos" that may be Related to Health Risk

Health studies suggest that of the four economically important forms of "asbestos," crocidolite has been responsible for the greatest health risk, followed by amosite, then chrysotile, and lastly anthophyllite [11]. If we

assume that the health hazard caused by the commercial "asbestos" minerals is due to some combination of their chemical, structural, and physical properties, we can make some predictions about their relative biological activity.

All commercial "asbestos" minerals separate into very thin fibrils; possible reasons for this have been discussed previously. The thickness, length, and flexibility of the fibrils apparently is important in determining to how the fibrils lodge in human tissue and how readily they are cleared from the lung areas. The straight fibrils of small diameter, particularly those of crocidolite, can more readily move to the periphery of the lung, where they are in a position to penetrate the pleura and thus produce mesotheliomas [11]. That curly fibrils, especially those of chrysotile, are more readily arrested in the upper respiratory tract, is given as a reason for the low incidence of mesotheliomas in chrysotile miners and millers [11, 19, 23]. Assessment of the role of fibril size in relation to lung cancer is less clear [11]; however, Gross [12] cited evidence that "asbestos" fibers less than 5 μm long cause negligible pathogenicity, both of the lung and pleura.

The problem of fibril size in relation to cancer incidence is of some importance, for the average ambient airborne "asbestos" fiber is shorter than the average fiber in the whole rock. Brulotte [2] reported that the average concentration of airborne dust particles in the chrysotile mining district of Thetford Mines, Quebec, was 80,500 ng/m^3 during active mining and 39,600 ng/m^3 during a 5-month period when the mines were closed. If we assume that the rock contains 4 weight percent chrysotile, these measurements suggest a minimum chrysotile dust concentration in the ambient air of 3220 and 1584 ng/m^3 .^{1/}

The total surface area of the inhaled fibrils and the chemical reactivity of this surface may have an important influence in the production of cancer.

1/ Conversion of these figures (nanograms chrysotile per cubic meter of air) to numbers of "fibers" per cubic centimeter of air (the value usually given in health studies) is estimated by using the following relations:

(1) density of chrysotile $\approx 2.5 \text{ g/cm}^3 = 2.5 \times 10^9 \text{ ng/cm}^3$

(2) volume of 1 ng chrysotile $= 4 \times 10^{-10} \text{ cm}^3 = 400 \text{ } \mu\text{m}^3$

(3) volume of chrysotile fibers in $\mu\text{m}^3/\text{cm}^3 = \frac{(\text{ng/m}^3)}{2500}$

(4) if a fiber having dimensions $1 \text{ } \mu\text{m} \times 1 \text{ } \mu\text{m} \times 5 \text{ } \mu\text{m}$ ($5 \mu\text{m}^3$) is designated as a "standard fiber," then

$$1 \text{ ng chrysotile} = 80 \text{ "standard fibers"}$$

(5) number of chrysotile "standard fibers"/ $\text{cm}^3 = \frac{(\text{ng/m}^3)}{12,500}$

Researchers have not yet determined whether this surface plays a direct part in the formation of cancerous tissue, or whether a carcinogenic chemical adheres to the mineral surface and the chemical itself later reacts with the tissue or in some way catalyzes the carcinogenic process. The high incidence of lung cancer in men who worked in the "asbestos" trades (textiles, brake-lining fabrication, insulating) and who also smoked [33] indicates that carcinogenic chemicals in the tobacco smoke may somehow interact with the "asbestos" fibrils. If many of the fibrils are not easily cleared from the lung, they may adsorb these chemicals and hold them indefinitely. Injection of "asbestos" fibrils directly into the pleura of animals causes a high incidence of mesothelioma [40]. These experiments suggest a direct relationship between the active fibril surface and production of pleural cancer. However, other dissimilar substances injected into animals also cause tumors; for example, nonfibrous hematite (Fe_2O_3), sanidine (KAlSi_3O_8), and corundum (Al_2O_3), [27].

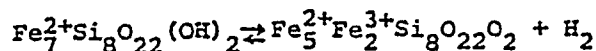
As a generalization, the relative chemical reactivity of the exposed fibril surfaces of the four important forms of commercial "asbestos" in aqueous solutions is:

chrysotile < anthophyllite < amosite < crocidolite.

Chrysotile, the least reactive of the four, is composed of rolled-up layers that possess no broken chemical bonds except where the edges of the layers are exposed at the ends of the tubes. The three amphiboles, on the other hand, have broken chemical bonds on all surfaces of the fibrils.

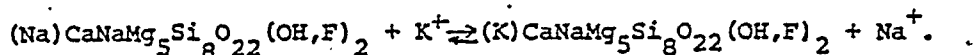
Anthophyllite can alter to various other silicates in aqueous solutions, as has been explained above. Similar alteration mechanisms might also exist for crocidolite and amosite, although to my knowledge, these have not been

documented. However, studies of the geochemistry of silicates indicate that the exposed surfaces of these two amphiboles present some interesting possibilities for chemical change. Amosite (and also crocidolite) can undergo oxidation-reduction reactions of the type,

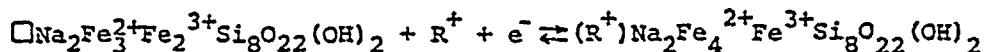


Ernst and Wai [6] have demonstrated that this reaction takes place in iron-bearing sodic amphiboles at 705°C. The complete reversibility of such a reaction in the chemically similar silicate mineral biotite, has been demonstrated by Wones [42] and by Takeda and Ross [35]. In the experiments of Wones, auto-oxidation was accomplished in a neutral atmosphere (flowing argon) at 500° to 700°C. Reduction was accomplished by passing hydrogen gas over the crystals. Analogous reactions can take place at much lower temperatures but also at much lower rates.

Cation exchange reactions take place in the amphiboles known as richterites [14]; exchange is accomplished within the A-site of the amphibole structure at 775-850°C by the reaction



Crocidolite having a partially filled A-site such as that from Bolivia [41] can also undergo exchange reactions with potassium being replaced by sodium and possibly ^{by} oxonium and ammonium ions. Crocidolite with a partially or completely vacant A-site may undergo exchange reactions coupled with oxidation-reduction, e.g.



where $\text{R}^+ = \text{K}^+, \text{Na}^+, \text{H}_3\text{O}^+, \text{or } \text{NH}_4^+$, and $\square$ = a vacant site.

Whether such reactions can take place within animal tissue is not known, but the charge^d and reactive surfaces of crocidolite and amosite fibrils appear to offer excellent sites or templates for the initiation of complex chemical changes.

The surface area^a available for adsorption is, of course, directly related to fibril thickness or diameter. The specific surface of chrysotile, as measured both by nitrogen adsorption and permeability, is about twice that of amosite and crocidolite [28]. Because chrysotile forms hollow tubes, this larger area for adsorption in chrysotile is predictable if the average fiber thickness is similar for all three minerals.

The strain-free layer of chrysotile has a radius of curvature of about 8.8 nm [5]; thus, the minimum diameter of the tube should not be much less than 17 nm. The most frequently measured tube diameter is about 26 nm. Bates and Comer [1] found in a study of chrysotile from Arizona and Quebec, a range of diameters from 11.4 to 85 nm; the average diameter was 25 nm. The fiber size ranges in the other forms of commercial "asbestos" have not come to my attention, although some crocidolite fibers from Western Australia [8] appear to be on the order of 50 nm wide.

"Asbestos" Health Risks in the Mining and Milling Industry and Environs

Although a significant health risk for those who work in the "asbestos" trades, particularly for those who smoke, has been well documented, such a risk is not clearly documented for those in the "asbestos" mining and milling industry and for those who reside in areas of such activity. The most detailed study of an "asbestos" mining community is that of the chrysotile mining areas of Quebec, Canada; the studies were started in 1966 and continue

to the present [20, 21, 22, 23]. Similar studies of chrysotile miners on a smaller scale have been undertaken by Kogan et al. [16] in the Urals, U.S.S.R., and by Vigliani [39] in Italy. According to McDonald [17, 18] these other studies came to the same conclusions on health risk as the Quebec studies, the latter of which have led the way in making some assessment of the health risk relative to the amount of dust to which the workers were exposed. Health-risk studies of workers in the "asbestos" trades, for the most part, have not given reliable dust-exposure figures, or even the relative amounts and types of "asbestos" inhaled.

Chrysotile has been mined in the Thetford Mines, Black Lake, and Asbestos localities of Quebec for nearly a century, beginning in 1886. Production has increased steadily since then, reaching 907,000 metric tons in 1956 and 1,500,000 metric tons in 1976. A tremendous amount of ambient dust has been generated over the years both by mining activities and by the winds blowing over the huge tailings piles. Even in 1974, when dust-emission controls had much improved over those of the earlier years (72 million particles per ft³ in 1950 to 4 million particles per ft³ in 1975 [20]) as a result of wet drilling, watering of haul roads, etc., emissions of particles from chrysotile mining and milling operations in the Province of Quebec amounted to 140,000 metric tons, of which about 4 percent (5600 metric tons) was "asbestos" dust [2]. The ambient dust levels for this region have already been discussed.

Is there a high incidence of cancer of the lung and pleura among the 35,000 residents of the Thetford Mines area of Quebec, 10 percent of whom are employed in the chrysotile industry? According to McDonald et al. [17, 18, 19, 20, 21, 22, 23], the cancer incidence for the male employees in the Quebec chrysotile industry is similar to the male cancer incidence in the whole of Canada. In table 1 is given the proportional mortality from lung

cancer and mesothelioma for the Quebec and North Italian chrysotile miners and millers and also for the entire populations of various countries in the year 1970. In the period 1936-1973 seven cases of mesothelioma have been reported in the Quebec mining and milling industry [19, table 12]. The world-wide incidence of mesothelioma in those who worked in the chrysotile mining and milling industry for the period 1958 to 1976 is 11 cases [19, table 4]. The Canadian studies do show an increased incidence (2.1 to 3.6 times) of lung cancer for those workers exposed to the highest concentrations of dust -- 400 to 800+ mpcf-yr². However, these studies show that little health risk is experienced by workers breathing less than 200 mpcf-yr for a working life of 50 years.

An unusually high number of deaths caused by lung cancer in Homestake gold miners during the period 1960 to 1973 has been reported by Gillam et al. [10]. The cohort consisted of 440 individuals who in 1960 had worked 5 years or more underground. Gillam et al. attributed the high incidence of lung cancer to inhalation of cummingtonite amphibole. They did not specify whether the hornblende amphibole, also present in the rock being mined, also contributed to health risk. In rebuttal to this work, McDonald et al. [24] reported on a health analysis of a cohort of 1321 Homestake miners whose working period was from as far back as 1937 to the end of 1973; each of the miners had more than 21 years mining service. Deaths resulting from malignant neoplasms were very close to those expected (93 observed, 90.5 expected); this includes the subcategories of malignant neoplasm -- respiratory, gastro-intestinal, and "other" cancers. The excess death found in the Homestake miners was due in fact to silicosis, silico-tuberculosis, and heart disease. McDonald et al. [24] stated, "The pattern of mortality of men with long employment in this

^{2/} This unit expresses (in millions) the average number of particles (including approximately 4% chrysotile) contained in each cubic foot of air inhaled during a worker's career in the mines or mills times the number of years the worker was employed. If the dust is assumed to contain 4% chrysotile, then working for 50 years at a dust level of 16 mpcf (800 mpcf-yr) is roughly equivalent to inhaling 23 chrysotile particles for every cm^3 of air taken into the lungs during the employment lifetime. A figure of 200 mpcf-yr is roughly equivalent to 6 particles of chrysotile/ cm^3 . Conversion from dust particle measurements to chrysotile fibers per cm^3 is difficult because chrysotile abundance varies from place to place.

industry indicates a serious pneumoconiotic hazard characteristic of hard rock miners but not of cancer."

Fears [7] has made an epidemiological study of cancer risk, including respiratory cancer, in 97 U. S. counties in 22 States known to be mining chrysotile or amphibole "asbestos." He found no excess of cancer mortality compared with cancer mortality rates in 194 demographically matched counties in which such minerals are not known to be mined; cancer mortality in both groups of counties was significantly below the national average.

At present, people are concerned about the possible health hazards associated with the quarrying of serpentine rock at Hunting Hill quarry near Rockville, MD, and its use as a surface material for roads, playgrounds, and parks. The rocks being quarried here are very similar geologically to those of the chrysotile mining localities of Quebec, except that they contain much less chrysotile -- about 0.5 weight percent. Rohl et al. [29] from Mount Sinai Hospital reported chrysotile fiber abundances of 500 to 4700 ng/m³ of air sampled adjacent to roads and a parking lot paved with loose crushed stone from the Hunting Hill quarry. The highest figures were measured during "moderate" motor vehicle use. The Mt. Sinai figures are equivalent to 0.2 to 1.9 µm³ of chrysotile per cm³ of air or 0.04 to 0.4 "standard fibers" per cm³ of air. Air samples taken near the perimeter of the Hunting Hill quarry gave chrysotile mass concentrations of from 0.02 to 64 ng/m³ or 2×10^{-6} to 5×10^{-3} "standard fibers" per cm³ of air (U. S. Bureau of Mines, State of Maryland, and McCrone Assoc., unpublished data). The present U. S. Government limits for "asbestos" content of air are 2 fibers/cm³ (OSHA) and 5 fibers/cm³ (MESA) where a fiber is defined as longer than 5 µm, less than 5 µm wide, and having a length-to-width ratio of 3:1 or greater.

The publicity about the possible health risk because of dust emission from the Hunting Hill quarry and its rock products had caused the quarry to lose about 30 percent of its business by July 1, 1977. Montgomery County, MD, expected to pay about \$2.3 million in its initial effort to seal the roads so as to reduce dust emissions and to remove loose stone from the parks (The Council Report, Montgomery County, vol. 6, no. 22, July 1, 1977). Apparently, other mining and quarrying operations along the "serpentine belt" of the eastern U. S. from Maine to Alabama also will be considered health risks to the general public [29]. Rohl et al. [29] suggested that exploitation of crushed amphibolite rock also raises the possibility of contamination of the air by "asbestos"-like minerals.

Discussion

The cancer incidence among those employed in the chrysotile mining and milling industry does not appear to be excessive when compared to national populations (table 1). However, the incidence of cancer among those employed in the "asbestos" trades is very high (table 1); incidence of lung cancer being 3 to 4 times that of the average population, incidence of mesothelioma being 130 to 220 times that of the average population. The "asbestos" trades generally utilized a variety of "asbestos" minerals including amosite and/or crocidolite, sometimes mixed into a paste for lagging. If we consider that 80 to 90 percent of all the commercial "asbestos" ever mined was chrysotile and that there is a low incidence of cancer in the chrysotile mining industry, we are led to conclude that either amosite and crocidolite are very hazardous or that there is an additional factor relating to health risk in the "asbestos" trades which has not yet been discovered. Previously, I have discussed some reasons why these two minerals may be more chemically reactive than chrysotile.

Definitive epidemiological studies of the amosite mining regions of South Africa and the crocidolite mining regions of South Africa, Bolivia, and Australia appear to be lacking; such studies are needed in order to understand the high cancer incidence in certain trades utilizing these minerals. It is important to point out that the "asbestos" minerals should be considered separately when analysing their effects on the worker's health. Reasoning by analogy is dangerous; high cancer incidence associated with one form of "asbestos" in a particular occupation does not necessarily mean that there will be the same incidence when utilizing another form of "asbestos" in that or another occupation. Unfortunately, this type of reasoning has led many to assume that any amphibole in any environment will cause high cancer mortality.

The operational problems in defining and characterizing fine mineral particles and the unknown health effects on humans by minerals not generally regarded as "asbestos" appears to be causing more and more investigators to accept rather broad definitions for "asbestos." The present analytical techniques used by the EPA and OSHA do not distinguish between amphibole cleavage fragments and the minerals geoscientists generally consider to be true "asbestos." In fact, if electron diffraction is not used expertly, many pyroxenes might be called "asbestos." For example, bronzite, a common orthopyroxene having the composition $(\text{Mg,Fe})_{8}\text{Si}_{8}\text{O}_{24}$, is very similar chemically to amphiboles of the cummingtonite-grunerite series, $(\text{Mg,Fe})_{7}\text{Si}_{8}\text{O}_{22}(\text{OH})_{2}$. Also, orthopyroxene gives an electron diffraction pattern similar to that of cummingtonite -- both patterns possess 0.52 nm spacings between the diffraction row lines in the h₀l reciprocal lattice net. A full interpretation of the patterns is necessary for positive identification. Similarly, calcic pyroxenes might be confused with amphiboles of the temolite-actinolite series

or with hornblende. Cumingtonite (and possibly hornblende) is considered an "asbestos" health hazard by health investigators from the National Institute of Occupational Safety and Health (NIOSH), as reported by Gillam et al. [10]. The Mt. Sinai group [29] suggested that crushed amphibole-bearing rocks (amphibolite) used as road-surfacing material may result in wide-spread "asbestos" contamination of community air.

Along with the general use of broader definitions of "asbestos" is a trend toward setting lower and lower limits on the acceptable amount of "asbestos" permitted in the environment (at present the OSHA standard is 2 fibers/cm³; the MESA standard is 5 fibers/cm³, but it will soon be changed to the OSHA value).

A more stringent "asbestos" health standard is presently being proposed by the National Institute for Occupational Safety and Health (Reexamination and Update of Information on the Health Effects of Occupational Exposure to Asbestos, December 1976; document prepared by NIOSH for transmittal to OSHA, as requested by the Assistant Secretary of Labor). This document states (p. 92-93): "Evaluation of all available human data provides no evidence for a threshold or for a safe level of asbestos exposure."

"In view of the above, the standard should be set at the lowest level detectable by available analytical techniques----."

"Since phase contrast microscopy is the only generally available and practical analytical technique at the present time, this level is defined as 100,000 fibers >5 μ m in length/m³ (0.1 fibers/cc)----."

A definition of "asbestos" to include many amphiboles, chrysotile, and possibly other minerals that appear fibrous or acicular in the electron microscope coupled with a fiber-concentration standard of 0.1 fibers/cm³ should serve to shut down a large number of our hard rock mines and quarries.

Also, nothing has yet been said about the effect of such standards on construction workers building highways, tunnels, bridges, or dams on amphibole-bearing rock, nor of the agricultural workers who are exposed to fiber-containing dust while working the croplands. If the present concept of low or "zero threshold" health risk and broad use of "asbestos" definitions continue, much of the crust of the earth could be considered a health hazard.

A way of minimizing the effect on the mining industry of the present and proposed "asbestos" standards, yet still maintaining a good level of health safety, is presented by the Canadian studies of the Quebec chrysotile workers. Here J. C. McDonald and his colleagues G. W. Gibbs, A. D. McDonald, M. R. Becklake, J. Siemiatycki, C. E. Rossiter, F. D. K. Liddell, O. A. El Attar, A. Harper, and many others [17, 18, 19, 20, 21, 22, 23] have undertaken not only to delineate areas of health risk in the Quebec environment but also to assess the exposure limits of rock dust where the incidence of cancer and other diseases is at an acceptably low level. No occupation can be considered to have a zero health risk. It would seem that similar studies in this field would be of value in the United States.

References

- [1] Bates, T.F., and Comar, J.J., Further observations on the morphology of chrysotile and halloysite, Clays Clay Min., 6, 237-247 (1959).
- [2] Brulotte, Raynald, Study of atmospheric pollution in the Thetford Mines area, cradle of Quebec's asbestos industry, Atmospheric Pollution, M.M. Benarie, ed., Elsevier Sci. Pub., Amsterdam, 447-458 (1976).
- [3] Campbell, W.J., Blake, R.L., Brown, L.L., Cather, E.E., and Sjöberg, J.J., Selected silicate minerals and their asbestiform varieties: mineralogical definitions and identification-characterization, U.S. *Bureau of Mines Information Circular 8751, 56 pp. (1977)*
- [4] Champness, P.E., Cliff, G., and Lorimer, G.W., The identification of asbestos, J. Microscopy, 108, 231-249 (1976).
- [5] Deer, W.A., Howie, R.A., and Zussman, Jack, Rock-forming Minerals, vol. 3, Sheet Silicates, Longmans, Green, and Co. Ltd., London (1962).
- [6] Ernst, W.G., and Wai, G.M., Mössbauer, infrared, X-ray, and optical study of cation ordering and dehydrogenation in natural and heat-treated sodic amphiboles, Am. Mineral., 55, 1226-1258 (1970).
- [7] Fears, T.R., Cancer mortality and asbestos deposits, Am. J. Epidemiology, 104, 523-526 (1976).
- [8] Franco, M.A., Hutchison, J.L., Jefferson, D.A., and Thomas, J.M., Structural imperfection and morphology of crocidolite (blue asbestos), Nature, 266, 520-521 (1977).
- [9] Gary, Margaret, McAfee, R^{best}, Jr., and Wolf, C.L., Glossary of Geology, Am. Geological Inst., Washington, D.C. (1972).
- [10] Gillam, J.D., Dement, J.M., Lemen, R.A., Wagoner, J.K., Archer, V.E., and Blejer, H.P., Mortality patterns among hard rock gold miners exposed to an asbestiform mineral, Annals. N.Y. Acad. Sci., 271, 336-344 (1976).

- [11] Gilson, J.C., Asbestos cancers as an example of the problem of comparative risks, Inserm Symposia Series, 52, IARC Scientific Publications No. 13, Environmental pollution and carcinogenic risks, 107-116 (1976).
- [12] Gross, Paul, Is short-fibered asbestos dust a biological hazard?. Arch. Environ. Health, 29, 115-117 (1974).
- [13] Hamley, J.J., Montoya, J.W., Shaw, D.R., and Luce, R.W., Mineral equilibria in the $MgO-SiO_2-H_2O$ system:II Talc-antigorite-forsterite-anthophyllite-enstatite stability relations and some geologic implications in the system, Am. J. Sci., 277, 353-383 (1977).
- [14] Huebner, J.S., and Papike, J.J., Synthesis and crystal chemistry of sodium-potassium rich^terite, $(Na,K)NaCaMg_5Si_8O_{22}(OH,F)_2$: A model for amphiboles, Am. Mineral., 55, 1973-1992 (1970).
- [15] Hutchison, J.L., Irusteta, M.C., and Whittaker, E.J.W., High-resolution electron microscopy and diffraction studies of fibrous amphiboles, Acta Cryst., A31, 794-801 (1975).
- [16] Kogan, F.M., Guselnikova, N.A., and Gulevskaya, M.R., The cancer mortality rate among workers in the asbestos industry of the Urals, Gig. Sanit. 37, 29-32 (1972).
- [17] McDonald, J.C., Cancer in chrysotile mines and mills, Biological effects of Asbestos, Lyon, International Agency of Res. on Cancer, 189-194 (1973a).
- [18] McDonald, J.C., Asbestosis in chrysotile mines and mills, Biological effects of Asbestos, Lyon, International Agency of Res. on Cancer, 155-159 (1973b).
- [19] McDonald, J.C., and McDonald, A.D., Epidemiology of mesothelioma from estimated incidence, Preventive Med., 6, 426-446 (1977).

- [20] McDonald, J.C., and Becklake, M.R., Asbestos-related disease in Canada, Hefte z. Unfallheilkunde, 126, 2. Deutsch-Österreichisch-Schweizerische, Unfalltagung in Berlin 1975, Springer-Verlag, Berlin, 521-535 (1976).
- [21] McDonald, A.D., Harper, A., El Attar, O.A., and McDonald, J.C., Epidemiology of primary malignant mesothelial tumors in Canada, Cancer, 26, 914-919 (1970).
- [22] McDonald, J.C., McDonald, A.D., Gibbs, G.W., Siemiatycki, J., and Rossiter, C.E., Mortality in the chrysotile asbestos mines and mills of Quebec, Arch. Environ. Health, 22, 677-686 (1971).
- [23] McDonald, J.C., Becklake, M.R., Gibbs, G.W., McDonald, A.D., and Rossiter, C.E., The health of chrysotile asbestos mine and mill workers of Quebec, Arch. Environ. Health, 28, 61-68 (1974).
- [24] McDonald, J.C., Gibbs, G.W., Liddell, F.D.K., and McDonald, A.D., Mortality after long exposure to ^mcumingtonite-grunerite (abstr.), Am. Rev. Resp. Disease, Supp., 115, no. 4, 230 (1977).
- [25] Nord, (Jr., G.L.), "State-of-the-Art" of the analytical transmission electron microscope, in Proc. Symposium on Electron Microscopy and X-ray applications to environmental and occupational health analyses, Ann Arbor Sci. Publ., in press (1978).
- [26] Papike, J.J., and Ross, Malcolm, Gedrites: Crystal Structures and intracrystalline cation distributions, Am. Mineral. 55, 1945-1972 (1970).
- [27] Pott, F., and Friedrichs, K.H., Tumoren der Ratten Nach I.P. Injektion faser formiger Staube, Naturw., 59, 318 (1972).
- [28] Rendall, R.E.G., The data sheets on the chemical and physical properties of the U.I.C.C. standard reference samples, in Pneumoconiosis, H.A. Shapiro, ed., Oxford U. Press, (1970).
- [29] Rohl, A.N., Langer, A.M., and Selikoff, I.J., Environmental asbestos pollution related to use of quarried serpentine rock, Science, 196,

1319-1322 (1977).

- [30] Ross, Malcolm, Papike, J.J., and Weiblen, P.W., Exsolution in clin-amphiboles, Science, 159, 1099-1102 (1962).
- [31] Ross, Malcolm, Smith, W.L., and Ashton, W.H., Triclinic talc and associated amphiboles from the Gouverneur Mining District, New York, Am. Mineral., 53, 751-769 (1968).
- [32] Ross, Malcolm, Papike, J.J., and Shaw, K.W., Exsolution textures in amphiboles as indicators of subsolidus thermal histories, in Mineral. Soc. Am. special paper no. 2, J.J. Papike, ed., pp. 275-299 (1969).
- [33] Selikoff, I.J., Hammond, E.C., and Churg, Jacob, Asbestos exposure, smoking, and neoplasia, J. Am. Med. Assoc., 204, 106-112 (1968).
- [34] Seshan, K., and Wenk, H.-R., Identification of faults in asbestos minerals and application to pollution studies, in Proc. Electron Microscope Soc. Am., 34th annual meeting, G.W. Bailey, ed., 616-617 (Claitor's Pub. Div., Baton Rouge, 1976).
- [35] Takeda, Hiroshi, and Ross, Malcolm, Mica polytypism: Dissimilarities in the crystal structures of coexisting 1M and 2M₁ biotite, Am. Mineral., 60, 1030-1040 (1975).
- [36] Veblen, D.R., and Burnham, C.W., Triple-chain biopyriboles: Newly discovered intermediate products of the retrograde anthophyllite-talc transformation, Chester, Vt. (abstr.), Trans. Am. Geophys. Union, 56, 1076 (1975).
- [37] Veblen, D.R., and Burnham, C.W., Biopyriboles from Chester, Vermont: The first mixed-chain silicates (abstr.), Geol. Soc. Am. Abstracts with Programs 8, 1153 (1976).
- [38] Veblen, D.R., Triple and mixed-chain biopyriboles from Chester, Vermont, Ph.D. thesis, Harvard University, Cambridge, Mass. (1976).

- [39] Vigliani, E.C., Asbestos exposure and its results in Italy, in Proc. International Conf. on Pneumoconiosis, Johannesburg, Oxford U. Press, 192-196 (1970).
- [40] Wagner, J.C., Berry, G., and Trimbrell, V., Mesotheliomata in rats after inoculation with asbestos and other materials, Brit. J. Cancer, 28, 173-185 (1973).
- [41] Whittaker, E.J.W., The structure of Bolivian crocidolite, Acta Cryst., 2, 312-317 (1949).
- [42] Wones, D.R., Physical properties of synthetic biotites on the join phlogopite annite, Am. Mineral. 48, 1300-1321 (1963).

TABLE 1. Proportional mortality from lung cancer and mesothelioma for selected male populations.

Group	Cohort	Deaths		
	No. men	All causes	% lung cancer	%mesotheliom
<u>General populations a/</u>				
Canada (1970)		82,052	5.3	0.03
USA (1970)		988,620	5.1	0.03
Finland (1970).		22,332	7.1	0.04
Italy (1970)		252,795	4.7	-
England - Wales (1970)		278,617	8.9	0.06 .
<u>Chrysotile mining-milling b/</u>				
Quebec (1936-73)	10951	3938	5.7	0.18
N. Italy (1932-70)	1098	270	2.2	0
<u>Anthophyllite mining-milling c/</u>				
Finland (1936-67)	900	216	9.7	0
<u>"Asbestos" trades d/</u>				
Insulators	26505	2137	19.6	6.7.
Asbestos factory	10781	1422	15.0	3.1

a/ Entire male population over 24 years of age [19, table 13]

b/ [19, table 12; 20, p. 525]

c/ [19, table 12]

d/ Composite figures [19, table 12]

FIGURES

Figure 1. Structural relationship between the upper double chain of linked $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra and the octahedra part of the amphibole strip or "I-beam." The circles represent Mg, Fe, or Al atoms in octahedral coordination; at the apices of the polyhedra are oxygen atoms. Tetrahedral Si and Al atoms are not shown. The "I-beams" extend infinitely in a direction parallel to the c-axis (the fiber axis). The width of the "I-beam" in the b-direction is three octahedra. Figure is modified from Papike and Ross [26].

Figure 2. Arrangement of the amphibole strips or "I-beams" in (A) orthoamphibole (space group $P_{21}ma$) and (B) clinoamphibole (space group $C2/m$). The "I-beams" are viewed end-on (parallel to the fiber c-axis). The central portion of the "I-beam" is composed of $(\text{Mg}, \text{Fe}, \text{Al})\text{O}_6$ octahedra; the upper and lower portions are composed of double chains of $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra. The "I-beams" are stacked in two ways: (1) $+++...$ (clinoamphibole), and (2) $+ - + -$ (orthoamphibole). Figure modified from Papike and Ross [26].

Figure 3. Mineral stability relations in the system $\text{MgO}-\text{SiO}_2-\text{H}_2\text{O}$ as a function of log of molality of aqueous silica and temperature, at 1 kilobar H_2O pressure. Figure modified from Hemley et al. [13].

Figure 4. Adaptation of the enstatite-anthophyllite-talc-forsterite stability relationships at 1 kbar H_2O to show a possible stability or metastability field of "talcholo asbestos" (stippled). Figure modified from Hemley et al. [13]. Anth. = anthophyllite.

Figure 1

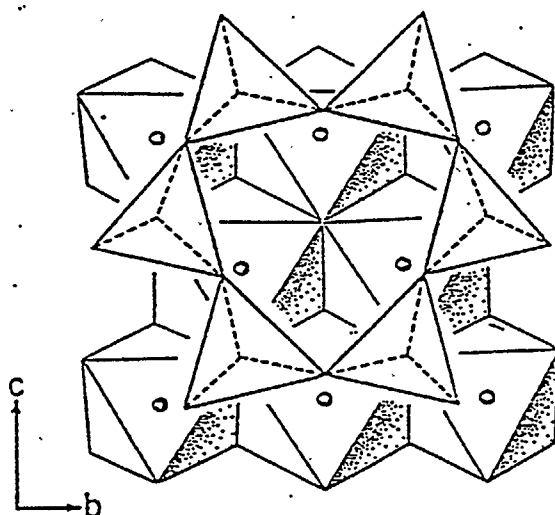


Figure 2

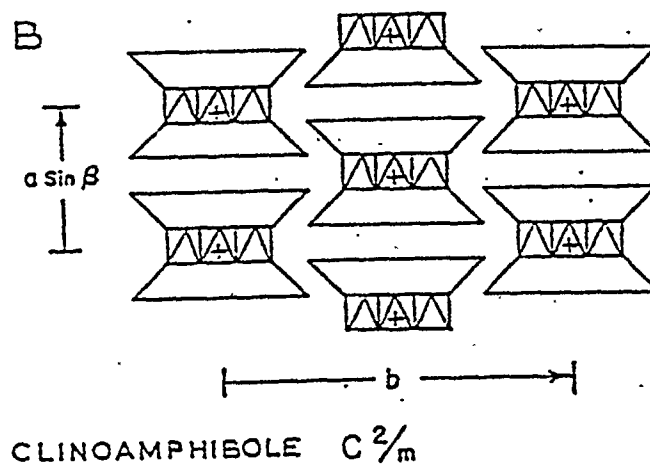
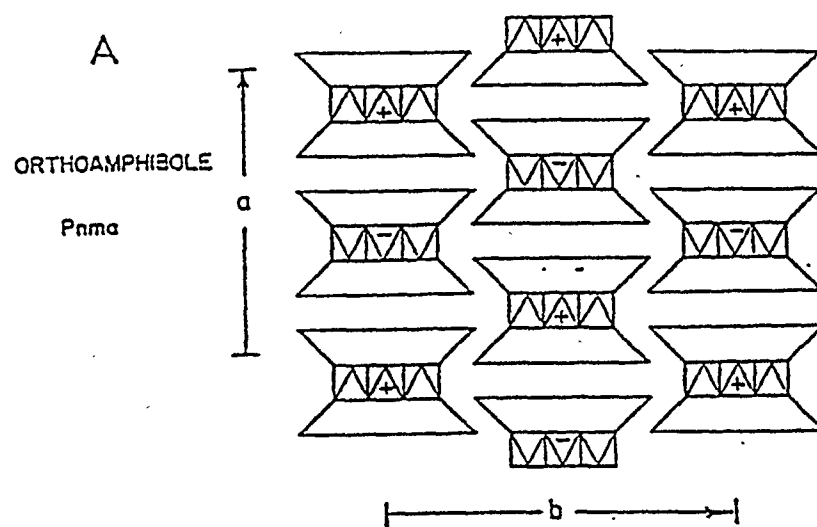


Figure 2