ASBESTOS AND OTHER FIBEROUS MATERIALS

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Mineralogy, Crystal Chemistry, and Health Effects

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Preface

In 1971 the National Academy of Science published a 40-page report, "Asbestos: The Need for and Feasibility of Air Pollution Controls," (Cooper, 1971) summarizing the illnesses associated with occupational exposure to asbestos and the risks of developing asbestosis, pleural calcifications, and cancers of the pulmonary and gastrointestinal tracts and thoracic cavity. Based on the evidence, the committee recommended control and reduction of dust containing fibrous inorganic materials in the workplace; it also discussed nonoccupational exposure to asbestos.

Since this report was published, the government has imposed regulations. The maximum allowable exposure to asbestos fibers in the ambient air of the workplace is now mandated. The workers affected include not only the miners extracting mineral fibers from rock but also the people who manufacture or use products containing asbestos—construction workers, for example. More significant, the emphasis has shifted to the hazards associated with nonoccupational exposure to asbestos. The public has become acutely aware that the environment contains a large quantity of asbestos. It is used as insulation material in homes, schools, other public buildings, and ships, in the brake linings of cars, in hair driers, and in many other products. All of us have been, and continue to be, exposed to asbestos. What are the dangers to the public of this low-level exposure, and what can or should be done about them?

In spite of the publication of thousands of articles on asbestos, and its role as a hazard, the ability to assess the risks to low-level exposure is limited. Many basic scientific and medical questions remain unanswered. For example, we are still a long way from understanding the material known as *asbestos,* much less the relationship between it and disease.

Asbestos is a fibrous inorganic material. It is mined and exploited because of its unique chemical and physical properties, in part the result of its distinctive fibrous form. The hazards, as we understand them, are also attributed to this fibrous character, but asbestos represents only a fraction of the many inorganic fibers now in use. Furthermore, although it is a readily recognizable form, *fiber* has no precise scientific or technical definition. Thus, to address the health effects of asbestos, federal government (OSHA—Oc-

cupational Safety and Health Agency) regulators had to define fiber and to establish the criteria for their regulations.

The purpose of this book is to introduce fibrous inorganic materials, their unique features, and their chemical and structural variety. This survey of fibrous materials, together with a summary of their health and biological effects, provides an opportunity to examine the current theories of disease induction and the hazards associated with exposure, not only to asbestos but to other inorganic fibers as well.

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May 1988

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Many people volunteered their time and expertise from the inception of this effort of a National Research Council/National Academy of Sciences interdisciplinary panel, which was created to review the data on fibrous materials as health hazards. To the members of the panel, especially John Craighead, Graham Gibbs, Irving Kessler, Richard Link, Elburt Osborne, Adrianne Rogers, Andrew Reeves, Paul Weiblen, and Tibor Zoltai, we owe much of our present understanding of the range of problems associated with fibrous materials. We are extremely grateful for the discussions and for written materials they graciously allowed us to use in preparing this book. In addition, many others have assisted and guided us—V. Timbrell of Llangdoch Hospital, Penarth, Wales; M. Hobbs of the University Hospital, Perth, Western Australia; Ian Webster of the South African Institute for Medical Research, Johannesberg, South Africa; Jack Harrington of the National Cancer Association of South Africa, Johannesburg, South Africa; and many colleagues in the United States including Hatten Yoder, E-an Zen, Peter Buseck, Joan Clark, Bernard Gee, Daryl Carter, Karen Antrum, Raymond Yesner, J. Wister Meigs, Irving Selikoff, Art Langer, David Veblen, Hilton Lewinsohn, and William Petrie, to name only a few. We thank them all but hold ourselves responsible for the book's accuracy and the interpretations presented herein.

No book is ever contemplated or completed without the patience and dedication of the editor and staff. To Joyce Berry of Oxford University Press, one long and resounding "hurrah!"

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What Is an Inorganic Fiber?

FIBERS AND HISTORY

Fibers are everywhere around us. They are essential parts of the human body, our hair, for example; the threads in our clothing, natural or synthetic; the insulation in our houses. Natural fibers have been useful to humans for more than ten thousand years. They were mixed with clay before firing to strengthen and reinforce pottery vessels, making them more durable. Textiles that combined the fibers of flax and asbestos were known in ancient times for their seemingly magical resistance to fire and decay. It was industrialization, however, that caused a dramatic increase in the use of natural inorganic or mineral fibers. By the late nineteenth century asbestos had become an important commodity with a variety of commercial applications. It served as insulation to control heat generated by engines and, because of its incombustibility, as a fire retardant in its more recent general use as building insulation.

Asbestos fibers are found worldwide in many products: as reinforcement in cement water pipes and the inert and durable mesh material used in filtration processes of chemicals and petroleum, for example. However, asbestos is not the only inorganic fiber in use today. Synthetic inorganic fibers abound. Glass fibers have replaced copper wire in some intercontinental telephone cables. Fiberglas (a trade name) has become the insulation material of choice in construction. Carbon and graphite fiber composites are favored materials for tennis racket frames and golf clubs. Fibrous inorganic materials have become commonplace in our everyday lives.

As the use of inorganic fibers increased, there were some indications that fibers might be hazardous to our health. Since the first century A.D. it was suspected that asbestos might be the cause of illness among those who mined and processed the material. Asbestosis, a debilitating and sometimes fatal lung disorder, was documented and described in the nineteenth century. Within the last 25 years, lung cancer and mesothelioma have also been linked to asbestos exposure among construction and textile workers, as well as others exposed to dusts containing asbestos fibers. Although the etiology and specific mechanisms that give rise to these two cancers are not yet understood,

concern for the health of exposed workers led the governments of the United States and other countries to specify the maximum allowable concentrations of asbestos in the ambient air of the workplace. To enforce these regulations, it was necessary to measure and monitor concentrations of asbestos. The methods devised for monitoring were based on the fibrous nature of asbestos, a material composed of fibers or fibrils (small fibers).

As the most widely distributed inorganic fiber, asbestos has become the focus of intense scrutiny and discussion. Hardly a week passes without a local newspaper reporting on some aspect of the risks associated with this material: the ripout of asbestos in a school, a lawsuit brought by workers against a mining company or manufacturer of asbestos-based products (such lawsuits now number in the thousands), a debate over how to evaluate environmental health risks using the documented example of asbestos. The attention has prompted researchers to review and reexamine the data gathered on asbestos from many perspectives.

The indictment of asbestos as a health hazard focused attention on inorganic fibers in general, particularly on how they might cause disease. In spite of, or possibly because of, their widespread occurrence and usefulness, the diversity of inorganic fibers has not been appreciated. From the medical perspective, for those in industry or commerce engaged in producing and distributing fibrous materials, and for consumers as well, there is a need to understand the reactions of inorganic fibers in the biological, and specifically the human, environment. This need, coupled with some urgency, created controversy based largely on the definition of the term "fiber."

DEFINITIONS OF FIBER

The term *fiber* originally referred to biologically produced substances such as cotton or muscle fiber. Today the term is applied to many substances, and any small elongate piece of matter can be called a fiber, or fibrous, regardless of its source or composition. Fibers can be biologic or nonbiologic, organic or inorganic, natural or synthetic. *Webster's Third New International Dictionary* defines fiber as "a thread or a structure or object resembling a thread: as (a) (1) a slender root, . . . (2) an elongate tapering cell . . ."; the lengthy entry continues as follows:

> . . . (c) a natural or man-made object that has a length usu. many hundred or thousand times greater than its width, that possesses considerable tensile strength, pliability and resonance esp. against heat, light, some chemicals, and mechanical abrasion, that is obtained from animals (as wool, hair, silk, fur), vegetable matter (as cotton, flax, hemp, straw), or minerals or metals (as asbestos, aluminum, gold) or that is synthesized industrially (as rayon, nylon, glass fiber), and that may be wholly crystalline like asbestos and metal wires, wholly amorphous like glass, or, in the case of the most widely used fibers, which are high polymers, partly crystalline and partly amorphous. . . .

Despite the many applications of the term, no precise scientific definition exists. A search of more than 50 technical and scientific texts, glossaries,

and dictionaries produced no authoritative definition of fiber or fibrous that is applicable to asbestos and appropriate for use by health professionals.

Texts from the fields of mineralogy, petrology, and mining often contained no entry under "fiber" or "fibrous," Where the term fibrous was included, it was presented as synonymous with "asbestos," as in this entry from a nineteenth-century handbook of geological terms: "Fibrous: applied in geology or mineralogy to rock and mineral textures which consist of or resemble fibers as amianthus or asbestos" (Page, 1865). In a more recent dictionary of mining and mineral terms, fibers are defined as "the smallest single strands of asbestos or other fibrous materials . . ." (Thrush, 1968). A book on inorganic polymers, for example, characterized most commercially produced synthetic inorganic fibers (glass fibers, mineral wools, and fused silica) as amorphous polymers of various sizes. The rest of the fibers in this study were grouped as polycrystalline compounds with "unusual fibre-forming tendencies" (Ray, 1978). The entry under "fiber" in the *Encyclopedia of Chemical Technology* (1984) mentions only hydrocarbon polymers—surely nonbiologic and fibrous, but are they a subset of inorganic or organic fibers? Glass and ceramic fibers are listed separately in the same volume, as are the several types of synthetic crystalline fibers known as *whiskers*. Some of the best known whiskers can also contain carbon—for example, silicon carbide.

Responding to those concerned with the health effects of inorganic fibers, the Occupational Safety and Health Administration (OSHA) specified the maximum allowable concentrations of asbestos in the ambient air of the workplace. The following General Industry Standard was given: "the 8 hour time-weighted average airborne concentration of asbestos fibers to which any employee may be exposed [can]not exceed 5 fibers longer than 5 micrometers per cubic centimeter of air . . ." (Occupational Health and Safety Agency, 1972). In 1976 the exposure limit was lowered to 2 fibers per cubic centimeter, and in 1983 an emergency temporary standard of 0.5 fibers/cc was suggested, but it has not been imposed. In June 1986, OSHA proposed 0.2 fibers per cubic centimeter (Federal Register, 6/20/86). *Fiber* in these standards is a particle 5 micrometers or longer, with a diameter-to-length ratio of at least 1 to 3 (National Institute of Occupational Safety and Health Rept., 1981). The British Health and Safety Executive defined fiber as a particle having a length greater than 5 micrometers and a diameter less than 3 micrometers (Asbestos, 1977).

Fiber has been given a legal, if not operational definition, at least as it applies to asbestos. Unfortunately the definition bears little relationship to the present use of the term. It was essential to set standards to reduce occupational exposure but the detection, identification, and suppression of asbestos materials opened several areas of problems that remain unsolved. For example, six minerals are included in the definition of asbestos. Are they all equally hazardous? If not, why not? There are many other inorganic particles with diameters of less than 3 micrometers and a diameter-to-length ratio of 1:3. Should we be concerned that they too might be hazardous to our health?

Whatever distinguishes asbestos fibers—their composition, structure, or other peculiar properties that may contribute to the health hazard—they need to be examined in context, as representative of a class of inorganic fibrous materials. Perhaps then the factors that initiate adverse biologic reactions, and might be responsible for the induction of disease, could be identified.

In this book we define inorganic fibers in a general sense: as small elongate solid objects composed of any compound or element; usually nonbiologic in origin and often exhibiting distinctive physical, especially mechanical, properties. Inorganic fibers can occur naturally, that is, as mineral fibers or can be produced synthetically.

Our definition encompasses the enormous diversity of materials at present subsumed under the term. The definition, however, requires amplification.

NOMENCLATURE

The most common, and certainly the most familiar, inorganic fibers are the mineral fibers known as asbestos. Several minerals have been mined as asbestos (Fig. 1.1A, C; see chapter 2 for a detailed discussion of the asbestos minerals). These minerals are widespread in nature, but mining is economical only when they occur as continuous fibrous aggregates (veins) crosscutting rock masses. The veins are made up of hairlike fibers in parallel array that, on close inspection, appear bent (Fig. 1.1B). Not surprisingly, a mineralogical term, *asbestiform*, has been used to describe this subset of inorganic materials.

The term asbestiform has also been applied to other minerals and to synthetic materials when they occur as fibrous aggregates. Nemalite, the fibrous variety of the mineral brucite (Fig. 1.1D), has been described as asbestiform. A strong physical resemblance exists between nemalite and chrysotile (Fig. 1.1B), the most common asbestos mineral. However, in our view the term *asbestiform* is incorrectly applied to nemalite. Nemalite, with the chemical composition $Mg(OH)_2$, is a magnesium hydroxide, whereas the minerals mined as asbestos are all silicates. Nemalite has a different chemical composition, and it does not exhibit the strength and resilience typical of the asbestos minerals. The only similarity to the asbestos minerals is its fibrous morphology. The more general term *fibrous* more appropriately describes nemalite and other nonasbestos mineral or synthetic fibers. *Fibrous* adequately describes the appearance and obviates misleading associations or incorrect identification of a sample that has not been chemically analyzed.

Difficulties also arise when the terms *fiber* and *fibrous* are used instead of more precise terms. For example, not all elongate inorganic particles obtain their distinctive morphology through growth. Some small, long, and thin objects result from the disintegration of large solid particles. Many scientists would argue that these particles should not be called fibers or fibrous but *acicular*, to indicate a needlelike morphology. Five of the six minerals that have been marketed as asbestos occur much more commonly as large,

nonfibrous crystals scattered throughout the rocks (Fig. 1.1E). When crushed, these crystals yield slender, nonflexible, rod-shaped particles, and are best described as prismatic or acicular in form. The term *acicular* can be applied to any needlelike particle whether single and isolated or in an aggregate. The term is discussed further in the section on amphiboles in chapter 2.

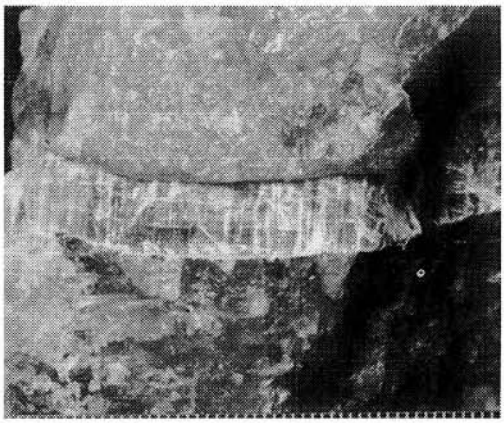
The inclusiveness of the term fibrous, however, can lead to ambiguity. For example, many elongate crystalline mineral fragments, because of their size and shape, are called fibrous but are neither asbestos nor asbestiform. If the fragments are obtained from crushing one of the minerals that is also mined as asbestos, confusion may ensue. Three samples of the amphibole mineral tremolite illustrate the dilemmas that may develop. Fig. 1.1F shows tremolite-asbestos, which has grown in fibrous form; Fig. 1.1E shows a large crystal of tremolite; Fig. 1.1G shows acicular tremolite—the result of crushing tremolite. The difference in appearance between the fibrous mineral and the acicular fragments of the same mineral is obvious with the luxury of direct comparison and magnification. However, many people use the term fibrous to describe the elongate mineral particles of Fig. 1.1G. The use of the term seems reasonable and practical, but when these particles come from a mineral cited in the definition of asbestos, should they be regulated? In our survey of inorganic fibrous materials for this book we included all materials labeled fiber or fibrous, acicular, and asbestiform.

A fiber, on close inspection, may be seen to have other distinctive characteristics besides its elongate shape. Frayed ends observed on a fibrous particle indicate that it is composed of still smaller *fibrillar* components, usually referred to as *fibrils*. The surfaces of a fibrous particle may be planar or curved, the result of growth or fracture. For example, glass fibers extruded like spaghetti through the fine pores of a bushing appear curved under magnification, and exhibit an oval or rounded cross section. Many natural fibers are cylindrical. A unique scrolled structure, typical of several silicate minerals, produces fibrils with rounded outlines (see the high magnification photo of chrysotile in Fig. 2.4 of chapter 2). Graphite fibers have a similar structure and appear to be composed of cylindrical fibrils (see Fig. 2.27).

An isolated, free-standing fiber, especially a crystalline fiber that has grown unimpeded, may show an equant, bladed, or lathlike cross section, depending on the number, growth rates, and geometric relationships of the bounding crystal faces. When such a fiber grows in an open space, both the lateral boundaries and the tip can exhibit planar crystal faces. Each natural and synthetic single-crystal fiber (whisker) exhibits crystalline faces typical of the compound. Occasionally single-crystal fibers have hollow cores, resembling drinking straws. A synthetic single-crystal fiber with a central hole is called a *capillary whisker*.

Alternatively, a fiber can be one member of a group or aggregate, as a fibril is one part of a fiber. Spherulites (Fig. 1.1H), fan-shaped fibrous crusts or rosettes, and the veins depicted in Fig. 1.1A are examples of aggregates created when many crystalline fibers grow in close proximity. During fibrous growth, lateral interference may produce planar but irregular bound-

A



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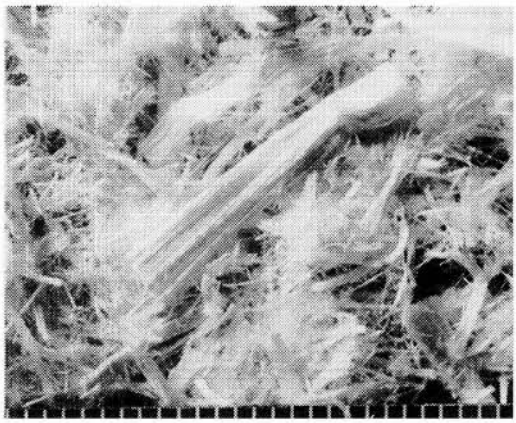

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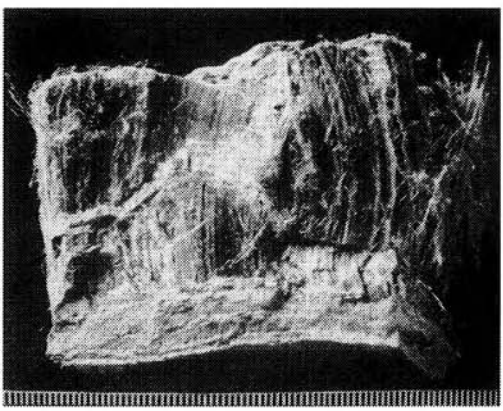

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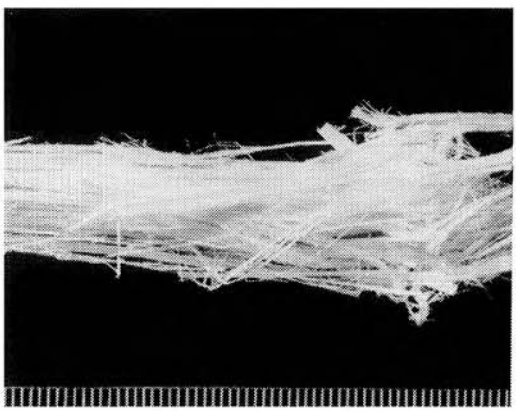

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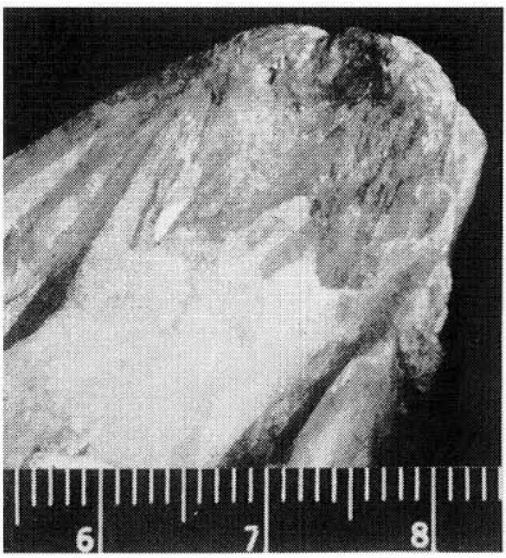

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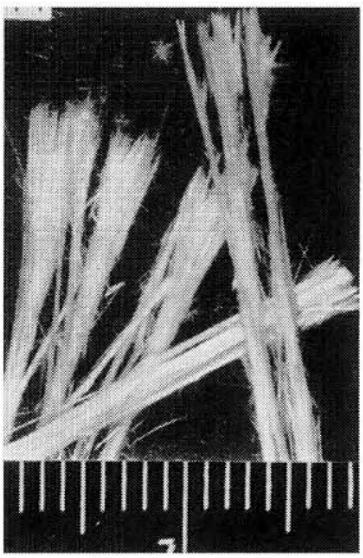

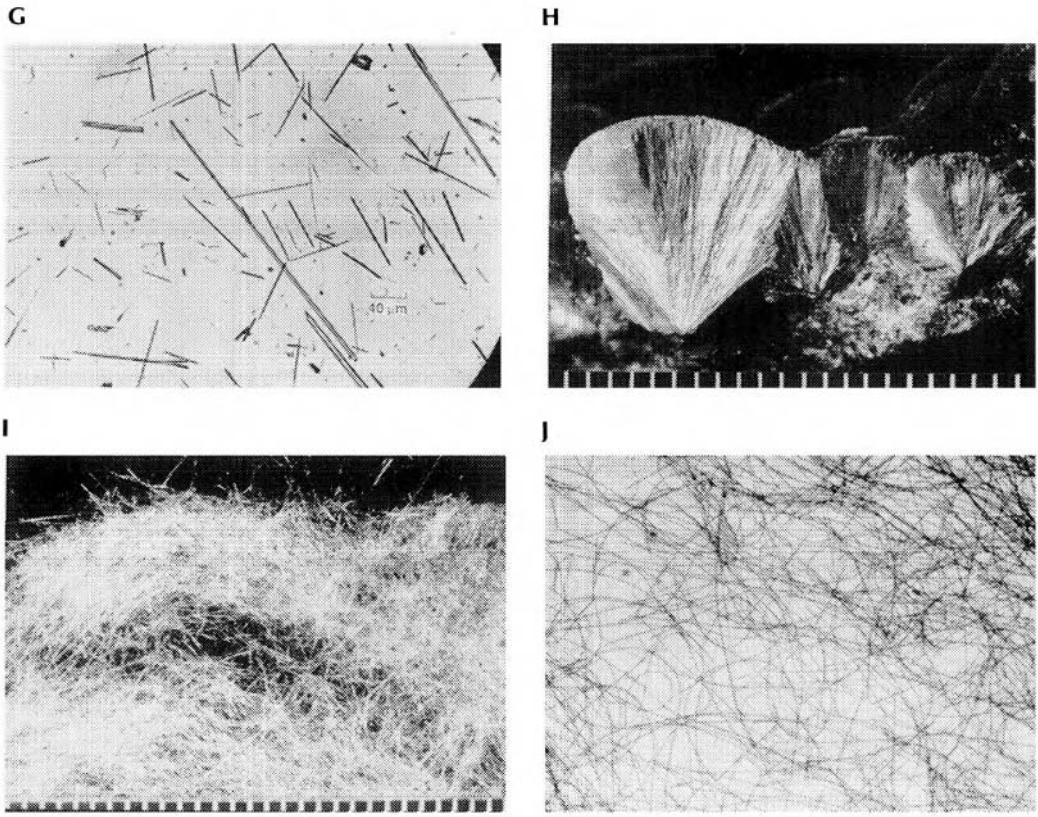

Fig. 1.1 Examples of Fibrous Materials. (**A**) Hand-sized specimen of serpentinite, the host rock containing a vein of the serpentine mineral chrysotile. The crysotile is an aggregate of crystalline fibers that have grown in parallel array and stretch approximately one centimeter across the vein opening. Sample from Sierra Aucha Mountains, Arizona, Yale Collection # B 6065 (mm scale). (**B**) Chrysotile, $Mg_5Si_2O_5(OH)_4$, or White Asbestos. Fluffy, fibrous character of commercial asbestos. Sample from Montville, New Jersey, Yale Collection # B 3496 (mm scale). (**C**) Crocidolite, fibrous riebeckite, $Na_2(Fe^{+2},Mg)_3Fe^{+3}{}_2Si_8O_{22}(OH)_2$ or Blue Asbestos. Parallel growth of the amphibole fibers very similar to the chrysotile in Fig. 1.1A. Sample from Prieska, South Africa, Yale Collection # B 38 IV (mm scale). (**D**) Fibrous brucite, $Mg(OH)_2$, usually called nemalite. Appearance deceptively similar to chrysotile (cf. Fig. 1.1B). Sample is from Asbestos, Quebec, where many tons of asbestos, presumably chrysotile, have been mined. Yale Collection # B 3065 IV (mm scale). (**E**) Tremolite, $Ca_2(Mg,Fe^{+2})_5Si_8O_{22}(OH)_2$. Hand-sized sample showing prismatic crystals of the mineral, a common occurrence. Sample from the Adirondacks, New York. Photograph contributed by the Bureau of Mines, courtesy G. Hyde and R. Virta (bar scale is 3 mm). (**F**) Tremolite-asbestos. Sample is a fibrous form of tremolite from Rajasthan, India. Photograph contributed by the Bureau of Mines, courtesy G. Hyde and R. Virta (mm scale). (**G**) Acicular tremolite. Needle-like fragments obtained by milling tremolite. Photograph contributed by the Bureau of Mines, courtesy G. Hyde and R. Virta (bar scale is 40 micrometers). (**H**) Spherulites of Millerite, NiS. Parallel fiber growth radiating from a point often results in rounded aggregates (spherulites). A section through such a spherical mineral crust shows a tufted fan shape. Sample from the Gap Mine, Lancaster County, Pennsylvania, Yale Collection # B 1562 (mm scale). (**I**) Glass fibers. Sample taken from the commercial product marketed as insulation by Johns Manville (mm scale). (**J**) Silicon carbide, SiC, whiskers (magnification 200 ×). From Evans, 1972, Fig. 2, p. 11.

aries on an individual fiber. The acicular particles created by comminution also have irregular lateral surfaces.

Materials described as fibers or fibrous vary greatly in size. Depending on context, fibers may be macroscopic, microscopic, or submicroscopic. The general perception of elongate objects as fibers is not limited by either length or thickness, although particles with diameters greater than a few millimeters would probably be described by other terms such as rod.

Filaments, or fibrils, are similarly variable in size. When the terms refer to portions of a fiber, their dimensions are also usually unspecified but are relative to the fiber itself. Fibrils of glass or inorganic polymers that have been measured are often less than 10 nanometers in diameter and form bundles of aligned fibrils 0.2 to 10 micrometers in diameter and up to 100 micrometers in length (Ray, 1978). Occasionally, minerals with diameters of a few millimeters and lengths of hundreds of centimeters have been described as fibrous. Most objects called fibers, however, are microscopic, with maximum dimensions of less than a millimeter.

There is a relationship that accommodates the wide range of fiber sizes and is independent of the composition or constitution of the fiber or fibrous material. The *aspect ratio,* or the relationship of the length to the thickness of the particle (length/thickness), can be calculated or estimated with relative ease.

When the aspect ratio of a particle is 10 or greater, mineralogists use the term fiber. Below 10, terms such as columnar, prismatic, blocky, and—at an aspect ratio of 1—equant are applied. Aspect ratios, ordinarily much greater than 20 for the fibers of asbestos samples, may be as high as 5000.

If a fiber is less than a few micrometers thick, mineralogists may emphasize its fineness with the term *fine-fibrous*. Particles with diameters of a few mils (1 mil = 25 micrometers; see Table 1.1) must be examined under a microscope. Electron microscopy is employed for the finest materials, and high-resolution electron microscopy is required to image fibrils with diameters of a few angstroms (1 angstrom = 10^{-10} meter or 0.1 of a nanometer). At any resolution, the aspect ratio can be estimated or measured as part of the identification of the fiber.

Table 1.1 Common Units of Length or Diameter

Units	Value in Meters		
Meter (m)	1	or	10^{-1}
Decimeter (dc)	0.1		10^{-2}
Centimeter (cm)	0.01		10^{-3}
Millimeter (mm)	0.001		10^{-4}
	0.0001		10^{-5}
Micrometer (μm)	0.00001		10^{-6}
Mil = 25 micrometers			
	0.000001		10^{-7}
	0.0000001		10^{-8}
Nanometer (nm)	0.00000001		10^{-9}
angstrom (Å)	0.000000001		10^{-10}

THE PROPERTIES OF INORGANIC FIBERS

Crystal Chemistry

Inorganic fibers are solids, and a solid may be crystalline or amorphous. Crystalline solids are characterized by an atomic structure that has a regular, three-dimensional, geometric order. Amorphous solids are a special group of solids that lack internal order. Glass, for example, has an amorphous structure. Many varieties of crystalline inorganic fibers exist, and a large proportion of synthetic inorganic fibers are glasses. Some inorganic fibers, such as carbon fibers, combine crystalline and amorphous materials.

Many common inorganic fibers are solids formed through polymerization, the repetition of a chemical unit in linear array. The chemical unit can be simple, such as the element carbon, or complex, such as the aluminum-silicate cage that characterizes the zeolite mineral erionite. (Both of these fibrous materials are discussed in chapter 2.) A fiber visible to the naked eye is formed by the aggregation of thousands of elongate submicroscopic linear arrays, or chains, in parallel. This preferred side-by-side aggregation is enhanced by interchain bonding and the surface character of the chains. The microscopic fiber is, therefore, actually a collection of many smaller elongate units or fibrils.

Inorganic fibers can also be produced from substances that do not form polymers. Under special conditions, virtually any compound can grow as a fibrous solid. These conditions occasionally exist in nature, but today many inorganic fibers are custom-crafted. A compound synthesized in fibrous form usually possesses additional and desirable mechanical properties over the compound in any other form.

Fracture

Minerals and synthetic materials alike tend to be brittle and fracture into smaller fragments when crushed. The shapes of the fragments depend on the internal atomic geometry of the solid, and the fracture surfaces may be planar or irregular.

Cleavage is the term used when a solid fractures along special planes dictated by the crystal structure. The orientation of the cleavage planes reflects the differing strengths of the atomic bonds in the solid. The direction or directions of cleavage are distinctive for each crystalline compound. Cleavage is described in terms of the quality of the surfaces created by fracture (*perfect,* if the surfaces are flat and even); the ease of fracture (*easy*); and the specific orientation of the cleavage direction to the crystal structure. (For a full discussion of cleavage, consult a standard mineralogy text such as Hurlbut and Klein, 1985.)

A crystalline solid with cleavage in one direction yields platy fragments on fracture. Mica is a well-known example of a mineral with one direction of perfect cleavage. Two directions of cleavage yield prismatic or acicular

fragments (depicted for tremolite in Fig. 1.1G). Minerals with three or more directions of cleavage tend to yield equant fragments.

Another kind of planar fracture called *parting* occurs in the presence of mechanical weakness in a crystal. Sites for parting are created during growth by the concentration of impurities or submicroscopic voids within the crystal. Parting usually produces relatively rough and uneven surfaces and odd-shaped fragments, unlike the uniform particles created by cleavage.

The fracture patterns of noncrystalline or partly crystalline, partly amorphous materials are unpredictable. Conchoidal fracture is typical of glass and yields odd-shaped flakes of various sizes.

The fracture of aggregates of fibrous crystals usually involves mechanical separation along boundaries of individual crystallites or fibers. However, as might be anticipated, the ease of mechanical separation of fibers varies widely. Crocidolite, the variety name for one of the fibrous amphiboles mined as asbestos (Fig. 1.1C), contains clumps of fibers that can be picked from the sample with the fingers. Electron microscopy and electron diffraction show that the fibrils in crocidolite lie parallel but rotated relative to one another around the fiber axis (Alario-Franco et al., 1977), suggesting limited interfibrillar bonding. Individual fibers or groups of fibers might, therefore, easily separate along the fiber length into finer fibrous particles, that is, fibrils.

Not all fibers yield fibers on comminution. Fibrous varieties of quartz (SiO_2), for example, are formed from tightly bonded, aligned helical "fibers" that cannot be separated mechanically (Frondel, 1978). Fibrous calcite ($CaCO_3$), when crushed or ground, breaks into equant grains of rhombic shape. The fragments reflect the cleavage characteristics of the mineral.

The fracture patterns of fibrous materials may be distinctive, but inspection alone rarely provides sufficient information to identify a fiber or its source accurately.

Surface Properties

Fibers with high-aspect ratios have very large surface areas in relation to unit mass. The higher the aspect ratio, the greater is the surface area per unit mass. The number of ions, molecules of water, or other liquids or gases adsorbed on a fiber, can be used to estimate the surface area. The nature of the adhering species is affected by the kind and distribution of charges on the fiber surface, which, in turn, is directly related to the composition and structure of the surface and ultimately of the material itself.

The surface characteristics of substances with simple structures—metals and metal oxides, for example—and the chemical reactivity of these surfaces have been investigated using low-energy electron diffraction (LEED). The experiments show that the distances between atoms and even the atomic configuration on the crystal surfaces differ from the configurations and interatomic distances in the crystals' interior (Rhodin et al., 1969). However, the study of surfaces—especially the surfaces of fibers—has inherent experimental difficulties that cannot be overstated. LEED employs a large-

diameter source beam, and a fibrous aggregate rough surface complicates the interpretation of the diffracted energy spectrum. The tunneling microscope, a new instrument capable of examining areas as small as the diameter of single fibers, may provide data on fibrous material surfaces (Golovchenko, 1986).

Thus far, studies employing standard chemical methods have provided some information about the surfaces of a few fibers. Ralston and Kitchener (1975), for example, examined the chemical reactions of amosite, an amphibole asbestos. They detected a small amount of surface dissolution under mild leaching, and strong adsorption of some cationic surfactants, indicating specificity of surface reactions. Schiller et al. (1980) showed that short mineral fibers and blocky cleavage fragments have a smaller net charge than more elongate particles. Moreover, fibrous particles and cleavage fragments of the same mineral may have similar dimensions and even the same net surface charge, but different specific charge and charge distribution. Charge, and its distribution, is an expression of the specific chemistry of a surface. A crystalline fiber would have different charges on the several faces developed during growth or fracture. And any particle can change its net charge or charge distribution if placed in a new environment. Placing a fiber in aqueous media, for example, alters the local chemistry as ions adhere to the fiber surface. The charge associated with the fiber can change. At present, such differences are virtually impossible to assess, much less to predict, for a particular fiber; however, one might expect the reactivity of fibrous particles to be enhanced by their large surface areas, and if a fibrous particle has residual charge, the distribution of the charge to impart distinctive surface characteristics to the fiber or fibril.

In summary, the surface properties of fibers are influenced by the composition of the material, the environment during growth or generation, and the "history" of the particle. The term *history* refers to any changes in the surface after the fiber is formated. The charge or charge distribution affects the reactions of a fiber.

Flexibility and Mechanical Strength

Hemp rope, once widely used, has largely been replaced by nylon cord. The flexibility and mechanical strength of hemp, a nettle plant fiber, also characterize nylon synthetic and several other inorganic fibers in common use.

Fig. 1.1B illustrates fibers typical of commercial asbestos, while Fig. 1.1I shows Fiberglas and Fig. 1.1J silicon carbide whiskers. Some of the fibers in these examples are bent, occasionally through 180°, indicating considerable flexibility. Whiskers of other compounds can also bend but the tensile strength of these materials is their most remarkable feature. The measured values (Table 1.2) are at least ten times higher than those observed for the same compounds in bulk or in another morphology (Walker and Zoltai, 1979). The numerous investigations into the causes of this unique response have produced several hypotheses.

Table 1.2 The Tensile Strength (σ) of Selected Inorganic Fibers

Material	σ (kg/cm^2)	Reference
Chrysotile	31×10^{-3}	Hodgson (1979), p. 93
Crocidolite	35×10^{-3}	Hodgson (1979), p. 93
Tremolite	$<5 \times 10^{-3}$	Hodgson (1979), p. 93
Copper wire	4.4×10^{-3}	Brenner (1956)
SiC	9.9×10^{-3}	Cook (1970)
αSiC	72×10^{-3}	Webb et al. (1966)
Carbon	13×10^{-3}	Nicoll and Perry (1973)
Glass		
69% SiO_2	2.4×10^{-3}	Griffith (1921)
High-strength	35×10^{-3}	Loewenstein and Dowd (1968)

The strength of a material depends on the crystal structure and interatomic bonding of the compound. The ultimate tensile strength of materials, the extension limits of elastic bodies, is readily determined through the use of Hooke's law, o = eE, where o is tensile strength, e is strain, and E is Young's modulus, a proportionality between normal stress (force/unit area) and resulting normal strain (change in length/unit length). The direction of the applied stress during testing usually coincides with the direction of elongation of the fiber which is often the direction of growth, of the parallel alignment of chemical polymeric units, or, in crystalline fibers, a special direction in the three-dimensional array.

The strain developed in the material in response to external stresses can be relieved by simple displacements, translation, elongation (stretching, for example), or a combination of distortions. The type of response is influenced by the rate at which the stress is applied as well as the composition and crystallinity of the solid. Metal wire subjected to moderate tension is ductile, extending through slippage along preferred planes in the crystal structure of the metal. If the wire appears bent or otherwise changed in shape after stress is released, the elastic limit of the material has been exceeded. On the other hand, a brittle material extends minimally when stretched, exhibiting limited or no planar slippage. The crystal structure and bonding character of nonmetallic compounds usually reduce, and may preclude, the ductile response. Exceedingly high tensile stress applied to either ductile or brittle materials eventually leads to fracture.

Most whiskers up to 1 micrometer in diameter obey Hooke's law to the point of fracture, regardless of their composition (Evans, 1972). Whiskers of brittle and ductile materials with larger diameters respond to stress differently. Metallic whiskers fail under tension by shear, whereas other compounds fail through fracture.

Measuring the bending strength of a fiber—in effect, quantifying its flexibility—is a more complicated procedure. One side of the curve is under tension and the opposite side under compression (Evans, 1972). The reactions of a particular fibrous solid nevertheless depend on the material's chemical

composition and crystal structure, as well as on the disposition of the forces during flexion, and any surface phenomena.

More than 250 years ago it was observed that the strength of small-diameter wires increased proportionally as the diameter decreased (Musschenbroek, 1727). The inverse relationship between elastic strain and diameter has also been noted for whiskers of brittle or ductile materials of less than 20 micrometers in diameter (Evans, 1972).

The enhanced strength of whiskers and natural fibers, by comparison to the strength of materials of the same composition in another morphology, could be a coincidental: in these crystalline synthetic and mineral fibers, a particular crystal direction is parallel to the direction of the applied stress. However, the inverse diameter–strength relationship indicates that factors other than crystal structure contribute to the mechanical strength of fibrous materials.

There are different schools of thought concerning the strength of fibrous materials. It has been proposed that small-diameter fibers may be closer to ideal crystals, and hence have fewer flaws or imperfections per unit volume than large crystals (Walker and Zoltai, 1979). By using high-resolution electron microscopy with a resolution of about 0.3 nanometers (nm), we can directly observe the internal molecular arrangements of crystals. Veblen and Buseck (1980) found stacking faults and other defects in the orderly aggregation of the silicate chains in well-crystallized samples of amphibole minerals (Fig. 2.9). Studies of the asbestos equivalents of the same amphiboles (Veblen, 1980) disclosed similar stacking faults. Veblen suggested that the flaws could be the sites at which strain was dissipated, a factor that might contribute to the extraordinary flexibility and enhanced mechanical strength of some asbestos. The relief of strain through localization at microcracks was previously suggested by Griffith (1921) to explain the enhanced strength of glass fibers.

The large surface area of fine fibers may contribute significantly to mechanical strength. Surfaces may provide a distinct structural or chemical zone where strains are dissipated. A surface structure distinctively different from the core has been discovered during optical examination of some fibers (Woods, 1955). Inverted cones developing at the tips of fiberglass and asbestos fibers subjected to chemical attack suggest that the fiber surface is more chemically resistant than its interior (Hrapka, 1977, 1978). An example of the sophistication achieved through research on fibrous materials is the discovery that coating a synthetic fiber as it is drawn or extruded prevents oxidation and hydration of the compound and imparts a different, useful surface. In engineering industrial fibers to maximize those properties best suited to a particular application, coatings are often added. Coatings alter the surface properties of glass fibers, for example, increasing stability and resistance to abrasion while maintaining fiber flexibility and strength.

Just as flexibility cannot be judged by observation alone, extraordinary mechanical strength cannot be assumed for all fibers with high aspect ratio.

If a particle appears bent, the designation *fiber* is obviously appropriate, in accordance with the original definition, and the particle probably possesses enhanced mechanical strength. However, the term *fiber* is usually applied to any small elongate inorganic particles without consideration of flexibility or mechanical strength.

CLASSIFICATION OF INORGANIC FIBROUS MATERIALS

The physiochemical environment of the earth has placed certain elements in common association and produced a variety of minerals. Minerals, classified according to a well-known and well-documented system based on the chemistry of the compounds, have been presented in several compendiums (e.g., Strunz, 1941; Palache, Berman and Frondel, 1944). Several glossaries aid in identifying minerals and cross-reference the more than 6000 names that have been used for the approximately 3000 known minerals (Embrey and Fuller, 1980; Fleischer, 1987). Each year about 100 new minerals are proposed to the International Mineralogical Association Commission on New Minerals and Mineral Names, of which about half are accepted as new species (Skinner and Skinner, 1980).

Most minerals occur in a variety of morphologies. Although it is not exhaustive, the list we recorded as occurring in fibrous form (Appendix 1) contains more than 350 entries, each with a reference. The format follows that proposed in Dana's System of Mineralogy, (Palache, et al., 1944), one of the standard references in the field. The names of fibrous minerals are alphabetically arranged within each chemical group; that is, elements, oxides, hydroxides, carbonates, sulfates, phosphates, and so on. A similar, parallel system has been adopted for the list of synthetic fibers (Appendix 2). The list of synthetics includes glassy fibers produced from natural materials, as well as whiskers.

Over the past 40 years a great deal of research has been done on the nucleation and growth of fibers for industrial uses. The predominant industrial fiber is a silica-based glass. Whiskers, with a high degree of internal structural perfection, have been produced under a variety of special conditions from an extraordinarily wide range of compounds.

The published information on industrial materials is found in patent literature and compendiums such as those of Wilke (1973) and Bracke (1984). For many synthetic fibers, information on the precise chemical composition is unavailable or buried in a patent that describes a series of commercial fibers distinguished from each other by exceedingly small variations in composition.

The data in the references provided for each entry in the Appendices are extremely variable. Except for those of the asbestos minerals, the general descriptions of most minerals give little more than cursory mention of their occurrence as fibers. A journal citation indicates some information on composition, crystal structure, size, morphological characteristics, and other

physical data such as tensile strength may be presented. For those with short-form references, and especially the synthetic compositions with patent numbers, the entry only confirms the synthesis of a fiber. Detailed information on the unique properties of these materials as fibers, regardless of their chemical composition or source, is extremely limited.

Compiling the lists confirmed an early impression: data on fibrous materials is within the purview of the field called materials science, but information is segregated and published within specialized fields and subdisciplines. For example, naturally occurring fibrous materials are investigated by mineralogists whereas synthetics, some of identical composition, are produced by solid-state physicists, polymer chemists, or metallurgists. The Appendices demonstrate the wide compositional ranges of fibrous inorganic materials; only a few of the fibers listed have been studied in any detail.

In Chapter 2 we introduce some basic concepts from mineralogy and materials sicence before describing several mineral and synthetic fibrous inorganic materials. In Chapter 3 we outline the physiology of the human lung, cellular biology and the diseases associated with asbestos exposure—the pertinent information for discussions of the health effects of asbestos and other inorganic fibers.

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2

Fibrous Minerals and Synthetic Fibers

FIBROUS MINERALS

A mineral is a naturally occurring, crystalline inorganic compound with a specific chemical composition and crystal structure. Minerals are commonly named to honor a person, to indicate the geographic area where the mineral was discovered, or to highlight some distinctive chemical, crystallographic, or physical characteristic of the substance. Each mineral sample has some obvious properties: color, shape, texture, and perhaps odor or taste. However, to determine the precise composition and crystal structure necessary to accurately identify the species, one or several of the following techniques must be employed: optical, x-ray diffraction, transmission electron microscopy and diffraction, and chemical and spectral analyses.

The long history of bestowing names on minerals has provided some confusing legacies. Many mineral names end with the suffix "ite," although not most of the common species; no standard naming practice has ever been adopted. Occasionally different names have been applied to samples of the same mineral that differ only in color or shape, but are identical to each other in chemical composition and crystal structure. These names, usually of the common rock-forming minerals, are often encountered and are therefore accepted as synonyms or as varieties of bona fide mineral species. The Fibrous Minerals list (Appendix 1) includes synonyms.

A formal description of a mineral presents all the physical and chemical properties of the species. In particular, distinctive attributes that might facilitate identification are noted, and usually a chemical analysis of the first or "type" specimen on which the name was originally bestowed is included. As an example, the complete description of the mineral brucite ($Mg(OH)_2$), as it appears in *Dana's System of Mineralogy,* is presented as Appendix 3. Note the complexity of this chemically simple species and the range of information available. In the section on Habit (meaning shape or morphology) both acicular and fibrous forms are noted. The fibrous variety, which has the same composition as brucite, is commonly encountered (see Fig. 1.1D) and is known by a separate name, "nemalite."

Tables to assist in the systematic determination of a mineral species are

usually based on quantitative measurements of optical properties (using either transmitted or reflected light, as appropriate) or on x-ray diffraction data. More accurate data on known species, or the data for new species, is continually added to keep the tables of both optical and x-ray diffraction properties current. Identification of a mineral requires familiarity with these methods of analysis, and critical judgment must be exercized to accommodate the complexities and nuances of evaluation. Underlying the evaluation process are several basic mineralogy comcepts that are applicable to all fibrous inorganic materials, both natural and synthetic. The following overview focuses on the crystal chemistry of silicate compounds, and uses minerals that are often found in fibrous forms as the examples.

THE CRYSTAL CHEMISTRY OF MINERAL MATERIALS

Many mineral species have the same or similar chemical basic units within their atomic structure. All common silicate minerals, for example, are characterized by the association of four large oxygen ions (O^{-2}) bonded to a small silicon ion (Si^{+4}). The shape of the complex ion is a tetrahedral unit, with the composition $(SiO_4)^{-4}$. The two- and the three-dimensional expressions of the silicate ion are presented in Fig. 2.1, parts A and B, respectively. The three-dimensional figures emphasize the potential variations in orientation between the ions as they have been observed in minerals.

The silicate tetrahedra can polymerize by sharing oxygen atoms to form other complex ions such as $(Si_2O_7)^{-6}$, $(SiO_3)^{-2}{}_n$, $(Si_4O_n)^{-6}{}_n$, and so forth. Individual mineral species are identified by determining the specific Si ... O array (hence the degree of polymerization), and by the cationic composition. A few of the polymerized arrays identified in silicate minerals found as fibers, or described as fibrous, are illustrated in the remainder of Fig. 2.1. The names and formulas appended to the arrays indicate that they are typical of well-known minerals. The polymerized ion configurations were determined through detailed crystal structure analyses using x-ray diffraction of single crystals. Rarely have fiber samples of the mineral species been used for structural analyses.

Many minerals are characterized by the polymerized ion that presents as a single silicate chain with a Si:O ratio of 1:3, as is illustrated in Fig. 2.1A′ and B′. Such chains bond through cations to form three-dimensional crystalline structures in which each tetrahedron shares two of its oxygen ions with adjacent tetrahedra. A group of minerals containing such complex ions are the pyroxenes (Fig. 2.1C). Other single-chain silicate species, given different names, exhibit similar regular chains with distinct repeat patterns and cation associations. For example, wollastonite, has a single chain characterized by a 3-tetrahedral repeat unit (Fig. 2.1D), and rhodonite has a 5-tetrahedral repeat unit (Fig. 2.1E). The habit of these minerals is often described as acicular. Wollastonite is discussed later in the section "Pyroxenoids."

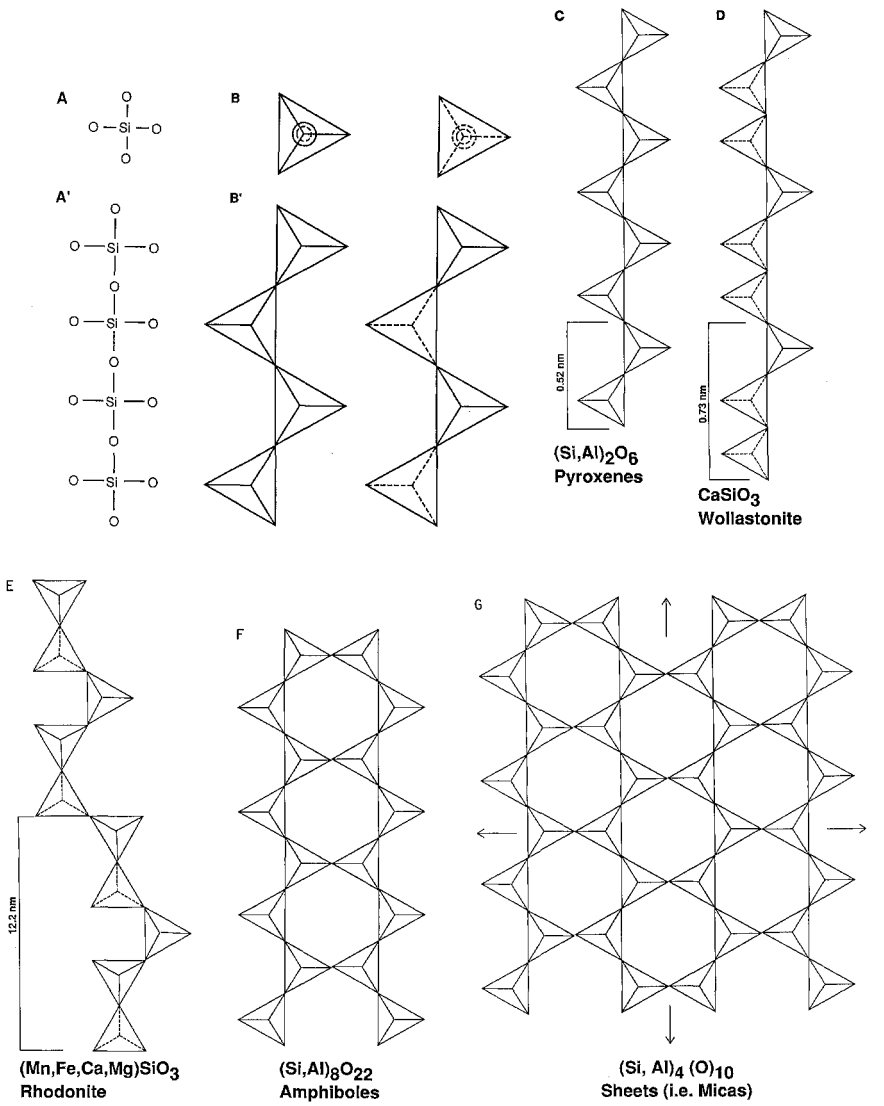


Fig. 2.1 Configurations of the tetrahedral units and chain, double chain, and sheet structures in the silicate and aluminosilicate minerals. (**A**) Two-dimensional representation of a single silicate tetrahedron. (**A'**) Two-dimensional representation of an extended silicate chain. (**B**) Three-dimensional representations of single tetrahedra in two orientations. The apexes of the tetrahedra point above or below the plane of the paper. (**B'**) Three-dimensional representations of extended silicate chains showing different orientations of the tetrahedra in two of the many possible configurations. Single chain: pyroxenes (**C**), wollastonite (**D**), rhodonite (**E**). Double chains: amphiboles (**F**). Sheets: as found in the serpentines, micas, and clays (**G**).

Polymerization into $(Si_4O_{11})^{-6}$ units gives rise to minerals characterized as having double chains. The configuration depicted in Fig. 2.1F is common and typical of the amphiboles, a mineral group of special interest because five amphiboles have been mined as asbestos.

When three of the oxygens in the tetrahedra are shared (Si:O ratio = 2:5), the complex ions that form take on a sheetlike configuration. The sheets can be stacked, and the associated cations are found between the sheets. Micas and clays are sheet-structure minerals with distinctive habits and physical properties, that reflect the planar silicate sheet structure (Fig. 2.1G). These normally platey minerals may also occur with fibrous-growth habits. The special crystal chemistry that produces such a distinctive habit is discussed later.

When all four oxygens of the tetrahedra are shared (Si:O = 1:2), a fully polymerized ion results, and a three-dimensional framework is formed. Quartz, an example of this type of silicate array, is discusssed in the section on silica minerals.

Some of the diversity that characterizes the properties and compositions of the silicate minerals stems from the ability of the aluminum ion (Al^{+3}) to substitute for silicon in the tetrahedral unit. When silicate tetrahedra in a mineral are replaced by aluminum-containing tetrahedra, concomitant changes occur in the size of the tetrahedron (usual Si—O bond length = 0.160 nm.; Al—O bond length = 0.178 nm) and in the cations or protons that balance the tetrahedral unit charge. Regular substitutions with distinct chemistries and structures lead to the formation of groups of discrete minerals called aluminosilicates.

Since silicates and aluminosilicates are by far the predominant rock-forming minerals, the crystal structures of most species have been determined. Liebau (1980) presents an overview of the structures of silicate and aluminosilicate minerals, and one can consult Berry, Mason, and Dietrich (1983, especially pp. 382–389) or other mineralogy texts for an introduction to the subject. The multivolume work of Eitel (1965) provides a general treatment of the crystal chemistry of all types of silicate materials.

The Chemical Formulas of Minerals

In the remainder of this chapter, specific examples of fibrous minerals are presented. The chemical formulas are given as well as the mineral names. A formula is a shorthand notation that describes the elemental composition of the compound plus the specific ion associations, as determined by three-dimensional structure analysis of the species. Because every mineral sample is not completely analyzed, an ideal formula—one that summarizes the chemistry and associations of the ions—is usually presented.

The Polymorphism of Minerals

Some chemical compounds exist in more than one structural form. For example, the idealized chemical formula for both of the mineral species chrys-

otile and lizardite is $Mg_3Si_2O_5(OH)_4$. The two minerals possess similar polymerized silica ions and associated magnesium (Mg) ions, but the three-dimensional configuration, or crystal structures, are different. The structure of chrysotile is quite complicated and is discussed later. However, Fig. 2.1B′ presents a simplified version of the general concept. The figure depicts single chains in two different orientations. Such variations do not necessarily change the composition but would create the opportunity for different three-dimensional structures. Two minerals with the same chemical composition but different crystal structures are *polymorphs*. The mineral world contains many examples of *polymorphism*. Diamond and graphite, both composed of the element carbon, are familiar examples of polymorphism.

Mineral Series

In addition, many mineral species, such as the chain silicates, contain identical basic chemical units, and hence exhibit very similar crystal structures but have different chemical compositions. These minerals may be members of a mineral series if the chemistry varies predictably. The variations, known as atomic substitution, are based on Pauling's rules.

The potential for each atom of an element to combine with others to form molecules and compounds is based on its electronic structure and charge. We have already mentioned the silicon–oxygen association that forms the tetrahedral ion $(SiO_4)^{-4}$, for example. Aluminum is similar to silicon size and bonding potential, and forms a similar stereochemical configuration with four oxygen ions, although with a different charge—reflecting the fact that the cation is Al^{+3} rather than Si^{+4}. In effect, Al ions substitute for Si ions in fourfold or tetrahedral coordination. The substitution results in the complex ion, AlO_4^{-5}.

Substitutions of ions for one another take place readily, provided the site they occupy accommodates the small differences in size and electronic configuration. Ca^{+2}, for example, may be found in six-, seven-, or eightfold coordination with oxygen ions in different minerals. Mg^{+2} substitutes for Ca^{+2} at the sixfold sites, whereas larger ions, such as Sr^{+2}, substitute for Ca^{+2} in the eightfold coordination sites. When cations of similar size, stereochemical, and bonding characteristics occupy identical sites in the crystal structure of the mineral, an ideal formula is written to indicate the equivalency, that is, the formula $(Mg,Fe)_2SiO_4$, indicates Mg and Fe are substituting for each other in special atomic positions (sites) in the crystal structure. If all of the sites are filled with only one of the elements, the mineral formula is $(Mg)_2SiO_4$. The minerals with such predictable chemical variations may be members of a *mineral series*.

Mineral series are composed of species whose basic chemistry and three-dimensional structure are so similar that they differ in a well-documented, predictable manner, based on the substitution of comparable chemical elements. Such a series is usually defined by the end members, that is, the compounds that contain only one of the substituting cations. End members

are given distinct mineral names. Other species within the series are referred to in terms of the end member or occasionally given specific names. An example is the amphibole mineral series, whose end members are

cummingtonite–grunerite

$$Mg_7Si_8O_{22}(OH)_2–Fe_7Si_8O_{22}(OH)_2$$

Intermediate members of the series that contain both Mg^{+2} and Fe^{+2}, may be identified as iron-rich cummingtonite, for example. Alternatively, a fibrous species whose composition and structure resembles grunerite occurs in South Africa. It is mined as asbestos and known commercially as amosite. Amosite is a varietal mineral name that has been used in the trade to describe mineral materials within the cummingtonite–grunerite series. The name is an acronym for asbestos mines of South Africa. Because it is not a proper mineral name, it may not be found in lists of minerals in standard mineralogical texts.

Actinolite–tremolite is another mineral series whose names are well-known because of their fibrous habit. Tremolite, the magnesium end member of the series is depicted in Fig. 1.1E. Other minerals of similar structure but containing iron as well as magnesium were called actinolite. Ferroactinolite, is the name of the ideal 100% iron (Fe) end member. An accurate designation of the series is

tremolite–actinolite–ferroactinolite

$$Ca_2Mg_5Si_8O_{22}(OH)_2–Ca_2(Mg_{0.2}Fe_{0.8})_5Si_8O_{22}(OH)_2–Ca_2Fe_5Si_8O_{22}(OH)_2$$

Names are assigned to members of this series somewhat arbitrarily. For example, the term actinolite may be used when the magnesium content of the sample is as low as $(Mg_{0.1}Fe_{0.9})$ and when the magnesium content is well above that of the ideal formula (20% Mg in place of Fe).

Table 2.1 presents chemical analyses for actual samples in this mineral series. Note the compositional variations of the main cationic species, reported as oxides—SiO_2, MgO, CaO, FeO, and Fe_2O_3—and the small amounts of other elements—Na_2O, Al_2O_3, MnO, TiO_2.

Mineral Groups

Minerals and mineral series with the same basic chemical units, such as the silicate polymerized ions, and very similar crystal structures are related and referred to collectively as *mineral groups*. The amphiboles are a group composed of several mineral series, two of which were cited in the preceding examples. The several series that make up the amphibole group reflect the changes in the size and location of cations associated with the polymerized silicate chains. Because several amphibole species occur in fibrous form, we discuss this group in much greater detail, and include an idealized crystal structure.

Table 2.1 Chemical Analyses of Mineral Samples from the Tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$–Actinolite–Ferroactinolite ($Ca_2Fe_5Si_8O_{22}(OH)_2$ Series in the Amphibole Group

Compound	Tremolite[a]	Actinolite[b]	Ferroactinolite[c]
SiO_2	59.45	54.73	49.30
TiO_2	—	0.021	—
Al_2O_3	0.49	1.46	1.30
Fe_2O_3	0.00	—	2.15
FeO	0.07	9.60	30.50
MnO	0.38	0.16	3.48
MgO	25.19	17.94	0.66
CaO	11.88	12.76	10.73
Na_2O	—	1.44	—
H_2O	2.27	2.77	2.13
	99.73	100.57	100.25

Analyses selected from Table 38 in Deer, W. A., R. A. Howie, and J. Zussman (1963). *Rock-Forming Minerals*, Vol. 2, pp. 251–253. John Wiley & Sons, New York.

[a]Tremolite—from skarn, Balmat, New York (Weeks, 1956, p. 251).

[b]Actinolite—from schist, South Devon (Tilley, 1938, p. 252).

[c]Ferroactinolite—from Tamarack Mine, Idaho (Sundius, 1946, p. 253).

Supergroups: The Biopyriboles

Similarities of composition, polymerized species, and crystal structures have been noted in several aluminosilicate mineral groups. Thompson (1978) suggests that although the mica, pyroxene, and amphibole mineral groups, are characterized by distinct aluminosilicate chemistries and crystal structures, they are related. Each group also has distinct polymerized species. The pyroxene species are single chains, the amphiboles are cross-linked double chains, and the micas are cross-linked aluminosilica sheets. Each group contains many mineral species and several mineral series. If one considers the three groups together as a supergroup, the commonality of specific cation substitutions relative to the polyanions is striking. The term *biopyribole* is a contraction of *bio*tite, a mica mineral, *pyr*oxene, and amph*ibole*. It subsumes several hundred species of minerals. The biopyriboles illustrate the range of composition and complexity of one sector of mineral materials.

Growth of Minerals, Fibrous Minerals, and Synthetic Fibers

It is not unusual to find minerals from different series or groups clustered in intimate association within a single rock. Minerals are products of chemical reactions that normally produce one or more mineral species. If, after the original mineral is produced, the environment in which it grew changes, one or all of the solid phases in the rock may alter or disappear. It is possible—indeed probable—that additional, distinctly different, species will form. Minerals are solids that reflect the physicochemical environment during their formation, and they respond to any change in the environment. Though they

are inorganic and inanimate, minerals are not immutable; they are subject to alteration.

The number and variety of minerals, and hence of mineral fibers, is limited. The range of chemical compositions that can form fibers in nature is restricted by the geochemical abundance of the chemical elements in the earth's crust and by variations in the local concentrations. The crust is heterogeneous; some chemical elements are abundant in certain geological environments while others are absent or unavailable for chemical reactions. The number of chemical reactions is therefore circumscribed in nature but this is not the case in the laboratory. Investigators can construct sythetic substances without regard to availability. It should not be surprising that scientists have created many distinctly different synthetic fiber species as well as families of fibers, with a range of chemical compositions analogous to mineral series and groups.

Fibrous minerals have been formed under physicochemical conditions that are difficult to define. When the advantages of inorganic materials in fibrous form were appreciated and fibrous minerals became commodities of commercial importance, the number of sources increased but the variability of natural products was recognized. Laboratory synthesis of fibers followed. It is true that laboratory procedures, especially those that produced fibers of compositions approximating minerals, have provided some information pertinent to the natural conditions of fiber generation. However, the synthetic investigations are driven by a different goal: to engineer materials that maximize the inherent advantages of the fibrous form itself, and its distinctive physical properties. In delineating the diversity of fibrous inorganic materials we see that the opportunity to create new fibers is in its infancy. Research on the chemically more complex mineral fibers should stimulate future synthetic endeavors and vice versa.

SILICATE AND ALUMINOSILICATE MINERALS THAT FORM FIBERS

A systematic classification of the most common minerals, the silicates, is based on the polymerization type of the silicate ions, $(SiO_4)^{-4}$, and the structural variations that arise through association with different cations. Mineral groups and series used as examples in the preceding section also illustrate the classification scheme. We now discuss in some detail the mineral groups noted for their fibrous morphology—the serpentine, amphibole, and zeolite mineral groups. We also outline some of the information available on clays, chlorites, silica, and other species to illustrate the compositional range of naturally occurring silicate fibers.

The most important of these groups is the serpentine mineral group, because it includes the fibrous mineral species chrysotile, which is the most common fibrous mineral and the one most widely mined, processed, and manufactured as asbestos.

The Serpentine Mineral Group

At least seven of the minerals belonging to the serpentine mineral group, occur in fibrous forms. Table 2.2 lists the varieties, together with the crystal chemical data needed to identify them.

Chrysotile is commonly fibrous whereas the other common serpentines, lizardite (a polymorph) and antigorite, are usually platy or massive, and rarely occur in fibrous forms.

Crystal Chemistry of the Serpentine Minerals

The crystal structures of all the minerals in the serpentine group contain the same basic building blocks. The basic unit is composed of a silicate sheet of composition $(Si_2O_5)_n^{-2n}$, in which three of the O atoms in each tetrahedron are shared with adjacent tetrahedra (Fig. 2.2A), and a nonsilicate sheet of composition $[Mg_3O_2(OH)_4]_n^{+2n}$ (Fig. 2.2B). These two sheets are bonded together to form a double layer in which the fourth (or free), apical, oxygens of the $(Si_2O_5)_n^{-2n}$ sheet are shared with the oxygens of the $[Mg_3O_2(OH)_4]_n^{+2n}$ sheet. Fig. 2.3 is a stereoscopic presentation of this layered structure, characteristic of the serpentine group of minerals, viewed from the side.

Alternate stacking arrangements of the double layers produce different crystal structures and different minerals in the group. The designations of hexagonal, orthorhombic, and monoclinic, listed in Table 2.2, reflect these structural variations (polytypes). Determinations of the crystal system and *unit cell* contents and dimensions (obtained by x-ray diffraction analysis) distinguish the several mineral species. Optical examination using the petrographic microscope is another technique often employed to identify minerals; it can detect and discriminate between the small variations related to composition or crystal symmetry. Because the values for the members of the group overlap, or are very close, definitive identification requires sensitive application of optical measurements and either x-ray or electron diffraction analyses, and often in combination (Hodgson, 1979; Wicks and Zussman, 1975).

In nature, samples usually contain different cations from those used to describe the double-layer structure: Al^{+3} and Fe^{+3} may substitute for Si^{+4}, and Fe^{+2}, Fe^{+3}, Mn^{+2}, and Ni^{+2} can all substitute for Mg^{+2} to a greater or lesser degree. The substitutions may be summarized in a chemical formula written as

$$(Mg_{3-x-y}R_x^{+2}R_y^{+3})(Si_{2-y}R_y^{+3})O_5(OH)_4$$

where $R^{+2} = Fe^{+2}$, Mn^{+2}, Ni^{+2} and $R^{+3} = Al^{+3}$, Fe^{+3}. Table 2.3 presents chemical analyses of chrysotile from four commercially important mines. Very small amounts of Na^{+1}, K^{+1}, and Ca^{+2} that appear in the chemical analyses of serpentine minerals are usually attributable to admixed trace amounts of other minerals in the analyzed samples. The composition of chrysotile is commonly quite close to the ideal $Mg_3Si_2O_5(OH)_4$.

Table 2.2 The Major Serpentine Group Minerals: Composition, Polytype, and Unit Cell Dimensions

Minerals	Composition	Polytype[a]	Crystal System	Unit Cell Dimension			
				a (nm)	*b* (nm)	*c* (nm)	*B*° (degrees)
Chrysotile	$Mg_3Si_2O_5(OH)_4$	1M	monoclinic	0.534	0.935	0.731	93.3
orthochrysotile		2O	orthorhombic	0.534	0.920	1.463	
Lizardite	$Mg_3Si_2O_5(OH)_4$	1M	monoclinic	0.531	0.920	0.731	90.0
Antigorite	$(Mg,Fe^{+2})_3Si_2O_5(OH)_4$	1M	monoclinic	0.533	0.93	0.746	91.6
		1M	monoclinic	4.35[b]	0.926	0.728	91.4
Orthoantigorite		2O	orthorhombic	0.532	0.922	1.453	
Jenkinsite	Fe-rich antigorite						
Garnierite	Ni-rich antigorite						
Amesite	$Mg_2Al(Si,Al)O_5(OH)_4$	2H	hexagonal	0.531		1.401	
		6H	hexagonal	0.531		4.212	
Greenalite	$(Fe^{+2},Fe^{+3})_{2-3}Si_2O_5(OH)_4$	1M	monoclinic	0.554	0.959	0.719	90.0
Cronstedtite	$Fe_2^{+2}Fe^{+3}(Si,Fe^{+3})O_5(OH)_4$	1H	hexagonal	0.549		0.7085	
		2H	hexagonal	0.549		1.417	
		3H	hexagonal	0.549		2.121	
Berthierine	$(Fe^{+2},Fe^{+3},Mg)_{2-3}(Si,Al)_2O_5(OH)_4$	1M	monoclinic	0.541	0.933	0.704	104.5
		1O	orthorhombic	0.537	0.931	0.706	

From Deer, R. A., W. A. Howie, and J. Zussman (1963). *Rock-Forming Minerals*, Vol. 3, p. 170. John Wiley & Sons, New York.
[a]Polytype = the crystallographic designation of the stacking order of tetranedral and octanedral layers.
[b]Layers display 4.35-nm corregation periods.

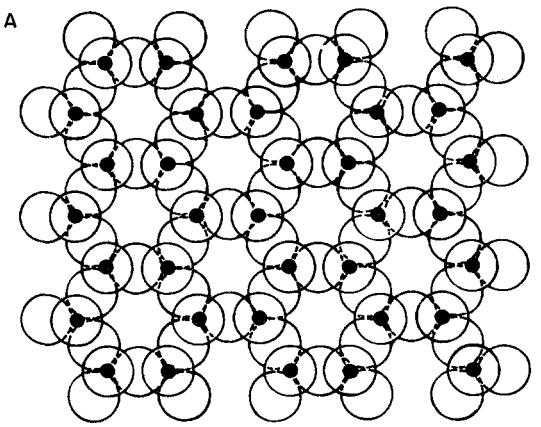


Fig. 2.2A Schematic representation of the structural components of the serpentines. The tetrahedral (**T**) sheet. The composition can be expressed as $[(Si_2O_5)^{-2}]_n$, is formed when three of the four oxygens in the tetrahedon are shared. The large open circles represent oxygen ions; the small solid circles are silicon ions. The open circles concentric with the silicon atoms represent oxygen atoms located vertically, above the silicon (apical oxygens).

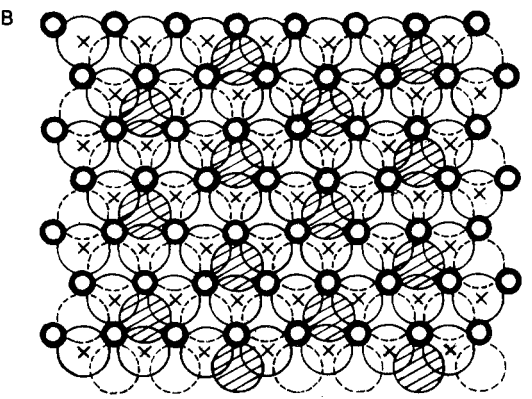


Fig. 2.2B The octahedral (**O**) sheet. The composition can be expressed as $[(Mg_{3-x-y}R^{+2}{}_xR^{+3}{}_y)O_2(OH)_4]_n$. The dashed circles represent the apical oxygens of the underlying T sheet. These ions replace the hydroxyls in the octahedral sheet and are common to the T and O sheets. The cross-hatched circles represent the remaining hydroxyls. The circles with crosses represent hydroxyls at the upper portion of the octahedral sheet. The small circles represent magnesium ions.

Chrysotile

Most serpentines and other layered silicate minerals, such as micas and clays, are composed of tetrahedral and octahedral sheets that lie virtually flat. In chrysotile samples, however, the layers curl, rolling up like a carpet, to form concentric hollow cylinders (Fig. 2.4). The average diameter of a cylinder, which is a chrysotile fibril, is about 25 nanometers (25 nm = 0.025 mi-

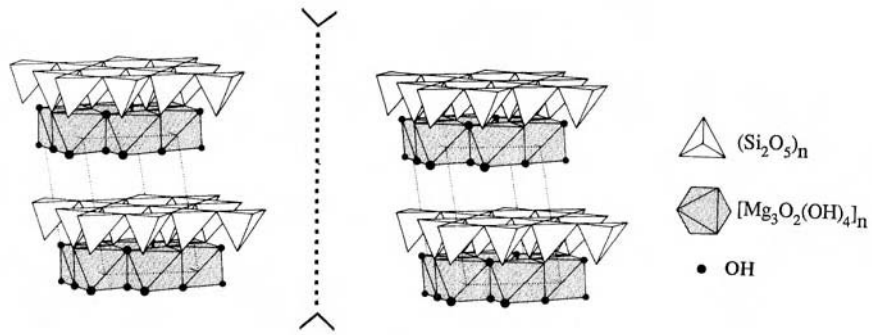


Fig. 2.3 Stereoscopic diagram of a serpentine structure (idealized). Polymorphs of $MgSiO_2O_5(OH)_4$ arise through stacking variations of the double T and O sheets. Oxygen ions are the corners of the silicon tetrahedra and magnesium octahedra. Hydroxyl ions are marked with a dot at the corners of the octahedra. Chemical bonds between the T and O sheets indicated by dotted lines, are weak. For a three-dimensional view of the structure, place a piece of paper perpendicular to the page along the dotted line separating the two images. Bring your face toward the page with one eye on either side of the paper, focusing on the drawings until they merge into one image at approximately 5 inches above the plane of the page.

crometers). It has been suggested that the curling is the consequence of a "misfit" between the two sheets of the double layer. The distances between apical oxygens in a regular (idealized) silicate layer (see Fig. 2.2A) are shorter (0.305 nm) than the O–O distances in the ideal Mg-containing layer (0.342 nm) (see Fig. 2.2B). The misfit can be accommodated by curling with the silicate or tetrahedral layer inside and the Mg or octahedral layer on the outside of the curve. However, the crystallographic analyses of several researchers (Steinfink and Brunton, 1956; Blount, Threadgold, and Bailey, 1969; Wicks and Whittaker, 1975) on serpentine and comparable tetrahedral–octahedral layered structures (the clay minerals: kaolinite, dickite, nacrite) show the tetrahedra are not in the ideal hexagonal arrangement of Fig. 2.2A, but are rotated and tilted. In many mineral species, therefore, the apical O–O distance of the tetrahedral sheet apparently matches the O–O distance in the octahedral sheet. Nevertheless, the chrysotile found in many localities is a curled fibrillar version of a double-layered crystal structure. In fact, variations in stacking sequences of the double layers have been shown to result in curling in different crystal axial directions (Whittaker, 1956). The specific factors that predispose some chrysotile samples to adopt a rolled (secondary) structure while others lay flat are not easily determined nor fully understood. This interesting fiber type and the tetrahedral–octahedral relationship is discussed more fully in the section on Clays, later in this chapter.

The individual cylindrical chrysotile fibrils undoubtedly contribute to the occurrence of this mineral species in fibrous form and may account for some of the flexibility and enhanced tensile strength of chrysotile fibers. Aveston (1969, p. 632) commented that asbestos was "inferior [in tensile strength]

Table 2.3 Chemical Analyses and Calculation of Formulas for Commercial Chrysotile Asbestos Samples from Four Countries

	Origin of Samples[a]			
	Canada (1)	USSR (2)	Zimbabwe (3)	Swaziland (4)
SiO_2	38.75	39.00	39.70	39.93
Al_2O_3	3.09	4.66	3.17	3.92
Fe_2O_3	1.59	0.54	0.27	0.10
FeO	2.03	1.53	0.70	0.45
MnO	0.08	0.11	0.26	0.05
MgO	39.78	38.22	40.30	40.25
CaO	0.89	2.03	1.08	1.02
K_2O	0.18	0.07	0.05	0.09
Na_2O	0.10	0.07	0.04	0.09
H_2O^+	12.22	11.37	12.17	12.36
H_2O^-	0.60	0.77	0.64	0.92
CO_2	0.48	1.83	2.13	1.04
	99.79	100.20	100.51	100.22
	number of ions on basis of the ideal formula $Mg_3Si_2O_5(OH)_4$[b]			
Si	1.845	1.851	1.885	1.882
Al	0.155 } 2.000	0.149 } 2.000	0.115 } 2.000	0.118 } 2.000
Al	0.018	0.112	0.062	0.100
Fe^{+3}	0.057	0.019	0.010	0.004
Fe^{+2}	0.081	0.061	0.028	0.018
Mn	0.003	0.004	0.010	0.002
Mg	2.823 } 3.047	2.704 } 3.013	2.853 } 3.025	2.827 } 3.016
Ca[c]	0.045	0.103	0.055	0.052
K[c]	0.011	0.004	0.003	0.005
Na[c]	0.009	0.006	0.004	0.008

[a]Key to country of origin of four sample: (1) King Beaver Mine, Thetford Mines, Quebec; (2) Asbest, Urals, USSR; (3) Shahani Mines, Zimbabwe; (4) Havelock Mine, Swaziland.

[b]To express mineral chemical formulas the cations or anions substituting in a unique site in the structure are combined.

[c]These cations may be the result of adventitious inclusion of other minerals.

only to pristine glass fibers and whiskers" (see Table 1.2). Chrysotile (from Canada) exhibited the highest value he obtained for any natural fibers, a characteristic he ascribed to interfibrillar adhesion.

Chrysotile, sometimes called *white asbestos*, with its unique fibrous form, is an expression of the subtle structural variations that can be found in crystalline solids. These characteristics illustrate the need to go beyond the simple, or standard, chemical and crystal analyses used for identification, to understand the distinctive qualities of fibrous inorganic materials.

Other Serpentine Minerals

Antigorite is another serpentine mineral. It is similar in composition to chrysotile except that small amounts of Fe^{+2} substitute for some of the Mg^{+2} in its structure (see Table 2.2). This subtle difference in composition produces a limited sheet structure with corregated stacking of the octahedral–tetra-

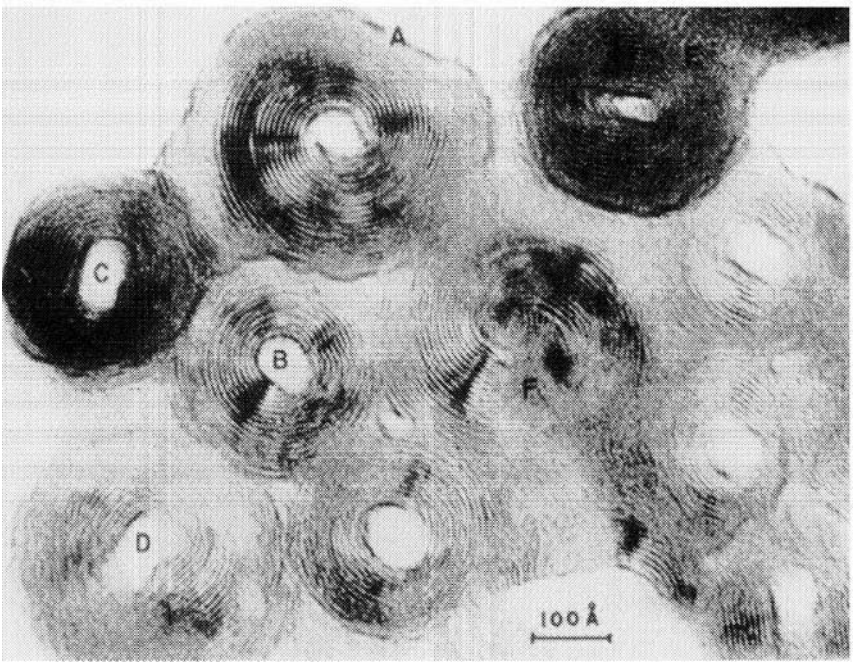


Fig. 2.4 Chrysotile asbestos sectioned perpendicular to the fiber axis. Electron micrograph showing typical lattice images of the layers of this serpentine mineral rolled into hollow cylinders (fibrils).

hedral layers. Two fibrous varieties of antigorite, known as *picrolite* and *povlen chrysotile,* respectively, are more brittle and stiffer than fibrous chrysotile. Povlen chrysotile fibers form segmented rather than continuous scrolls. Fig. 2.5 is an electron microscope photograph of a cross section through such fibers.

Other minerals in the serpentine group with structures similar to those depicted in Figs. 2.2 and 2.3 contain elements in addition to Mg in the octahedral layer (e.g., garnierite, a Ni-containing antigorite, and jenkinsite, an Fe-containing antigorite; see Table 2.2). These minerals also crystallize occasionally in fibrous forms. At present there is no definitive explanation of the mechanism of fiber formation, nor is there a means of predicting whether a particular structural or chemical modification will predispose a serpentine mineral to crystallize as a fiber.

Comprehensive reviews of the serpentine minerals can be found in Whittaker and Zussman (1956), Wicks and Whittaker (1975), and Zussman (1979).

The Amphibole Mineral Group

Few mineral groups contain as many species, or occur over as wide a range of geological environments, as the amphibole group. The forms and habits

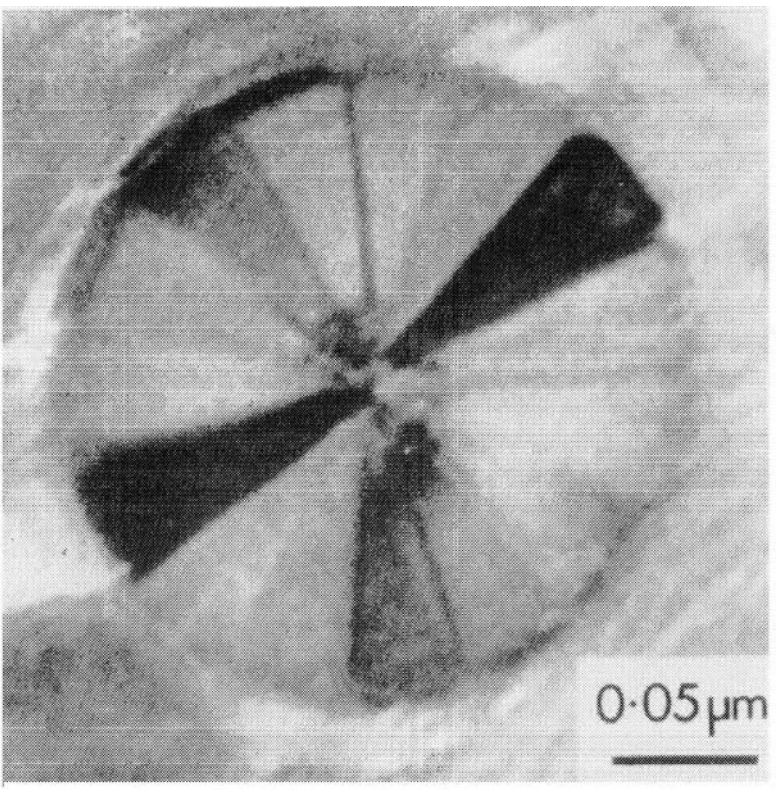


Fig. 2.5 Electron micrograph of Povlen (sectored) chrysotile. Each sector is a collection of flat serpentine layers.

adopted by the amphibole minerals are also diverse, but specimens are commonly columnar, acicular, or fibrous. Fibrous amphiboles have been discovered in veins cutting rock masses, an occurrence similar to that of chrysotile shown in Fig. 1.1A. Several amphibole minerals have been commercially exploited and are discussed separately in the following section on asbestos. The amphiboles have perfect prismatic cleavage, a distinctive physical property found in nearly all samples of the these minerals, regardless of habit. Cleavage produces fine, acicular fragments when the minerals are crushed, ground, or milled.

Crystal Chemistry of the Amphibole Minerals

A general formula for amphibole minerals can be written as

$$A_{0-1}B_2C_5T_8O_{22}(OH,F,Cl,O)_2$$

where A, B, C, and T represent cation sites with distinctly different geo-

metries. The disposition of these sites, as well as the aluminosilicate array, has been determined through x-ray diffraction analysis of selected amphibole crystals. Various cations commonly substitute for one another within the sites. For each formula unit, zero to one Na^{+1} and K^{+1} ions enter the A site, two ions each of Na^{+1}, Li^{+1}, Ca^{+2}, Mn^{+2}, Mg^{+2}, and Fe^{+2} enter the B site, five ions of Mg^{+2}, Fe^{+2}, Mn^{+2}, Al^{+3}, Fe^{+3}, Cr^{+3}, and Ti^{+4} enter the C site, and eight ions of Si^{+4} and Al^{+3} enter the T site.

Table 2.4 lists the major amphibole mineral series and illustrates the chemical range of the group. The five commercial asbestos varieties are starred. Idealized chemical formulas for the amphibole asbestos minerals are as follows:

Grunerite (variety amosite)—$(Fe^{+2})_2(Fe^{+2},Mg)_5Si_8O_{22}(OH)_2$
Riebeckite (variety crocidolite)—$Na_2(Fe^{+2},Mg)_3Fe^{+3}{}_2Si_8O_{22}(OH)_2$
Anthophyllite—$Mg_7Si_8O_{22}(OH)_2$
Tremolite—$Ca_2Mg_5Si_8O_{22}(OH)_2$
Actinolite—$Ca_2(Mg,Fe^{+2})_5Si_8O_{22}(OH)_2$

Table 2.5 presents chemical analyses of selected materials from commercial deposits. These data illustrate the chemical range of minerals that have been mined as asbestos.

The crystal structures of all amphibole minerals, including the asbestiform varieties, are most easily understood as variations on a basic structural unit called an I-beam. The term *I-beam* alludes to the cross-sectional shape of the three-part structure consisting of corner-linked $(SiO_4)^{-4}$ and/or $(AlO_4)^{-5}$ tetrahedra (T) linked together into a double-tetrahedral chain that sandwiches a layer of edge-shared $R^{+2}O_6$ and $R^{+3}O_6$ octahedra (O). R elements, which are either divalent or trivalent cations, are those ions that occupy the B and C sites, respectively. Representational sketches of the crystal structure are given in Fig. 2.6. Fig. 2.6A shows the double tetrahedral chains (T), composition $[(Si,Al)_8O_{22}]_n$ and Fig. 2.6B shows the octahedral sheet (O), $[(R^{+2}R^{+3})_5O_{12}(OH)_2]_n$. Fig. 2.6C illustrates the superposition relationship of T and O into the T + O + T sandwich—the I-beam unit. The four-I-beam stack in Fig. 2.6D is the typical amphibole structure viewed along the *c* axis of the crystal, allowing the shared oxygen atoms at the sheet edges and the A site between the four I-beams to be seen. Fig. 2.6E shows a plan view of the structure. It illustrates the octahedral and tetraderal sheet superpositions and the relationship between the B and A sites.

The cations in the octahedral sheet may have a distorted octahedral coordination, depending on the cation size. B site ions, such as Ca^{+2}, can be in either six- or eight-fold coordination with oxygen. Such variations can cause local structural distortion. The cation occupying the A site can bond to as many as 12 oxygen atoms—6 in the tetrahedral layer above and 6 below.

Variations in the stacking of I-beams have been studied with single crystal x-ray diffraction. The stacking character distinguishes the different amphibole mineral series (Hawthorne, 1981). Such studies show that tetrahedra in the T sheet are rotated and tilted to accommodate the variations in the anion

Table 2.4 Amphibole Mineral Series with Fibrous or Asbestos Varieties

Mineral Series/Species	Chemical Formula A	BC	T	Anions	Crystal System
Low-calcium amphiboles					
Magnesiocummingtonite–	—	Mg_7	Si_8	$O_{22}(OH)_2$	Monoclinic
Grunerite	—	Fe_7^{+2}	Si_8	$O_{22}(OH)_2$	Monoclinic
(Amosite)[a,b]	—	$(Fe,Mg)_7$	Si_8	$O_{22}(OH)_2$	Monoclinic
Magnesioanthophyllite[a]–	—	Mg_7	Si_8	$O_{22}(OH)_2$	Orthorhombic
ferroanthophyllite	—	$Fe^{+2}{}_7$	Si_8	$O_{22}(OH)_2$	Orthorhombic
Magnesiogedrite–	—	(Mg_5Al_2)	(Si_6Al_2)	$O_{22}(OH)_2$	Orthorhombic
ferrogedrite	—	$(Fe_5^{+2}Al_2)$	(Si_6Al_2)	$O_{22}(OH)_2$	Orthorhombic
Calcium-rich amphiboles					
Tremolite[a]–	—	Ca_2Mg_5	Si_8	$O_{22}(OH)_2$	Monoclinic
ferroactinolite	—	$Ca_2Fe_5^{+2}$	Si_8	$O_{22}(OH)_2$	Monoclinic
Actinolite[a]	—	$Ca_2(Mg,Fe^{+2})_5$	Si_8	$O_{22}(OH)_2$	Monoclinic
Aluminomagnesiohornblende–	—	Ca_2Mg_4Al	Si_7Al	$O_{22}(OH)_2$	Monoclinic
Aluminoferrohornblende	—	$Ca_2Fe_4^{+2}Al$	Si_7Al	$O_{22}(OH)_2$	Monoclinic
Edenite–	Na	Ca_2Mg_5	Si_7Al	$O_{22}(OH)_2$	Monoclinic
ferroedenite	Na	$Ca_2Fe_5^{+2}$	Si_7Al	$O_{22}(OH)_2$	Monoclinic
Pargasite–	Na	Ca_2Mg_4Al	Si_6Al_2	$O_{22}(OH)_2$	Monoclinic
ferropargasite	Na	$Ca_2Fe_4^{+2}Al$	Si_6Al_2	$O_{22}(OH)_2$	Monoclinic
Magnesiohastingsite–	Na	$Ca_2Mg_4Fe^{-3}$	Si_6Al_2	$O_{22}(OH)_2$	Monoclinic
hastingsite	Na	$Ca_2Fe_4^{+2}Fe^{+3}$	Si_6Al_2	$O_{22}(OH)_2$	Monoclinic
Aluminotschermakite–	—	$Ca_2Mg_3Al_2$	Si_6Al_2	$O_{22}(OH)_2$	Monoclinic
ferroaluminotschermakite	—	$Ca_2Fe_3^{+2}Al_2$	Si_6Al_2	$O_{22}(OH)_2$	Monoclinic
Alkali amphiboles					
Glaucophane–	—	$Na_2Mg_3Al_2$	Si_8	$O_{22}(OH)_2$	Monoclinic
ferroglaucophane	—	$Na_2Fe_3^{+2}Al_2$	Si_8	$O_{22}(OH)_2$	Monoclinic
Magnesioriebeckite–	—	$Na_2Mg_3Fe_2^{+3}$	Si_8	$O_{22}(OH)_2$	Monoclinic
Riebeckite (Crocidolite)[a,b]	—	$Na_2Fe_3^{+2}Fe_2^{+3}$	Si_8	$O_{22}(OH)_2$	Monoclinic
Eckermannite–	Na	Na_2Mg_4Al	Si_8	$O_{22}(OH)_2$	Monoclinic
ferroeckermannite	Na	$Na_2Fe_4^{+2}Al$	Si_8	$O_{22}(OH)_2$	Monoclinic
Magnesioarfvedsonite–	Na	$Na_2Mg_4Fe^{+3}$	Si_8	$O_{22}(OH)_2$	Monoclinic
ferroarfvedsonite	Na	$Na_2Fe_4^{+2}Fe^{+3}$	Si_8	$O_{22}(OH)_2$	Monoclinic
Sodic-calcic amphiboles					
Richterite–	Na	$NaCaMg_5$	Si_8	$O_{22}(OH)_2$	Monoclinic
ferrorichterite	Na	$NaCaFe_5^{+2}$	Si_8	$O_{22}(OH)_2$	Monoclinic
Aluminowinchite–	—	$NaCaMg_4Al$	Si_8	$O_{22}(OH)_2$	Monoclinic
ferrowinchite	—	$NaCaFe_4^{+2}Al$	Si_8	$O_{22}(OH)_2$	Monoclinic
Aluminobarroisite–	—	$NaCaMg_3Al_2$	Si_7Al_1	$O_{22}(OH)_2$	Monoclinic
ferroaluminobarroisite	—	$NaCaFe_3^{+2}Al_2$	Si_8	$O_{22}(OH)_2$	Monoclinic

Source: Data from Hawthorne (1981) and Leake (1978).

[a]Asbestos varieties.

[b]Amosite and crocidolite are not *bona fide* mineral species. See the text.

and cation compositions of the different species. Fig. 2.7 is a stereographic presentation of the crystal structure of anthophyllite [$(Mg,Fe)_7Si_8O_{22}(OH)_2$].

Further explication of the complexities of the compositions and the crystal structures of the amphiboles can be found in works by Papike and Ross

Table 2.5 Chemical Analyses of Samples of Amphibole Asbestos[a]

	Amosite	Actinolite	Anthopyllite	Crocidolite	Tremolite
SiO_2	49.70	53.80	57.20	50.90	55.10
Al_2O_3	0.40	1.20	—	nil	1.14
Fe_2O_3	0.03	1.90	0.13	16.85	0.32
FeO	39.70	25.30	10.12	20.50	2.00
MnO	0.22	0.40	—	0.05	0.10
MgO	6.44	4.30	29.21	1.06	25.65
CaO	1.04	10.20	1.02	1.45	11.45
K_2O	0.63	0.40	—	0.20	0.29
Na_2O	0.09	0.10	—	6.20	0.14
H_2O^+	1.83	2.60	2.18	2.37	3.52
H_2	0.09	nil	0.28	0.22	0.16
CO_2	0.09	0.20	—	0.20	0.06
	100.26	100.40	100.14	100.00	99.93
	Recalculated to Ideal Formulas $A_2(BC)_5T_8O_{22}(OH)_2$				
T(Si,Al,Fe^{+3})	7.99	8.26	7.79	7.97	8.00
A	2.08	1.84	2.24	2.13	2.36
B + C	5.00	4.72	5.00	4.91	5.00

Source: From Hodgson (1979); pp. 80–81.

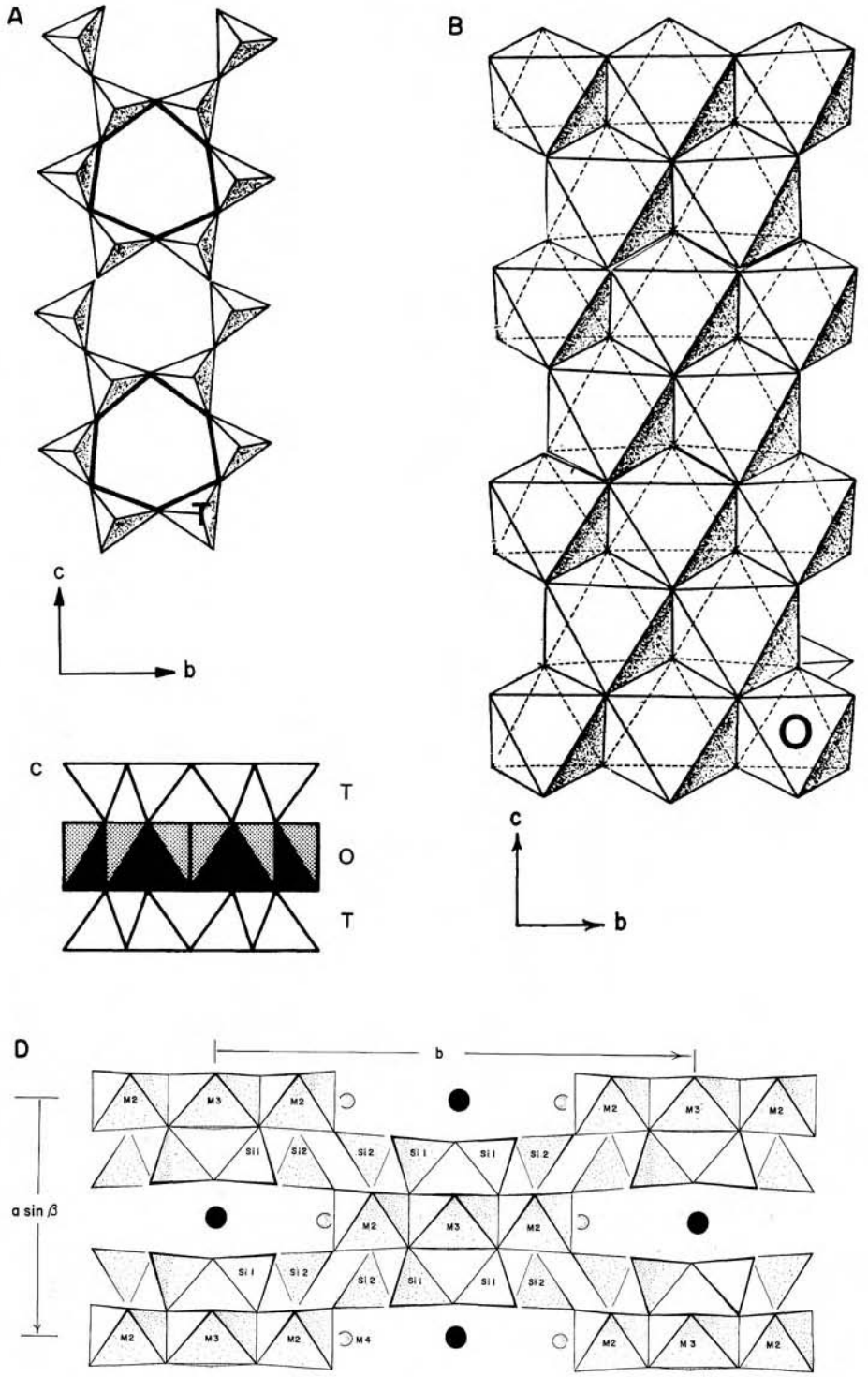
[a]Origin of samples: amosite—Penge, Transvaal, South Africa; actinolite—Koegas, Cape Province, South Africa (variety = prieskaite); anthophyllite—Paakkila, Finland; crocidolite—Koebas, Cape Province, South Africa; tremolite—Pakistan.

(1970), Zoltai (1981), Veblen (1981), and Veblen and Ribbe (1982). Special attention should be directed to the articles by Hawthorne (1981) and by Robinson et al. (1982). Clearly, accurate identification of a particular amphibole species requires considerable analytical effort and expertise.

Cleavage

The amphiboles exhibit prismatic cleavage, a distinctive physical property found in nearly all samples of these minerals, regardless of habit. There are two cleavage directions, both parallel to the length of the double-silicate chains. They separate the I-beams as shown in Fig. 2.8, producing fine, acicular fragments when the minerals are crushed, ground, or milled. The O—Si—O bonds within the tetrahedral double chains are much stronger than the O—R^{+2}—O or O—R^{+3}—O bonds that link the I-beams. The latter are the bonds broken during cleavage. Fig. 2.8A illustrates cleavage parallel to the crystallographic *c*-axis and around the T sheets. The orientation of Fig. 2.8B shows that the intersection of the two dominant planes of cleavage in amphiboles are at an angle of 56 degrees to each other, creating a rhombic cross section for the fragment. Cleavage perpendicular to (across) the I-beams is usually poor; therefore, fracture of amphibole crystals usually produces long rods or prisms, and repeated cleavage results in thinner rods with rhombic outline that consist of bundles of I-beams. The smallest amphibole fragment theoretically has a diameter about 0.84 nm (Fig. 2.8B).

High-resolution transmission electron microscopy has been used to study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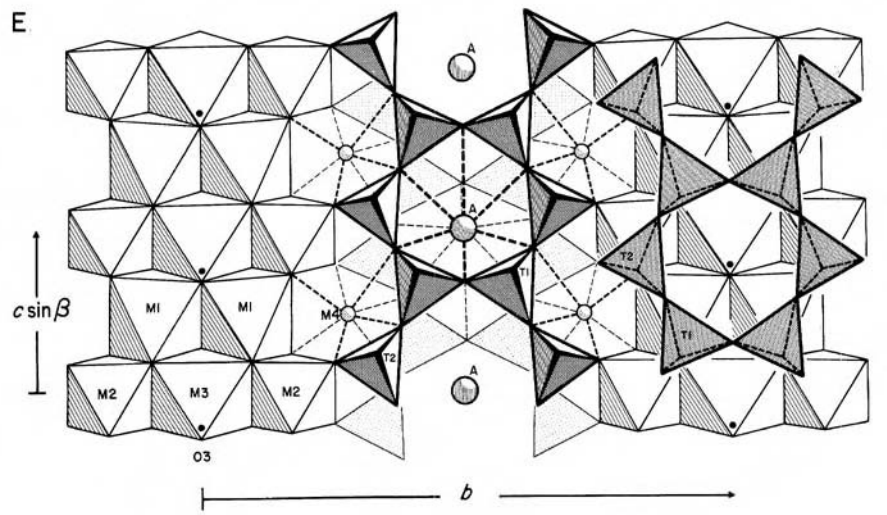


Fig. 2.6 Schematic representation of the structural components of the amphiboles. (**A**) The *c* and *b* vectors indicate the directions of the chains relative to the cell axes of the crystal structure unit cell axes. The double tetrahedral chain of composition $[(Si,Al)_4O_{11}]_n$ is formed from corner-linked SiO_4 or AlO_4 tetrahedra (T). (**B**) Octahedral chain of composition $[(R^{+2}R^{+3})_5O_{12}(OH)_2]_n$, formed from edge-shared $R^{+2}O_6$ and $R^{+3}O_6$ octahedra (O). (**C**) The superposition of the T + O + T sheets in the amphibole structure that forms the basic unit, or I-beam. Composition: $[(R^{+2},R^{+3})_5(Si,Al)_8O_{22}(OH)_2]_n$. (**D**) End-on view (down the c-axis of the crystal) of amphibole I-beams in staggered array, illustrating the sharing of oxygen atoms between the octahedral (M2) and tetrahedral portions (Si2) of adjacent units. Solid circles indicate the position of the cation A. The open circles are the M4 cations. Some amphiboles do not have cations in position A. The *a* sin β and *b* vectors give the orientation of the chains as determined by x-ray crystal structure analysis. (**E**) Plan view of a portion of the amphibole crystal structure. Compare the different orientation of this structure with that in Part D. The vectors *c* sin β and *b* instead of *a* sin β and *b*, indicate different directions in the three-dimensional structure determined for the amphiboles. The linkage between the tetrahedral and octahedral sheets is shown, with the amphibole double tetrahedral chains (*shaded*) superimposed on the octahedral sheet. To the right, the apex of the tetrahedra point down. In the center, one tetrahedral chain (light shading) points down and another (dark shading) points up. The A cation sites are partially shaded circles. On the left is the octahedral sheet with the B cation site indicated as M4 and the C cation sites indicated as M1, M2, and M3. The A, B, C, and T designations correspond to the general amphibole formula: $A_{0-1}B_2C_5T_8O_{22}(OH)_2$. The *c* sin β and *b* vectors indicate the orientation of the chains, as determined by x-ray crystal structure analysis.

these interesting minerals and to detect faults and defects in samples of amphibole asbestos minerals (Fig. 2.9) as well as other hydrous biopyriboles and sheet silicates (Jefferson et al., 1976; Mallinson et al., 1980; Veblen and Buseck, 1981). Although defects at the atomic level have been depicted,

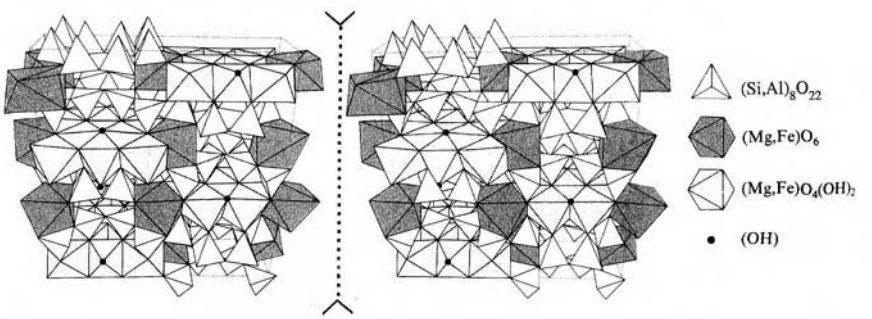


Fig. 2.7 Stereoscopic diagram of structure of the amphibole anthophyllite, $(Mg,Fe)_7Si_8O_{22}(OH)_2$. The position for three-dimensional viewing is indicated. The T sheet contains SiO_4, the O sheet $(Fe,Mg)O_6$ or $(Mg,Fe)O_4(OH)_2$. The (OH) positions are indicated by dots. Note the extensive distortion of the octahedra.

their specific contribution to the mechanisms of growth in a fibrous habit, or to the physical characteristics of fibrous minerals in general, has not yet been elucidated (Zoltai, 1981).

Hornblendes, one series of Ca–Al-containing amphiboles (see Table 2.4), are particularly common minerals. Their chemical and physical properties resemble those of the tremolite–actinolite series, but hornblendes generally do not occur in a fibrous habit. They contain Al^{+3} in both tetrahedral and octahedral sites, whereas the asbestos varieties of amphibole contain little Al^{+3}. This observation suggests that small variations in composition may be one of the important factors in generation of fibrous amphiboles.

Chemical factors other than the Al content have also been suggested as possible reasons for amphiboles to adopt a fibrous growth habit. One theory is that "large" cations inserted at certain sites produce local structural distortions and facilitate growth in one direction. Another theory suggests that multiple, rather than double, silica chains seen in certain high-resolution electron micrographs of amphibole samples (Fig. 2.9) cause local crystallization irregularities with a similar result—a preferential direction of growth (Zoltai, 1981). Alteration of the ideal crystal chemistry could, for example, affect not only growth but the reactions of a particular amphibole sample as well as the ease of the characteristic cleavage.

Amphibole Asbestos

The formation of amphibole asbestos, as with the previously described chrysotile asbestos, is the result of single-crystal fibrillar growth through preferential extension along one crystallographic direction. These fibrous minerals typically occur in veins created when cracks form in rocks during earth movement. Subsequently the cracks fill in with minerals. The opening of cracks produces regions of negative stress, which, together with the flow of solutions in the channels, probably influences the nucleation, growth, and direction of elongation of the mineral fibers (Ross, 1981).

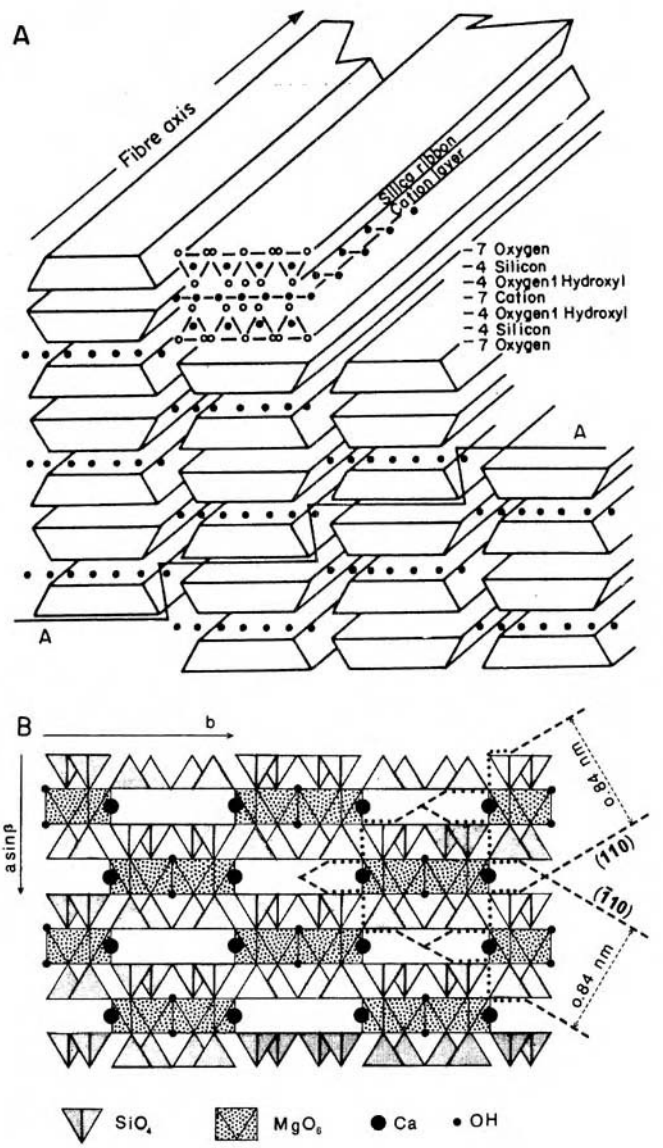


Fig. 2.8 Cleavage in the amphiboles. (**A**) Schematic representation of the characteristic stacked amphibole I-beams in the three-dimensional structure. A tetrahedral portion of an I-beam is labeled "silica ribbon." The octahedral portion is labeled "cation layer" and represented by solid circles. One of the possible cleavage directions (110) along planes of structural weakness is indicated by the line A-A stepped around the I-beams in the lower part of the diagram. (**B**) Cross section of the stacked I-beams with the directions of easy cleavage indicated. There is a lower density of bonds between I-beams in the crystallographic directions (110) and ($\bar{1}10$). These directions, parallel to the *c* axis and the length of the chains, are the planes of cleavage. The minimum thickness of a rhombic fragment produced through cleavage is 0.84 nm.

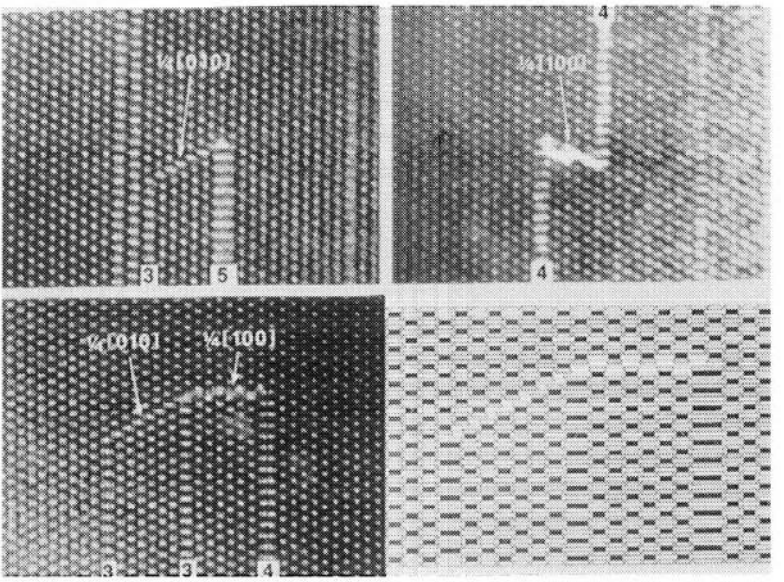


Fig. 2.9 High-resolution electron micrographs of anthophyllite. Displacive fault termination or "zippers," and an interpretation based on the 'I' beam structure of the amphiboles.

ASBESTOS

Historical Perspective

Asbestos has been known and used for millennia (Theophrastus, fourth century B.C.). The subject of much scholarly comment since Pliny's *Natural History* and Dioscorides' *De Materia Medica* in the first century, asbestos was known through a large quantity of fact and fable by the late seventeenth century when the modern era of mineral materials began (Plot, 1686; Ciampini, 1701; Gimma, 1730; Ledermuller, 1775; and Schroeter, 1772).

Although the etymologies of the numerous terms that have broadly been applied to asbestos are clear, their usage in many instances have not been consistent. The following illustrates the wide range of terminology, perceptions, sources, and ancient uses of the term *asbestos:*

1. The Greek *a-sbestos* means inextinguishable, but it is apparent from early descriptive comments that the characteristic of incombustibility was implicit (Luschen, 1968). Old synonyms for asbestos, such as "salamander stone," referring to a mythical animal that endured fire without harm encompass both meanings, as does the belief that tomb lamps with asbestos wicks burned indefinitely, or at least until all of the oil, but not the wick, was consumed (Theophrastus, trans. by Caley and Richards, 1956).
2. The Greek *a-mianto* was also used to refer to asbestos materials. The

term literally means unsoiled or undefiled, and the Latin equivalent, *amianthus,* originally pertained to the action of fire in removing stains from woven asbestos cloth. Some writers considered amianthus to be a synonym for asbestos. However, it was applied in particular to the long, silky asbestos fibers suitable for weaving. This use of long-fiber asbestos, and the advantages of asbestos (thermal insulation when coated on wood; enhancement of binding when mixed with clay in pottery), were recognized from the earliest times.

3. *Linon* and *linum* (Latin), meaning "linen," are often found coupled with asbestos, as is flax, the plant from which linen is obtained. The association refers to (a) the linenlike appearance of high-quality asbestos cloth, (b) the use of asbestos in the place of linen (crematory wrappings), and more generally (c) the use of flax as an aid in the weaving of asbestos. For example, a mixture of long-fiber asbestos and flax or another vegetable fiber is carded, moistened with oil to promote cohesion and tensile strength, and spun into thread. Cloth made from the dual composition fibers is then fired to burn off the plant (organic) fibers and oil (von Korbell, 1837).
4. The term *alumen plumosum* has had a long association with asbestos. Alumen (= alum) is a general term for naturally occurring hydrous alkali aluminum sulfates. These are efflorescent mineral materials of fibrous, feathery appearance. Confusion with the more durable silicate composition asbestos was not settled until 1741, by Tourneforte following a visit to asbestos deposits in Asia Minor.
5. Aside from occasional references to asbestos as vegetal (e.g., crematory cloth referred to as *linum vivum*), the ancients knew asbestos as a type of stone obtained at specified places. In seventeenth-century Germany the terms *Bergflachs, Bergleder, Bergholz,* and *Bergwolle* referred to the several varieties of fibrous mineral materials. *Berg,* a masculine noun in German, means "mountain," but as a prefix it carries the sense of mining (*Bergakademie* = mining school). The English translation was "mountain flax" or "mountain leather" instead of the more precise "mineral flax." These confusions in terminology persist today. Mountain leather is occasionally used to describe a tough flexible mineral aggregate that is partly tremolite-asbestos (one of the five amphibole minerals) and partly palygorskite (a clay mineral).

Thus, from the beginning, the term asbestos was used to describe any of several fibrous mineral materials, and usually those found as concentrated aggregates or in veins, and therefore amenable to mining. Many locations around the ancient Mediterranean—Greece, Crete, and Cyprus—as well as India and Egypt provided material for weaving. The most widely used minerals appear to have been either tremolite-asbestos or actinolite-asbestos. By 1764, twenty mines were said to be operating in Europe. The German localities produced minerals described as short fibers from areas now known to provide chrysotile (serpentine) asbestos. In fact, Reichenstein is the type

locality for chrysotile asbestos (von Korbell, 1834). The nomenclature we now apply to asbestos materials began in eighteenth-century Germany.

Occurrences in the United States were known as early as 1698 with numerous finds along Brandywine Creek in Pennsylvania (Frondel, 1988). The celebrated purse made from asbestos that Benjamin Franklin took to London in 1724, and which now resides in the British Museum of Natural History, may have been made of long-fiber asbestos from Newbury, Massachusetts. As a journeyman printer, Franklin made paper from asbestos, as did many Europeans. It was also used in making lamp wicks and cloth. Commercial mining in the United States took place some time after the first discovery of asbestos on Staten Island, New York, in 1818. (Asbestos continued to be mined at the site until 1876.) By 1825 more than seventy localities were known to produce asbestos in the United States (Robinson, 1825). However, as early as 1804 Jameson had recorded the mineralogy of the species and listed the numerous university, societal, and private mineral collections containing specimens of asbestos from U.S. localities and asbestos products of local manufacture.

The material called asbestos was first identified as fibers that were sufficiently flexible for weaving and white to gray color. It was generally known to be incombustible and to remain unchanged up to temperatures of red heat, which was considered a useful property. But its insolubility in water or mild alkaline and acid solutions seems not to have been recognized or mentioned.

By the first part of the nineteenth century asbestos was known to be different from other fibrous minerals. The open, flexible aggregates of "mountain flax," were distinguished from the stiff, harsh "mountain leather." About this time investigations were undertaken on a group of minerals called schorl. (Today schorl is a mineral in the tourmaline group with the chemical composition $NaFe^{+2}{}_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$.) In these initial scientific studies on green fibrous materials, a mineral was separated and named actinolite (a combination of the Greek words for "ray" and "stone"), in recognition of its stellate appearance (Kirwan, 1794). Werner and other European mineralogists of that time included asbestos in the category of actinolite, based on the known gradation of actinolite from columnar to acicular to fibrous forms.

Perhaps the most important early contribution to the precise characterization of the fibers came from the role played by asbestos in the discovery of the element magnesium. The Swedish chemist Bergmann, in the mid-1700s, analyzed some asbestos (now known to be the serpentine mineral chrysotile) from Reichenstein and established the presence of the element magnesium. From further crude analyses it was discovered that this asbestos was a silicate of magnesium containing variable and usually small amounts of calcium. Other analyses made in the early 1800s on different samples called asbestos correspond to the compositional ranges now defined for the amphibole asbestos minerals tremolite and actinolite. Measurements using an optical goniometer on free-standing coarse asbestos fibers (Kennegott, 1849) substantiated that one asbestos sample was identical to the large crystals and

cleavage fragments of the mineral actinolite. This was accomplished by showing that the interfacial angles (55°39′) of the prism faces on the fibers, were identical to those on a large crystal and on cleaved fragments of the mineral (Fig. 2.8B).

The confusion in the literature concerning asbestos materials over the past two centuries is not surprising in view of what we now know—that many fibrous minerals have similar chemistry and structures. *Serpentinite* is a rock and *serpentine* is a mineral group in the mineralogical literature of today. Both names come from the green stone with fibrous snakelike veins originally described by Pliny. The original stone probably contained several green magnesium silicate minerals from the serpentine group: antigorite, lizardite, and chrysotile. Chrysotile, formally described in 1834 by von Korbell, was first mentioned in Dana's *System of Mineralogy* in 1850 as a variety of serpentine, and it was separated from the amphibole asbestos minerals in the 1854 edition. The amphiboles also have a lengthy and convoluted history that starts with the introduction of the term *amphibole* by Hauy in 1801 to replace *hornblende*. Today, hornblende is but one of the many species and series included in the amphibole group (see Table 2.4).

The fibrous forms of amphiboles, and serpentines, in addition to occurring in aggregates amenable to mining, are widespread as minor constituents of many rocks. The fibers are also widely distributed throughout the soils and waters of the world. These occurrences, together with the many long-term uses for asbestos society has devised, ensure that the ubiquitous presence of asbestos in our environment.

Asbestos Today

Over the past several decades six different silicate minerals have been mined as asbestos and processed for industrial and commercial applications. The most commonly encountered asbestos mineral today is chrysotile. The five other minerals are tremolite, actinolite, anthophyllite, grunerite, and riebeckite. All five are members of the amphibole group of minerals, and each can occur as chunky, acicular, or equant crystals, as well as in fibrous form. When found as fine fibrous aggregates, in quantities appropriate for mining, they are usually distinguished as a special variety—for example, tremolite-asbestos.

The fibrous appearance of the asbestos minerals is achieved primarily through parallel growth of exceedingly fine and elongated crystals producing bundles of fibers. The fibers can be easily separated from the fibrous bundle, and they are themselves aggregates, or assemblages of fibrils, that reflect the crystal structure of the mineral. In the case of chrysotile the fibrillar unit is especially distinctive, a curled secondary structure of the usual primary layered silicate (see Serpentine Mineral Group).

Asbestos fibers usually have a diameter of less than 0.5 microns. They may have an aspect ratio of greater than 1000, but usually at least 20, and they exhibit very high tensile strength and flexibility. The chemical and ther-

mal stability prized by the ancients, when these pliable fibers were woven into cloth, is a result of the silicate composition.

Asbestos is a nonspecific, collective term for a group of fibrous minerals. A sample called asbestos may be composed of one or more of the six minerals listed above and may contain small amounts of other nonfibrous silicate minerals, such as quartz, feldspar, or mica. The definition of asbestos recently published by the American Society for Testing Materials (Ross et al., 1984) can be found in the Glossary.

Occurrence

Each asbestos occurrence is unique, and some variations of morphology, composition, and physical properties are expected from sample to sample, not only from one geographic source to another, but within a particular mine.

The modern industry began in Italy and England after 1860. Mines in Quebec, Canada, soon became prominent as the largest source of chrysotile asbestos. By 1900, roughly 200,000 to 300,000 tons of asbestos had been mined (mostly in Quebec), and by 1980 a total of more than 100 million tons worldwide, of which 90 percent was chrysotile. Approximately 75 percent of all the asbestos ever mined has come from four chrysotile mining areas located in Quebec, Canada, South Africa, and the central and southern Urals of the Soviet Union. The Soviet Union produced 46.1 percent of the world's total asbestos production in 1978, and Canada produced 28.9 percent, with the remaining being produced by Zimbabwe (3.8 percent), China (3.8 percent), Italy (2.9 percent), South Africa (2.1 percent), Brazil (1.8 percent), and the United States U.S. (1.7 percent). In 1984 mine production was down to a total of 4.3 million tons worldwide, with Canada producing 0.922 million tons (Mineral Commodity Summary, 1986).

Two to 3 percent of the world's total asbestos production has been of the crocidolite variety, most of which has come from South Africa. Western Australia was a minor producer of crocidolite between 1944 and 1966. All amosite has been mined in the Transvaal Province of South Africa (2 to 3 percent of the world total). The only significant anthophyllite production came from Finland, where about 350,000 tons were mined between 1918 and 1966. Table 2.6 lists the composition, optical, and diffraction characteristics of the six asbestos minerals. More information on individual mineral species can be found in the references accompanying the sections on serpentine and amphibole types. Discussion of the geology, terminology, and exploitation of the several types of asbestos can be found in Ross (1981).

OTHER CHAIN ALUMINOSILICATES THAT FORM FIBERS

In addition to the asbestos varieties many other examples of silicate and aluminosilicate minerals occur in fibrous form. In the following section we present data for a few selected species, indicating the types of chemical

Table 2.6 Comparison of the Diffraction, Optical and Mechanical Properties of the Six Asbestos Minerals

Mineral	Composition (Idealized)	Unit Cell Parameters[a]				Optical Parameters[b]		Tensile[c] Strength	Flexibility
		a (nm)	*b* (nm)	*c* (nm)	*B* (degrees)	*n*	n_y		
Chrysotile (Canadian)	$Mg_3Si_2O_5(OH)_4$	0.532	0.920	1.464	92.3	1.537–1.554	1.554–1.557	31	good
Actinolite	$Ca_2(Mg,Fe^{+2})_5Si_8O_{22}((OH)_2$	0.989	1.820	0.531	104.63	1.600–1.628	1.625–1.655	<5	fair to brittle
Amosite*	$(Fe^{+2},Mg)_7Si_8O_{22}(OH)_2$	0.951	1.830	0.533	101.06	1.670–1.675	1.683–1.694	25	fair
Anthophyllite	$(Mg,Fe^{+2})_7Si_8O_{22}(OH)_2$	1.850	1.790	0.529	90.00	1.578–1.652	1.591–1.676	24	fair to brittle
Crocidolite* (Cape Province, S. Africa)	$Na_2(Fe^{+2},Mg)_3Fe_2^{+3}Si_8O_{22}(OH)_2$	0.974	1.806	0.531	103.73	1.682–1.696	1.686–1.700	35	good
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	0.987	1.802	0.533	104.65	1.599–1.628	1.591–1.676	<5	brittle

[a]Zussman (1979) table 2.4, p. 61, and table 2.2, p. 53 (actinolite).

[b]Hodgson (1979) table 3.8, p. 95; crocidolite is length fast, and all other fibers are length slow.

[c]Hodgson (1979) table 3.6, p. 93.

*Variety names, not true mineral names. See text.

substitution, structural modification, and details of formation that can influence the occurrence of the fibrous morphology.

Single Chain

Pyroxenes

The pyroxenes are chemically complex but common rock-forming minerals. They resemble the amphiboles in many ways, but are actually single-chain silicates. The tetrahedral basic unit of the pyroxenes, $[(Al,Si)_2O_6]_n$, was schematically depicted in Fig. 2.1C. The general formula for the group is: $A_{1-p}(B, C)_{1+p}\ T_2O_6$, where A = Ca^{+2}, Fe^{+2}, Li^{+1}, Mg^{+2}, Na^{+1}; B = Mg^{+2}, Fe^{+2}, Mn^{+2}, Sc^{+3}; C = Fe^{+3}, Al^{+3}, Cr^{+3}, Ti^{+4}, and T = Si^{+4}, Al^{+3}. Within the group are several mineral series and several species that often occur in acicular or fibrous forms. One species that occurs in fibrous form is jadeite, $[Na(Al,Fe^{+3})Si_2O_6]$, a relatively familiar name because of the popularity of this material with Oriental sculptors.

Enstatite, $Mg_2Si_2O_4$, is a species within the group, where $p = 1$, although actual samples often contain small amounts of Ca^{+2}, Al^{+3}, and Fe^{+2}, presumably substituting for Mg^{+2}. The cations in the structure of enstatite could occupy two crystallographically distinct interchain sites, designated M1 and M2 on Fig. 2.10A. Changes in the relative positions of the pairs of silicate chains lead to polymorphism; that is, enstatite is orthorhombic while clinoenstatite is monoclinic (Fig. 2.10B). Another pyroxene mineral, diopside ($CaMgSi_2O_6$), contains Mg^{+2} ions in the B, or the M1 sites, while the Ca^{+2} ions are located preferentially in the A, or M2 sites. In diopside all chains are equivalent and staggered in a fashion similar to that depicted for clinoenstatite. However, diopside is a distinct structural type and a member of the compositional series $CaMgSi_2O_6$–$CaFeSi_2O_6$. It is unrelated to clinoenstatite. These small chemical and structural differences are significant. They influence the physicochemical reactions of a particular mineral species.

The pyroxene group of minerals, where cations substitute one for another at interchain sites, also have a tetrahedral Si^{+4} site that may contain Al^{+3}. Some of these substitutions, especially those at M2, can distort the ideal crystal structures, as is depicted in Fig. 2.10. The small distortions are detected as variations in bond lengths between adjacent atoms during crystal structure analyses. These data, combined with accurate composition analyses, could indicate some of the conditions present during growth of the crystal and contribute to our understanding of why some mineral species have formed as fibers. Unfortunately, few detailed crystal structural analyses have been performed on pyroxene minerals with fibrous habits.

As might be anticipated for minerals with chain structures, pyroxenes commonly occur in columnar, prismatic, rodlike, and acicular forms. Enstatite has been found in the form of rosettes of fine-fibrous crystals. Special names such as victorite, chladnite, and shepardite were assigned to different occurrences in this distinctive morphology, possibly because the fibrous aggregates were located in iron meteorites. However, the composition and crystal

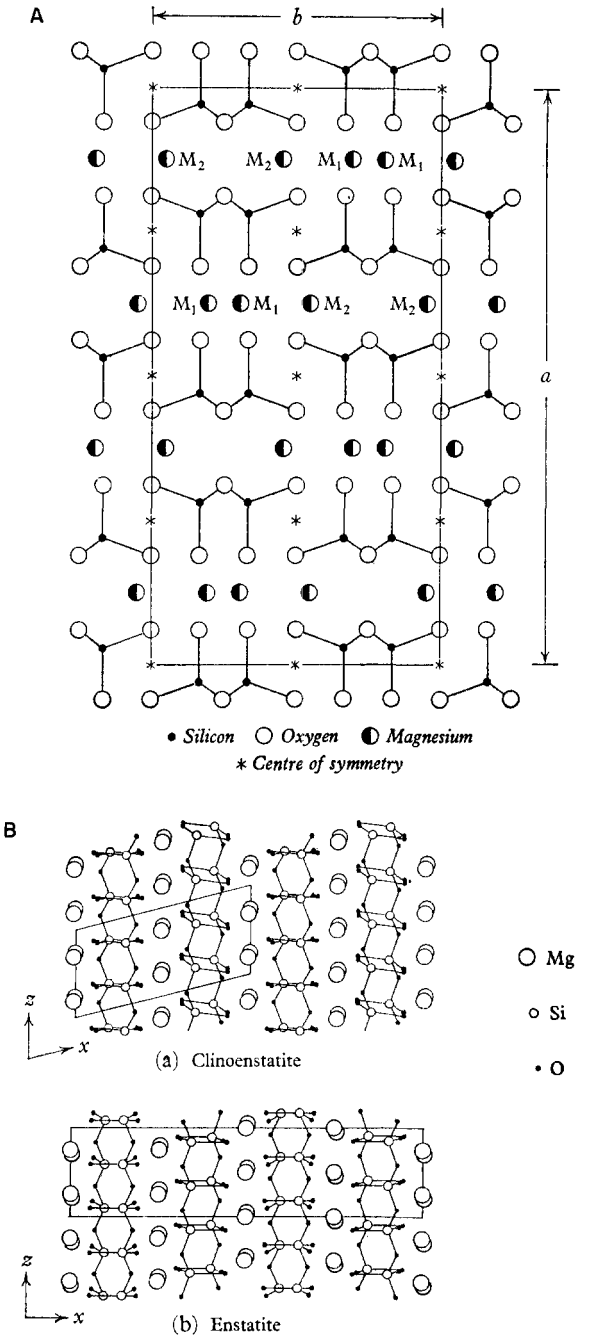


Fig. 2.10 Schematic structures of the pyroxenes, enstatite, and clinoenstatite. (**A**) Enstatite, (001) projection $Mg_2Si_2O_6$. (**B**) Comparison of the structures of enstatite and the polymorph clinoenstatite in a (010) projection. The large circles are Mg^{+2}, the small circles are Si^{+4} and the black dots are O^{-2}.

structure of all of these varieties have been shown to be virtually identical with those of enstatite, and the varietal names have been discarded.

Johannsenite, $Ca(Mn,Fe^{+2})Si_2O_6$, is a species in which $p = 0$. There is little additional trivalent ion (Al^{+3}, Fe^{+3}, or Cr^{+3}) substitution. The mineral is most commonly found as spherulitic aggregates of brittle fibers or prisms. Another pyroxene, acmite ($NaFe^{+3}Si_2O_6$), has been found as large (100 × 35 × 20 cm) single crystals of prismatic shape, as needles, as felted aggregates of fine fibers, and as capillary crystals.

These few examples illustrate the range of habits exhibited by minerals whose basic structural units are single chains. In addition, the pyroxenes, which have compositions quite similar to those of the amphiboles, are often found intimately intergrown with the latter double-chain minerals in what appears to be a single large crystal. An intergrowth of amphibole and pyroxene as a fiber, or in a fibrous aggregate, has not yet been described, but it is a likely occurrence.

Pyroxenoids

Wollastonite ($CaSiO_3$) is a single-chain silicate, with a structure similar to those of the pyroxenes. Known as a pyroxenoid, wollastonite frequently occurs as acicular crystals. Fibrous wollastonite from Devon, England, was investigated by Jeffery (1953) using x-ray diffraction techniques. He showed that the fibrous form was the result of an intimate intergrowth of fine crystallites of two polymorphs of $CaSiO_3$. The difference between the structures was the result of subtle changes in the orientation of the tetrahedral groups on adjacent chains. Both structures have virtually identical free energies of formation, and therefore both can apparently nucleate and grow with equal facility. The two types, in parallel aggregation, make up the crystalline fibers of wollastonite. It is possible that the fibrosity exhibited by other occurrences of wollastonite, and by other single-chain aluminosilicates, is the result of co-crystallization of similar, but not identical, fibrillar structural domains.

Fuchs (1971) identified acicular wollastonite from the Allende meteorite. Miyamoto et al. (1979) called these extraterrestrial crystals whiskers. Massive deposits of fibrous wollastonite in minable quantities occur in the Adirondack Mountain region of New York State.

Another pyroxenoid, bustamite, $[(Mn,Ca,)_3Si_3O_9]$, whose structure closely approximates that of wollastonite, has also been identified in fibrous form, but no detailed examination has been undertaken to check the possibility that a structural segregation similar to wollastonite exists in this mineral, and might contribute to the formation of fibers.

Pectolite $[NaCa_2Si_3O_8(OH)]$ is found as white to translucent acicular radiating crystalline aggregates, often in association with the zeolite group of minerals, which are discussed later. In the crystal structure of pectolite, Ca^{+2} and Na^{+1} occupy the sites between the single chains as described for pyroxenes. Chemical substitutions of Mn^{+2}, Mg^{+2} and Fe^{+2}, for Na^{+1} and Ca^{+2} are common. The substitutions may be detected optically because they pro-

duce changes in the indices of refraction. Optical methods can also be used to distinguish pectolite from wollastonite because the two fibers have different crystallographic axes of fiber elongation. Stacking disorder in pectolite, similar to that in wollastonite, has been demonstrated by Muller (1963).

Double Chain

Sillimanite

Sillimanite, the high-temperature polymorph of Al_2SiO_5, whose crystal chemistry is better expressed by the formula written as $AlO[(Al,Si)O_4]$, has been shown to have chains of alumina–oxygen tetrahedra that parallel tetrahedral chains in which silicon alternates with aluminum (Fig. 2.11A) (Burnham, 1963). Sillimanite commonly occurs in long prismatic crystals or as fibers.

At least some fibrous samples have been shown to consist of an intergrowth of sillimanite and quartz (Bell and Nord, 1974). The intimate association of Al_2SiO_5–SiO_2, called fibrolite, occurs in close geographic proximity with fibers composed of all sillimanite. Virtually identical in appearance, the two fiber types were detected when experiments using fibrous sillimanite, or an equant sillimanite crystal, gave different results depending on habit of the starting material (Holdaway, 1971). Examination of the fibrous sample using electron microscopy showed an intimate mixture of quartz and sillimanite (Fig. 2.11B). Adsorbed or entrapped water has also been reported as a constituent within a fibrous mass of sillimanite crystals. Vernon (1979) suggested that the mobility of hydrogen in the associated water might aid in the formation of fibrolite.

Investigation of a few fibrous samples of single- and double-chain aluminosilicates suggests that intimate intergrowth at the molecular level may be one mechanism leading to fibrous growth in minerals. Observations and investigations of other fibrous silicates, and indeed of other fibrous materials, with high-resolution techniques might be rewarding.

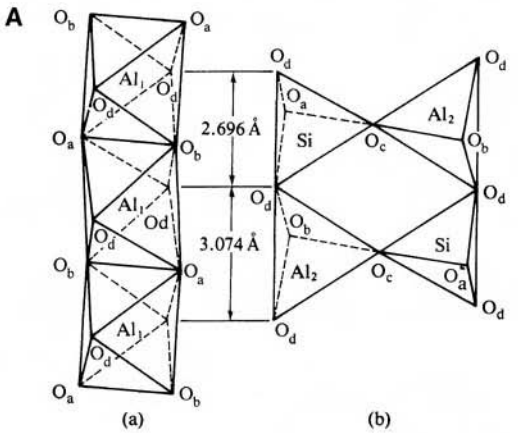
The minerals that adopt a fibrous morphology based on structural characteristics are certainly not confined to single- and double-chain aluminosilicates. To illustrate the variety of structural configurations that may produce fibers, we briefly outline other mineral groups in the following sections.

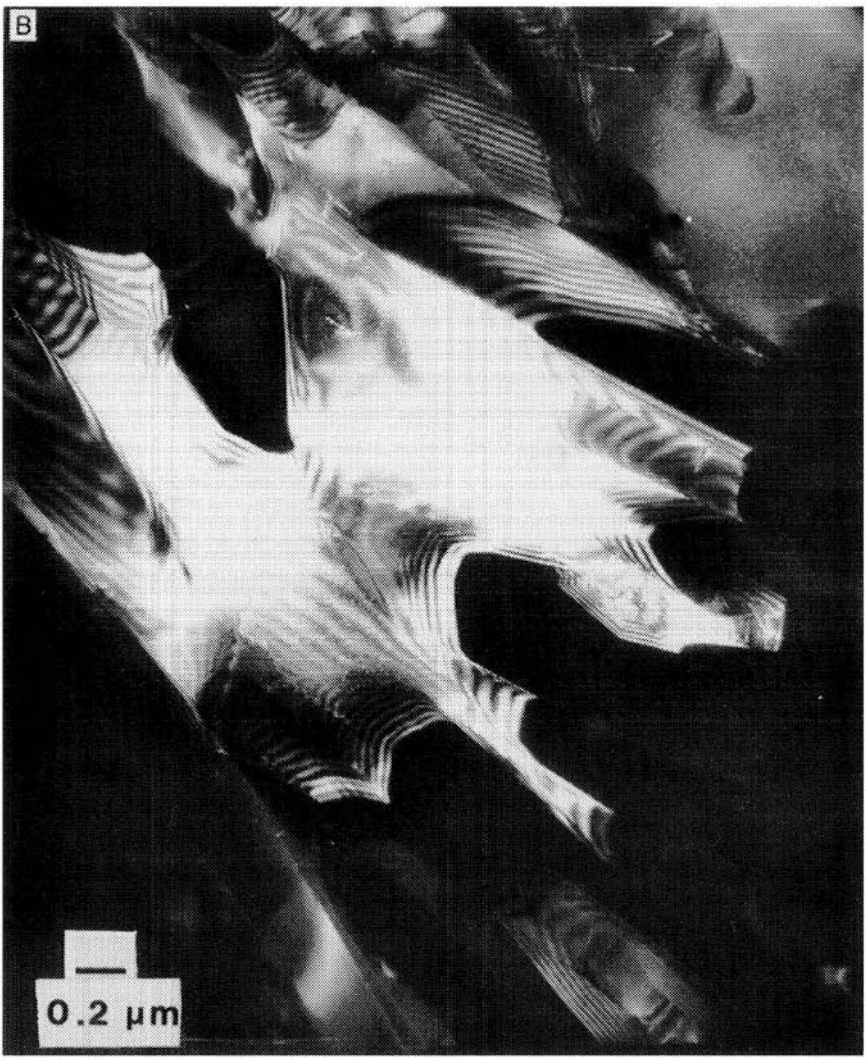
ALUMINOSILICATES WITH SHEET STRUCTURES THAT FORM FIBERS

The Mica Mineral Group

The third mineral group included in the category of *biopyriboles* is the micas. The micas are indicated by "bio," which comes from biotite, one of a large number of compositionally diverse species that make up the micas, a commonly encountered group of minerals.

The micas are characterized by extended silicate sheets rather than chains. Their structures resemble the serpentine mineral group in that they are dom-


A
2.696 Å
3.074 Å
Si
Si
(a)
(b)


B
0.2 µm

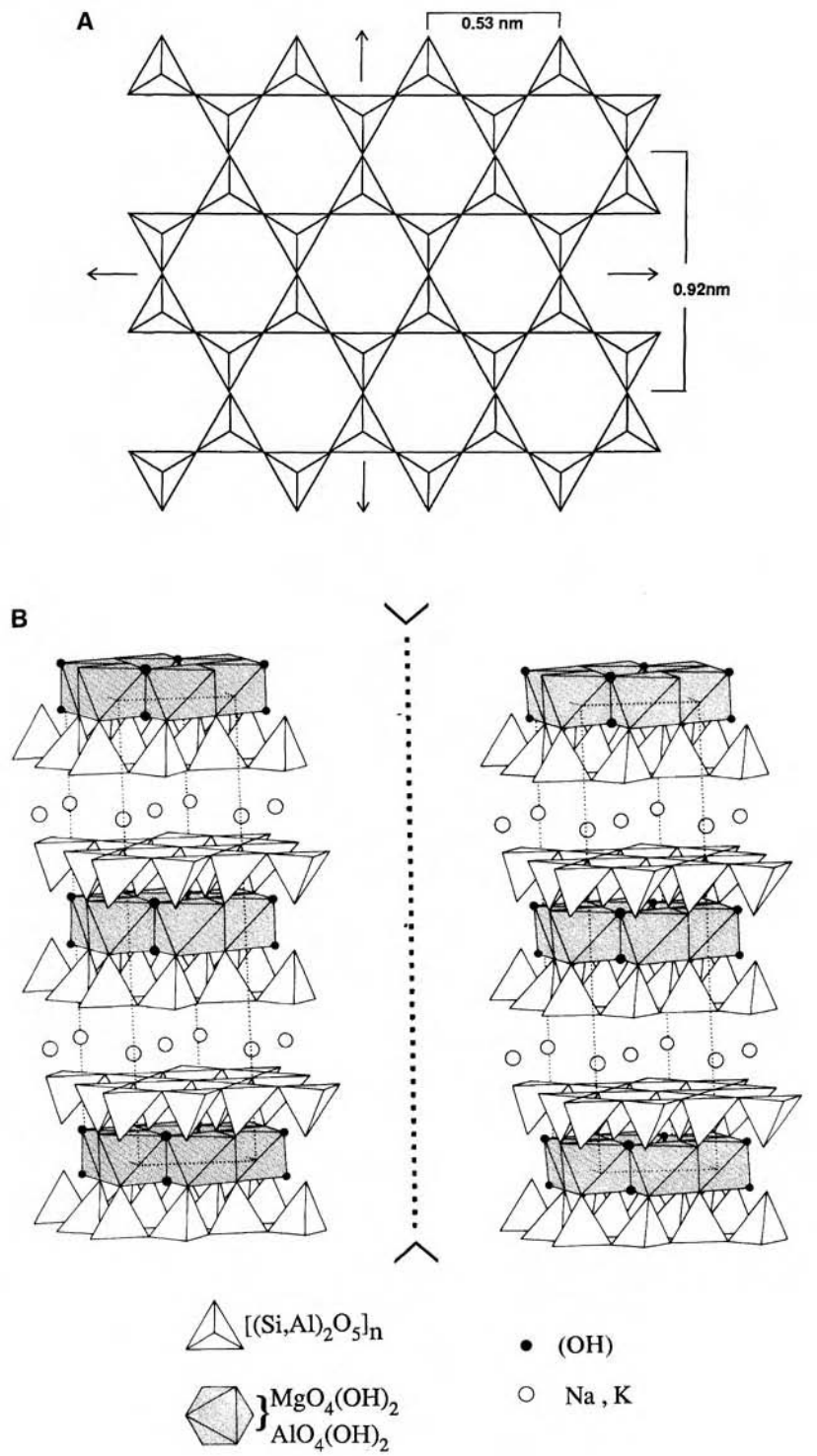
inated by sheets formed from tetrahedra sharing three of the four oxygens in a hexagonal ring arrangement (Fig. 2.12A). The apices of the tetrahedra within a sheet all point in one direction. The general formula for the mica sheet (T) can be expressed as $[(Si,Al)_2O_5]_n$, a unit with variable charge depending on the Al/Si ratio. If the ratio is 1 the charge is -3. The size of repeats within the sheet are approximately 0.53×0.92 nm.

Two sheets, apices pointing toward each other, are associated through magnesium (Mg^{+2}) or aluminum (Al^{+3}) ions that bond with six oxygens: two oxygens from each of the two tetrahedral sheets and two oxygens from the hydroxyl $(OH)^{-1}$ groups that are located in the centers of the hexagonal rings. The hexagons of the two connected tetrahedral sheets are not directly superimposed on this three-part, T–O–T or 2:1 continuous sandwich, or layer. Layers are held together by larger ions, such as sodium (Na^{+1}) or potassium (K^{+1}). These interlayer ions also bond with six oxygens, three from each of adjacent tetrahedral sheets in different layers (Fig. 2.12B). The general formula for the complete three-dimensional mica structure can be expressed as: $AB_{2-3}T_4O_{10}(OH,F)_2$, where A = K^{+1}, Na^{+1} or Ca^{+2}, usually, but Ba^{+2}, Rb^{+2}, Os^{+2} may be found, and B = Mg^{+2}, Fe^{+2}, Al^{+3}, or Fe^{+3}, as usual substitutions but Mn^{+2}, Co^{+2}, Ti^{+4}, Li^{+1}, or V^{+5} are also found at this site in these minerals. Considerable substitution of Al^{+3} for Si^{+4} always exists at the tetrahedral sites (T sheet). In muscovite, $KAl_2(Si_3Al)O_{10}(OH,F)_2$, one out of every four Si^{+4} is replaced by Al^{+3}. In addition, the site in the center of the hexagon, which is normally $(OH)^{-1}$, may contain fluorine (F^{-1}), or chlorine (Cl^{-1}). Not surprisingly the dominant physical characteristic of the micas is a single direction of perfect cleavage, parallel to the layers.

The 2–3 subscript for the B site in the formula expresses the fact that there are two families of mica structures, the dioctahedral and trioctahedral micas, based on the composition and occupancy of the intralayer octahedral sites. The trioctahedral micas have three divalent ions—for example, Mg^{+2} or a brucitelike $[Mg(OH)_2]$ intralayer, and the dioctahedral group—two trivalent ions—for example, Al^{+3} or a gibbsitelike $[Al(OH)_3]$ intralayer, between the tetrahedral sheets. In the dioctahedral micas, therefore, one-third of the octahedral sites are vacant or unoccupied (Fig. 2.12C).

The superposition of two aluminosilicate sheets to form a layer is influenced by the Al:Si ratio and by the composition of the octahedral sites (Fig. 2.12D). The charge on a layer is balanced by the interlayer ions in site A. The stacking sequence within or between layers is easily altered; often during growth one sequence changes to another, even though the mineral appears to be a single crystal. Smith and Yoder (1956) summarized the common stacking arrangements that produce the several distinct crystal structures observed in micas.

Fig. 2.11 Sillimanite. (**A**) Schematic structure of sillimanite showing the alteration of SiO_4 and AlO_4 tetrahedral groups in double chains and the associated octahedral chain of AlO_4. (**B**) Transmission electron micrograph of an intimate intergrowth of sillimanite and quartz known as fibrolite. The lamellae of sillimanite are dark and the quartz lamellae are light. The quartz lamellae show interference fringes.


A
0.53 nm
0.92nm
B
[(Si,Al)2O5]n
MgO4(OH)2
AlO4(OH)2
(OH)
Na , K

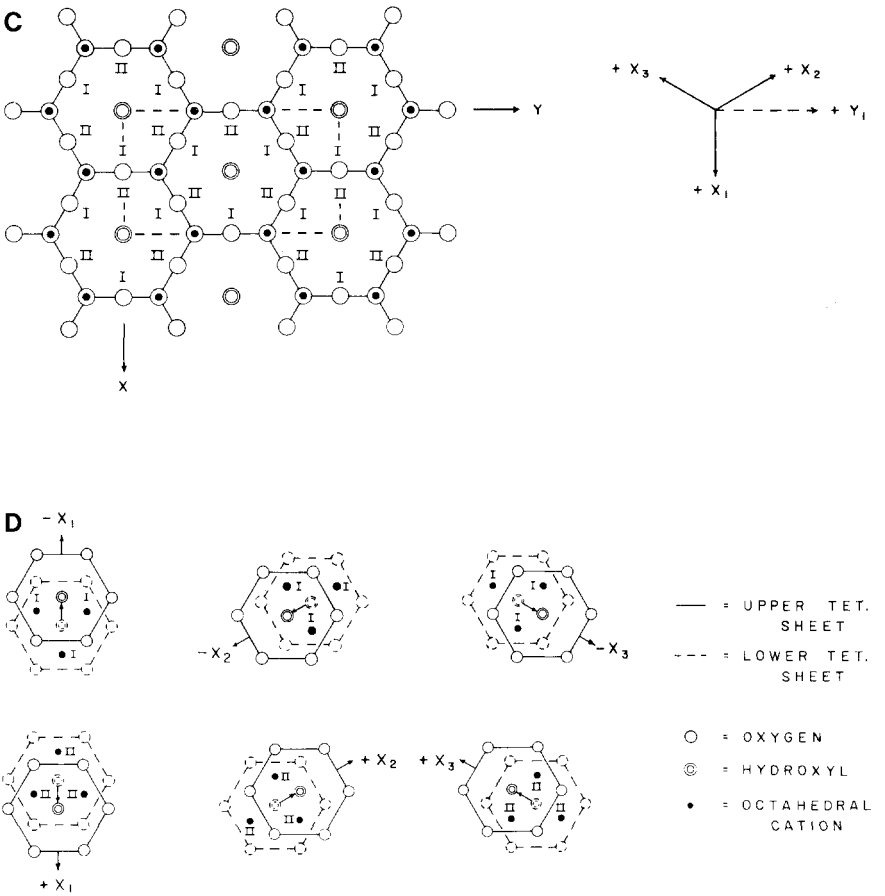
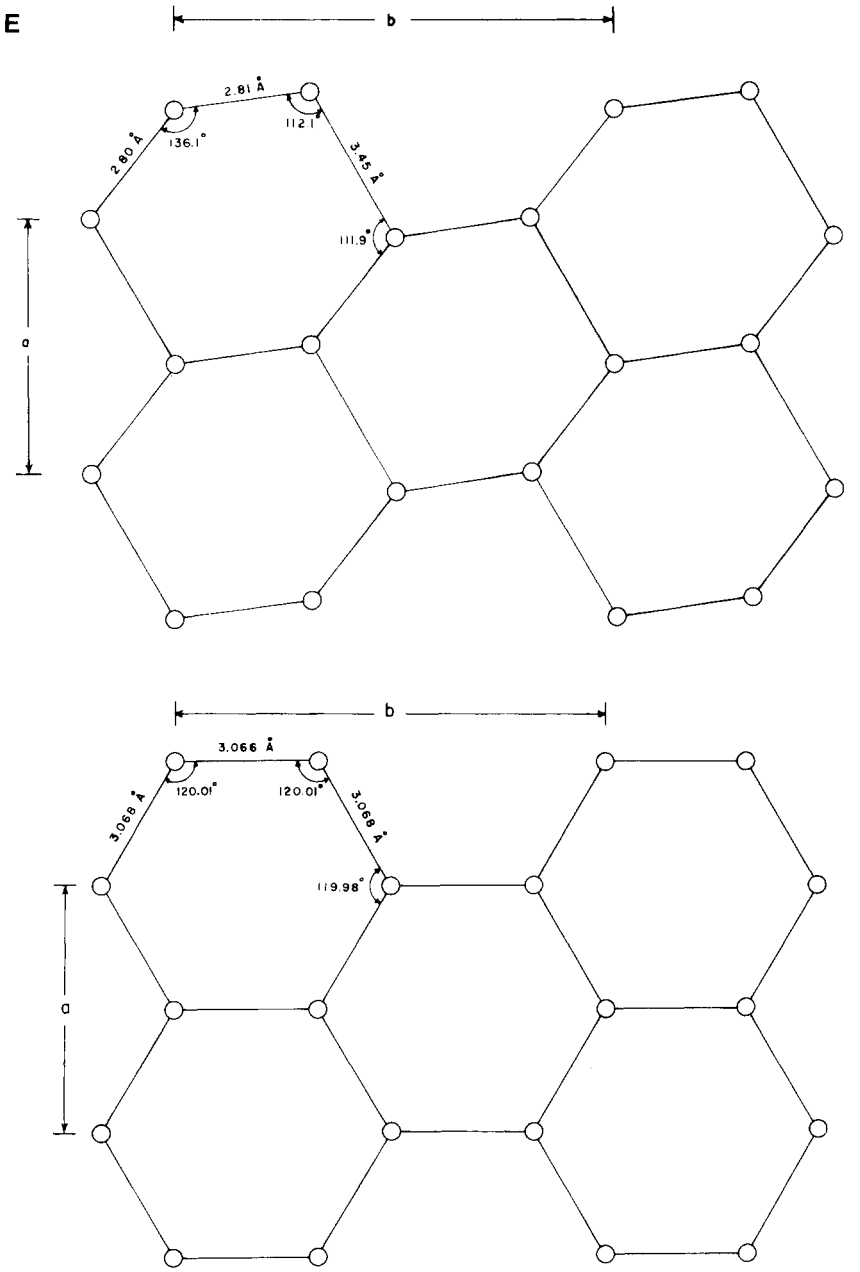


Fig. 2.12 Structural components and variations in the micas. (**A**) Plan view of the continuous aluminosilicate sheet (T), $[Si,Al_2O_5]_n$, a portion of the mica structure. (**B**) Stereographic representation of an idealized mica. The structure is composed of continuous layers containing two tetrahedral aluminosilicate sheets (T) that enclose octahedrally coordinated cations, Al^{+3} or Mg^{+2} (O). This layer or "sandwich," the T-O-T or 2:1 aggregate, is held together by K^{+1} or Na^{+1} ions. (**C**) The two possible positions (I and II) of octahedral cations in the micas. Sets of three locations for each are superimposed on the tetrahedral hexagonal aluminosilicate sheet. (**D**) The three possible directions of intralayer shift when octahedral set I (*upper*) or II (*lower*) are occupied. The dashed lines and circles represent ions below the plane of the paper. (**E**) Distorted hexagonal rings of apical oxygens in the tetrahedral sheet of dioctahedral micas compared with the undistorted positions of the apical oxygens in the tetrahedral sheet of trioctahedral micas.


E
b
2.81 Å
2.80 Å
136.1°
112.1°
3.45 Å
111.9°
a
b
3.066 Å
3.068 Å
120.01°
120.01°
3.068 Å
119.98°
a

The trioctahedral micas can be distinguished by x-ray diffraction from the dioctahedral type. The dioctahedral micas characteristically show distortions that are detected as variations in the bond angles of the hexagonal pattern, Fig. 2.12E (Bailey, 1984). Natural mineral samples often exhibit an "occupancy" of the B site of greater than 2 and less than 3, producing many variations that cannot be detailed here.

Muscovite, whose idealized formula is $KAl_2(Si_3Al)O_{10}(OH,F)_2$, is a common dioctahedral mica. Rutstein (1979) has described an intergrowth of a fibrous muscovite with chlorite, another mineral with sheetlike structure (discussed later). A fibrous "hydromuscovite" was identified (Brammall et al., 1941), and flexible fibers 1 cm in length and 0.003 to 0.335 mm in diameter, with the chemical composition $(K,H_2O)(Al_3Mg)\ (Si_6Al_2)O_{18}(OH)_6$, were described by Aruja (1944) and called gumbellite. In these last two species water appears to have taken the place of some of the K^{+1} at the interlayer, or A site, and $(OH)^{-1}$ or residual H^{+1} can be found in association with the T sheets. Approximately one-fourth of the Al^{+3} (B site) in gumbellite is replaced by Mg^{+2}, suggesting a composition intermediate between di- and trioctahedral mica structures. Substitutions in both the A and B sites in these sheet structures may aid the formation of fibers, or alternatively, the fibrous form may be another mechanism for relieving structural distortion.

Silicate minerals that usually occur as spherulitic aggregates of fibers have formed as a result of the alteration of the many minerals subsumed within the category of biopyriboles. Alteration of the micas under hydrothermal conditions produces compositional variants on recrystallization such as hydrous muscovite. Some of these samples have been labeled asbestiform, probably because they are found in veins that criss-cross rock masses. Fibrous micaceous minerals also occur as discrete disseminated particles, although few detailed analyses of crystallites from the disperse occurrences have been made. Fibrous mica found in veins usually grades (compositionally) into members of the serpentine mineral group, the clays or the chlorites.

It was suggested for the serpentines that compositionally induced distortions favored the production of fibers, but how can this be accomplished in materials with a basic sheetlike structure? Several specific examples of sheet structure minerals that occur as fibers (in addition to the micas) will be described before we examine some of these suggestions.

Pyrophyllite

The minerals of the pyrophyllite $[(Al_2Si_4O_{10}(OH)_2)]$–ferripyrophyllite $[(Fe^{+3}{}_2Si_4O_{10}(OH)_2)]$ series are related to the mica group. The structure of these minerals closely approximates that of muscovite with the two tetrahedral sheets and octahedrally coordinated intercalated ions, a 2:1 layering (Fig. 2.13) but there is little substitution of Si^{+4} by Al^{+3}. Only two-thirds

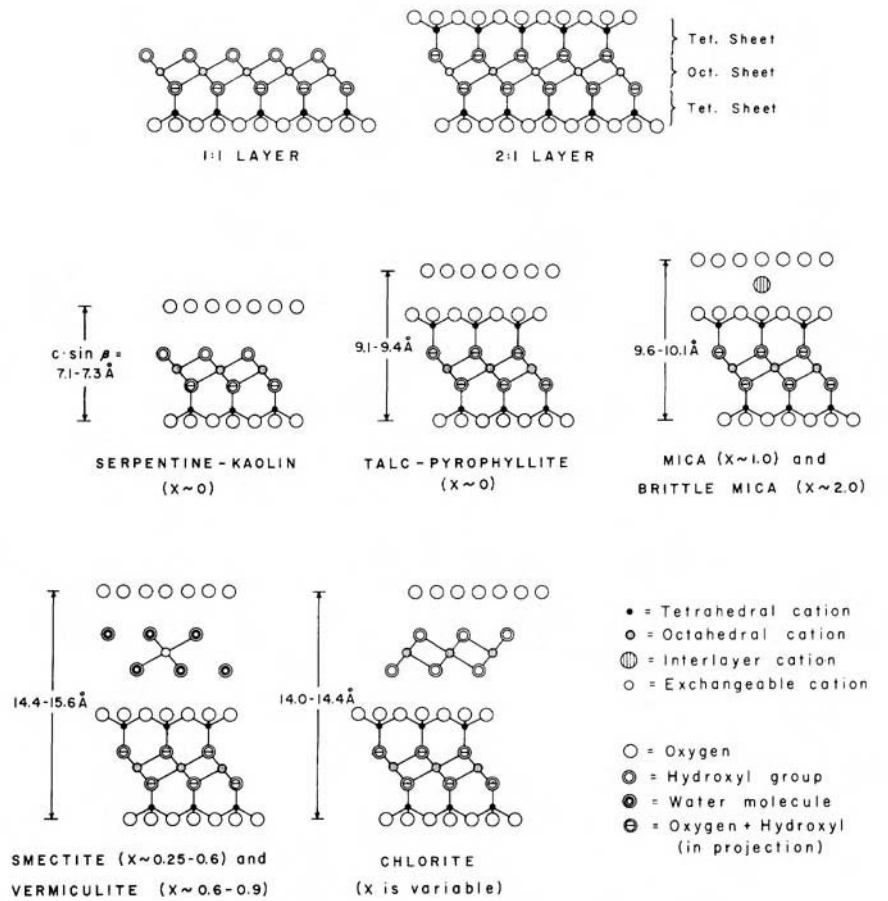


Fig. 2.13 The 1:1 and 2:1 layer arrangements in the sheet structure minerals and the (010) view of the structures of the serpentine, clay, talc, pyrophyllite, mica, and chlorite minerals. X = layer charge per formula unit. [From Bailey (1980), Fig 1.1, p. 3; Fig 1.2, p. 6.]

of the octahedral sites are occupied (dioctahedral) by Al^{+3} or Fe^{+3}, and there are no interlayer K^{+1} ions. Found singly as needles and as spherulitic aggregates, pyrophyllite crystals are often mistakenly identified as talc.

Talc

Talc [$(Mg_3Si_4O_{10}(OH)_2)$] was described by MacAdam in 1886. The mineral has all octahedral sites filled with Mg^{+2} (trioctahedral), resulting in an uncharged layer of three sheets (2:1). The characteristic ease of separation of talc layers is understandable in view of these crystallochemical factors. One can literally push flakes from a talc crystal by rubbing the sample between

one's fingers. Steatite, a name formerly used for massive impure talc, is still used as a rock name. Many temples in southern India are constructed of intricately carved steatite. Soapstone, compositionally similar to steatite, is not a technical term, but because both materials are popular with sculptors and are widely mined for the construction, ceramic, paint, paper, cosmetic, and pharmaceutical industries, the term *soapstone* continues to be used in common parlance. Soapstone deposits often contain tremolite as well as talc, and questions have been raised concerning the use of these materials, especially in cosmetics. In the materials mined at Gouverneur, New York, the tremolite is not fibrous, it occurs as large crystals. The stir over the potential health impact of this tremolite is indicative of the lack of understanding of mineral materials in general, and of the fibrous form in particular. This is an example of one of the many misunderstandings that prompted us to undertake this volume.

Stilpnomelane

Small flakes of the mineral stilpnomelane are often confused with the mica biotite. A fibrous form of stilpnomelane in veins with chlorite was recorded in North Wales by Hallimond in 1924. The material was labeled asbestiform. Stilpnomelane, ideally $K(Fe^{+2},Fe^{+3},Mg,Al)_{10}Si_{12}O_{30}(OH)_{12}$, is related to talc with several structural variants often occurring within one sample (Eggleton, 1972; Crawford et al., 1977). The variations, expressed as different symmetries of the layers, appear to result from ordering of intralayer cations and inversion of some tetrahedra within the sheets. These structural changes alter linkages between the sheets as well as displace the layers horizontally in relation to each other during the stacking process.

Minnesotaite

Minnesotaite resembles talc with Fe^{+2} substituting for some of the Mg^{+2} in the octahedral sheet: $(Fe^{+2},Mg)_3Si_4O_{10}(OH)_2$. Fibers of this material are abundant in the rock formations mined for iron in Minnesota (Gruner, 1944)—hence the name. In its fibrous form, about three-fourths of the octahedral sites are occupied by Fe^{+2}, rather than Mg^{+2}. Although also a layer silicate, minnesotaite has a complex structure that is not yet fully understood.

Rocks that contain talc, or the chemically and structurally similar minerals mentioned previously, are usually the result of alteration and recrystallization of rock formations that contained magnesian silicate minerals. Steatization or serpentinization are the terms given the processes that create layered (sheet) silicates from chain or other tetrahedral arrangements adopted by silicate minerals (see Fig. 2.1). The recrystallization process is expedited by temperature and pressure, and especially through the action of hydrothermal solutions.

The Chlorite Mineral Group

The chlorites are a group of sheet silicate minerals similar to the micas and talc. The general formula, $A_{5-6}T_4O_{10}(OH)_8$, is deceptively simple. The range of possible substitutions is enormous, for example, A = Mg^{+2}, Al^{+3}, Fe^{+2}, Fe^{+3}, Li^{+1}, Mn^{+2}, Ni^{+2} . . . and T = Si^{+4}, Al^{+3}, Fe^{+3}, B^{+3}. . . . A generalized structure for the many variations is composed of one talclike layer plus another $Mg(OH)_2$, or brucitelike, layer—that is, a 2:1:1 structure, which can be expressed as $[A_3T_4O_{10}(OH)_2] + [A_3(OH)_6]$. Crystals of these minerals are usually platy and flexible.

Chlorite crystals are characterized by semirandom stacking that, theoretically, could give rise to an astronomically large number of polytypes (Bailey and Brown, 1962) with orthorhombic, monoclinic, or triclinic crystal symmetry. Single crystal x-ray diffraction photographs usually show streaks and spots that document the random or semirandom stacking of the individual layers (Fig. 2.13). Nonrandom occupancy of tetrahedral sites by Al^{+3} and nonrandom Fe^{+2} in one of the octahedral sites promote an orthorhombic or monoclinic rather than a triclinic crystal structure, for example. There may also be some distortion of the hexagonal rings within sheets to accommodate the additional brucite layer. The potential for disorder within the sheets and in the stacking sequence, as well as the wide range of chemical compositions (both dioctahedral and trioctahedral forms of chlorites are known) make the chlorite group a premier example of the variety and gradations among a class of silicate minerals that have been found in fibrous form.

Clays

Clays are silicate minerals that may be platy or fibrous and are usually of exceedingly fine grain size, ranging from colloidal, a few nanometers in diameter, to a maximum of about a tenth of a micrometer. Similarly to other aluminosilicates, clays show considerable range in chemical composition with concomitant structural modifications (Fig. 2.13). A few of the clay minerals described as fibrous are briefly mentioned here.

The Kandite Mineral Group

One of the four compositional groups of clay minerals, the kandites include the minerals kaolinite, dickite, halloysite, and metahalloysite; all have virtually the same composition. The first two minerals are common and widely used in the production of ceramics; the latter two occur in tubular fibrous form.

Kaolinite, ideally $Al_2Si_2O_5(OH)_4$, consists of 1:1 layers, alternating sequences of silicate and hydrated Al-octahedra (dioctahedral) sheets. There is potential for disorder in the specificity of the site occupied by Al^{+3} and in the stacking of the sheets and layers, which give rise to the polymorphs dickite and halloysite.

Halloysite $[Al_2Si_2O_5(OH)_4]$ if hydrated with a single layer of water mol-

ecules between the layers (Fig. 2.14), is expressed in the formula $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$. The addition of water increases the layer repeat distance from 0.72 nm in kaolinite to 1.0 nm in halloysite, and also increases the potential for stacking disorder. A partially dehydrated species known as metahalloysite, in which most of the molecular water has disappeared but the stacking disorder remains, has a layer repeat near 0.72 nm. These minerals are normally found as fibers in the form of short tubes.

Tubular fibrous morphology has also been described for a hydrated kaolin (Honjo et al., 1954), a mineral known to have a structure different from that of kaolinite or halloysite.

Because the clays have a basic layered structure of aluminosilicate sheets the expectation was a platy habit. The creation of tubular forms was studied by Bates (1959). He postulated that the curved forms, observed by electron microscopic investigation of halloysite and chrysotile, originated through the relief of strain between sheets of unequal dimensions.

The silicate sheet in kaolinite, for example, has an O-O repeat distance in the sheet of 0.893 nm, whereas the octahedral or gibbsite sheet repeat is smaller, about 0.862 nm. Mismatch of the 1:1 sheets induces curvature with the smaller dimension sheet on the interior. The octahedral gibbsite layer in clays is postulated to be situated on the inside of the curve. This relationship contrasts with the hypothesis for chrysotile, in which the tetrahedral silicate sheet is smaller and is postulated to be the interior unit in the scrolled serpentine mineral.

Bates (1959) presented a method for estimating the degree of tube for-

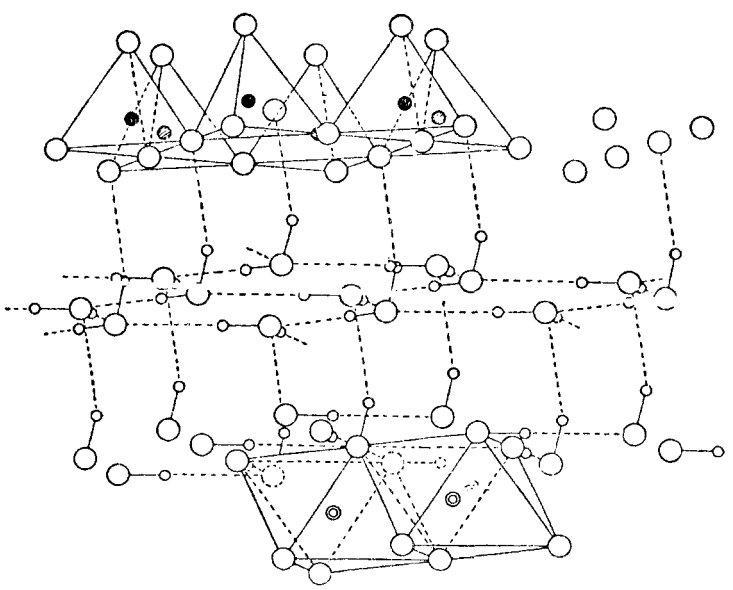


Fig. 2.14 The structure of halloysite. Hydrogen bonded interlayer water is shown in this 10 A or 0.01 nm. form.

mation through misfit based on chemistry. Accurate analysis of the cation composition, followed by assignment of the ions to the tetrahedral or octahedral sheets (and the concentration of H_2O, $(OH)^{-1}$ and H^{+1}), could give the relative size and bonding characteristic of the layers. A morphology index, based on these chemical considerations, was calculated for analyzed samples of clays, serpentines, and chlorites. The results indicated that misfit was highest in the samples of tubular kaolins and chrysotiles. The addition of the water molecules (i.e., in halloysite) is thought to weaken interlayer forces and to enhance the opportunity for curling in minerals with layer misfits. Chlorites, on which the calculations indicated less of a misfit, had, for example, an analyzed water content equal to the $(OH)^{-1}$ required for cation balance in the structures. Tubular form, it seemed, would be encouraged by increased amounts of H_2O, by substitution of trivalent ions (Fe^{+3}, Al^{+3}), by vacancies, and by the presence of H^{+1}, all of which could produce distortions.

Bates and his co-workers (1959) reaffirmed the suggestion of Sudo and Takahashi (1956) that tubular halloysite represents an intermediate morphology commensurate with increased aluminum and water content. For example, the hexagonal plates of well-crystallized kaolinite have a composition of $[(Al_2Si_2O_5(OH)_4]$, the halloysite tubes have a composition of $[(Al_2Si_2O_5(OH)_4]$ plus additional water, and allophane, an amorphous material described as randomly bonded silicate and aluminate tetrahedra with water, is considered a noncrystalline extreme. Hemni and Wada (1976) showed that allophane is a substance with variable composition, approximating $SiO_2/Al_2O_3 = 1:2$, with some Al^{+3} in octahedral as well as four-fold coordination, and with high and variable water content. Allophane is listed as a mineraloid without a precise chemical formula other than amorphous hydrous aluminosilicate.

The Illite Mineral Group

The illites, a group representing another chemical and structural range of minerals within the clays, can be identified only with a great deal of analytical difficulty. They are usually dioctahedral and are related to muscovite, which is obvious from the general formula, $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2, H_2O]$. Illites have fewer interlayer cations (less K^{+1}) and more SiO_2 and H_2O than micas, and hence have weaker forces keeping the layers together. More stacking disorder occurs as a result of the weaker forces. Gumbellite, the fibrous Mg-rich hydrous muscovite, is probably an illite.

Many samples of the fine-grained minerals called clays possess mixed-layer structures of montmorillonite and illite. Fine-scale interleaving of layers complicates interpretation of the analytical and x-ray diffraction results and might go undetected. A great deal of research has gone into identifying interstratified clays (Brindley and Brown, 1980), and investigators continue to search for appropriate and efficient techniques to obtain definitive analytical results (Nadeau et al., 1984). If any reinforcement of the difficulty of distinguishing between clay mineral species is necessary, it must be pointed

out that electron micrographs of illites exhibit few well-formed particles. Fibrous illites are apparently very common minerals in the sandstones that hold oil (reservoir rocks).

The Smectite Mineral Group

The smectite group of clay minerals is also poorly crystalline but perhaps better known because of their cation exchange capacity and their occurrence in the bentonite clays. A general formula for montmorillonite, which is one of the dioctahedral smectites is

$$(M^{+}_{y}, nH_2O)(Al_{2-y}, Mg_y)(Al,Si)_4O_{10}(OH)_2$$

where M^+ stands for exchangeable monovalent cations, that is, Na^{+1}, although Ca^{+2} sometimes appears, n stands for variable amounts of H_2O, and y is a variable number.

Montmorillonite, one of the most commonly encountered smectites, is similar to pyrophyllite (2:1) but has some interlayer cations and extra water. In pyrophyllite the layers are neutral because Si^{+4} in the tetrahedral sheet is not replaced by Al^{+3}. In the smectites there is substitution of Al^{+3} for Si^{+4} in the tetrahedral sheets, and occasionally Al^{+3} appears in octahedral locations as well (for the names assigned to the end members, see Brindley and Brown, 1980, pp. 169–170.) The charge imbalances of the substitutions are compensated by interlayer cations, usually Na^{+1} or Ca^{+2}. These cations are easily exchangeable. The hydration level of the smectites is also variable. These minerals are very responsive to changes in water content as well as to the salt contents of the water. Other liquids that might be associated with the minerals and temperature can also effect changes in the chemical and crystal structure.

Fibrous saponite, with the analyzed chemical formula $(Mg_{5.8}, Al_{0.1}, Fe^{+2}{}_{0.1})(Si_{6.76}, Al_{1.04}, Fe^{+3}{}_{0.2})\ O_{20}(OH)_4 \cdot 10H_2O$, also had $Ca_{0.1}$ and $Mg_{0.4}$ as exchangeable ions (Midgely and Grass, 1956). Saponite is an example of a trioctahedral smectite. The variable chemical compositions of the smectites adds to the difficulties of accurate identification of these minerals.

The Vermiculite Mineral Group

The fourth clay mineral group, vermiculites, have the general formula $(Mg,Fe^{+2},Al)_3(Si,Al)_4O_{10}(OH)_2 \cdot 4H_2O$. They can be classified as trioctahedral layer silicates intermediate between pyrophyllite and saponite. These minerals have a higher layer charge and slightly smaller interlayer spacing than the other clay mineral groups (Brindley and Brown, 1980), indicating a somewhat different crystal chemistry. Their name comes in part from their peculiar property of exfoliating on heating. Many a Fourth of July celebration has included a silent, nonexplosive vermiculite firecracker that grows into a black worm when lit. The name comes from the Latin term *vermis*, meaning "worm." This exfoliation property is related to the material's structure, which consists of a talclike layer (2:1), in which some of the Si^{+4} in the tetrahedral sheet is replaced by Al^{+3}, and the charge from this substi-

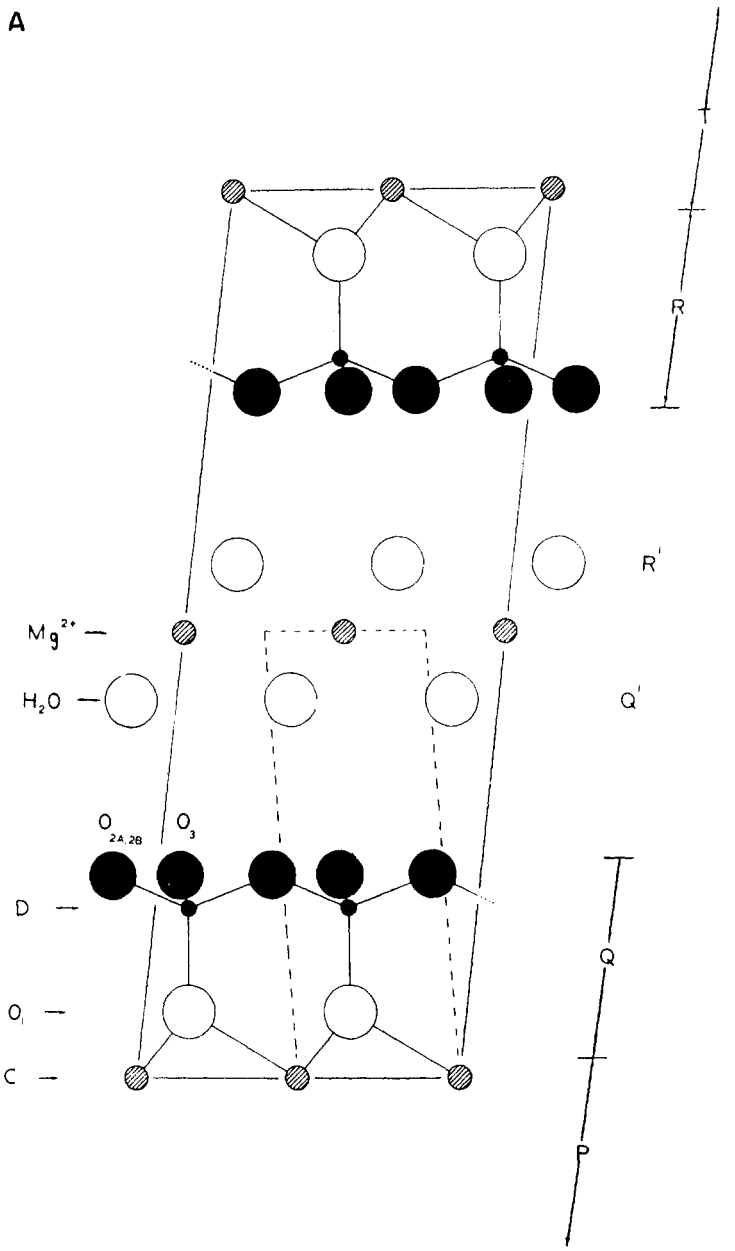
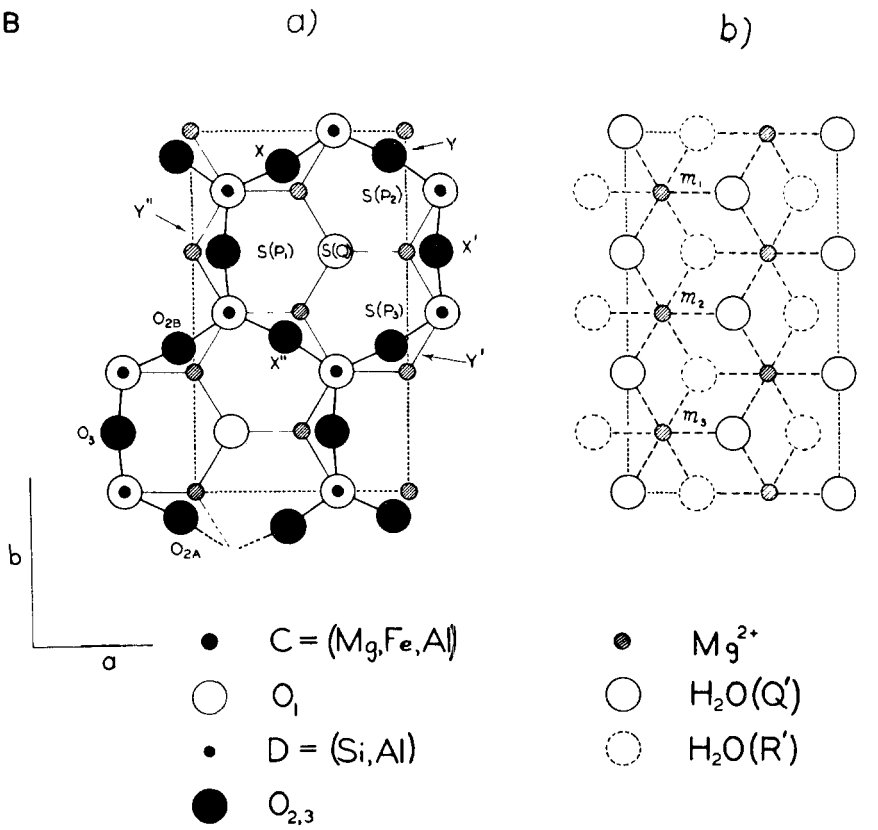


Fig. 2.15 Schematic representation of the magnesian-vermiculite structure. (**A**) The structure projected on (010) showing the layering of T and O sheets, 2:1, with the additional molecular water and Mg^{+2} ion sheet. (See Fig. 2.13 for comparison of vermiculite with other 2:1 layered structures.) Only half of a T sheet is shown at R′ and Q′. (**B**) Plan views showing ion distributions in the T and O sheets. (a) is at z = 0.000–0.114, T sheet, and (b) is at z = 0.213–0.287, O sheet, showing easily exchangeable water and Mg^{+2} positions.



tution is compensated by interlayer water and Mg^{+2} ions. An idealized crystal structure (Fig. 2.15 A and B give two projections) shows a double water sheet plus magnesium ions between the two talc layers. The water ions (H_3O^{+1}), form a distorted hexagonal ring, bonded to the silicate sheet, and to each other, through weak hydrogen bonds. The pairs of water planes are held together by exchangeable cations. The interlayer distance may be as high as 1.48 nm or as low as 0.902 nm, depending on the hydration and packing of the layers (Fig. 2.15A). The water sites are not necessarily fully occupied (even at high humidities), nor are the cation sites. The addition or exchange of these ions can take place without destruction of the crystal.

Vermiculites exist in various stages of dehydration. Because of the similar dimensions of the water-cation layer in vermiculite and the brucitelike layer in chlorite, vermiculites can be confused with the chlorites. The common substitutions of Fe^{+2} or Fe^{+3} for Mg^{+2} (in either the water or octahedral sheet of vermiculites), and Al^{+3} for Si^{+4} (in the tetrahedral sheets), as well as the hydration variations, present enormous potential for structural distortion in these types of minerals. Fibrous vermiculite was described by Weiss and Hofmann (1952).

Palygorskite and Sepiolte

Palygorskite (synonym = attapulgite) and sepiolite are clay minerals that usually occur as fibers and have been known for a long time as mountain flax or mountain leather. Microscopic fibers of palygorskite, 3 to 10 mm long by 0.7 to 1 mm wide, have been examined by electron microscopy (Liu, 1973). Transverse sections of the fibers exibit distorted hexagonal outline, with sharp edges. Several alternative structures have been postulated for palygorskite, but precise analyses have not yet been carried out (Brindley and Brown, 1980). X-ray diffraction analysis of fibers of sepiolite, 2 to 3 cm long and 10 nm wide, were used by Preisinger (1959) to suggest a crystal structure for the mineral.

Bearing in mind the difficulties of interpretation because of the lack of precise crystal structural detail characteristic of the diffraction data obtained from fibrous materials, chemical analyses indicate that the composition of sepiolite can be expressed as

$$(Mg_{8-y-z}\,R^{+3}_{y}\,[\ ]_z)(Si_{12-x}R^{+3}{}_x)O_{30}(OH)_4(OH_2)_4R^{+2}{}_{(x-y+2z)/2}(H_2O)_8,$$

and that for palygorskite as

$$(Hg_{5-y-z}\,R^{+3}{}_y[\ ]_z)(Si_{8-x}\,R^{+3}{}_x)O_{20}(OH)_2(OH_2)_4R^{+2}{}_{(x-y+2z)/2}(H_2O)_4,$$

where R^{+2} and R^{+3} stand for divalent and trivalent cations, respectively, and $[\ ]_z$ is a vacancy.

Both sepiolite and palygorskite contain tetrahedral silicate sheets (with a variety of substitutions for the Si^{+4}), but the apicies of the tetrahedra are thought to point up or down with the transition areas containing Ca^{+2} and Mg^{+2} ions, and bound or associated H_2O. The arrangement produces a continuous basal oxygen plane that is compartmentalized. Laths or ribbons three chains wide in sepiolite and two chains wide in palygorskite are separated by discontinuous octahedral areas (Fig. 2.16A and B).

Substitution and variations in the tetrahedral sites change the manner of side linkages for the ribbons, effecting the octahedral cation and water associations. In addition, different ribbon widths can lead to different numbers of octahedral cations. Variation in the width of chains and substitution of cations and water are easily accomplished, which means that accurate and consistent chemical and crystal structural data on these minerals are difficult or, at best, approximate. However, the minerals do form fibers with a consistent fiber axis repeat of about 0.512 nm (Preisinger, 1959; Rautureau et al., 1972). Sepiolite and palygorskite represent the widest possible structural and chemical diversity among fibrous silicate minerals.

OTHER ALUMINOSILICATES THAT FORM FIBERS

The Zeolite Mineral Group

The zeolites are another structure type of alumino silicate minerals. The eighteenth century identification of this mineral group was made on a few

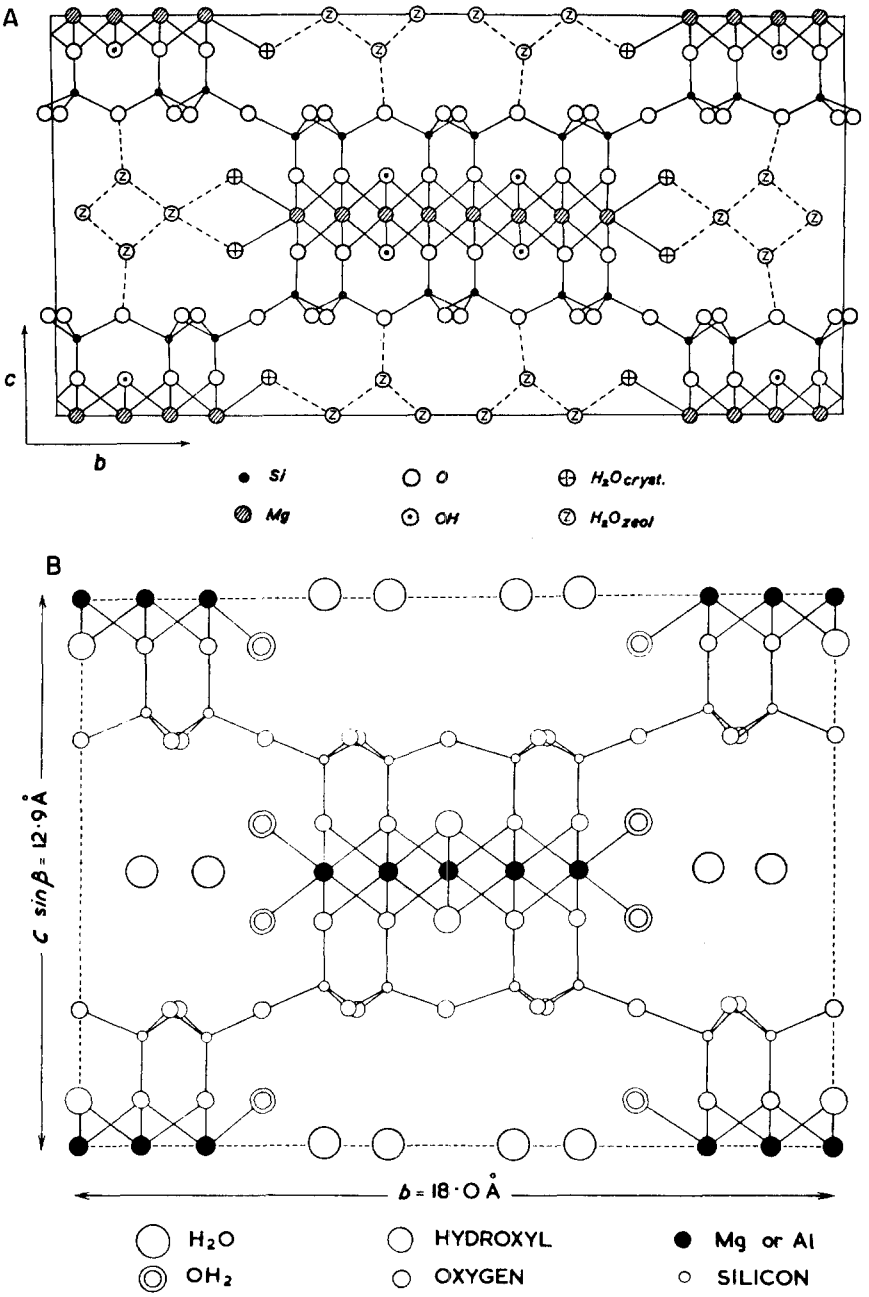


Fig. 2.16 Schematic representations of the structures suggested for sepiolite and palygorskite. The ribbonlike arrangement of silicate chains alternates with hydroxyl and water areas. (**A**) Sepiolite, the (001) projection, showing the cross section of three 2:1 silicate chains and associated water and hydroxyl groups. (**B**) Palygorskite, the (100) projection, showing the cross section of two silicate chains and associated water and hydroxyl groups.

isolated crystals collected from the sporadic vugs, or holes, in lava flows. Since 1960, however, sedimentary layers several feet thick and composed almost entirely of crystalline zeolites have been discovered (Hall, 1966). Mumpton (1977) estimates that about 40 zeolite mineral species have now been identified and at least 100 synthesized.

The discrepancy in numbers between natural and synthetic varieties is an expression of the usefulness of zeolitic materials in industry, a reflection of their unique physicochemical properties. The crystal chemistry of these aluminosilicates provides selective absorbtion and exchange of a remarkably wide range of molecules. Some zeolites have been called molecular sieves. This property is exploited in the purification and separation of various chemicals, such as in obtaining gasoline from crude petroleum, pollution control, or radioactive waste disposal (Mumpton, 1978). The synthesis of zeolites with a particular crystal structure, and thus specific absorbtion characteristics, has become very competitive (Fox, 1985). Small, often barely detectable, changes in composition and structure are now covered by patents. A brief review of the crystal chemistry of this mineral group illustrates their potential and introduces those that occur as fibers.

Crystal Chemistry of the Zeolite Minerals

Zeolite minerals are hydrous-aluminum-silicates whose general chemical formula can be expressed as

$$R_{2/n}OAl_2O_3xSiO_2 \cdot yH_2O,$$

where R can be any alkali or alkaline earth cation, such as Na^{+1}, Ca^{+2}, Mg^{+2}, K^{+1}, Ba^{+2} . . .; n = the valence of the ion; x = a number from 2 to 10; and y = a number from 2 to 7.

The range of the variables can be appreciated from Table 2.7, which presents examples of fibrous varieties from several of the zeolite mineral groups (using the classification system presented by Flanigen, 1977).

Zeolites have framework, or three-dimensional structures, that are known as clathrates. All four oxygens of the Al or Si tetrahedral ion are shared (the overall Al + Si:O is 1:2) with the tetrahedra combining into rings containing from 4 to 12 tetrahedra. Crystal structure analyses of a range of zeolite minerals have shown that some species contain several ring systems. In fact, more than thirty-nine different framework topologies have been observed in studies on natural and synthetic zeolites (Newsam, 1986). Synthetic analogs of zeolites, have been produced in which P^{+5}, Fe^{+3}, and Ga^{+3} substituted for Al^{+3} and Si^{+4} in similar frameworks. These synthetic zeolitic materials are chemically aluminophosphates, silicoaluminophosphates, gallosilicates, and ferrisilicates. The range of elements that can adopt the framework zeolite crystal structure is very wide.

The mineral natrolite ($Na_2Al_2Si_3O_{10} \cdot 2H_2O$), a member of the group of zeolites that usually occur in acicular or radiating spherulitc aggregates, has a structure based on four tetrahedra, a four-membered ring, connected in the third dimension by a fifth tetrahedron. The result is a chain (Fig. 2.17A)

Table 2.7 Composition and Structural Characteristics of Some Fibrous Zeolites

Mineral[a]	Composition (Idealized)	Composition[b] (unit cell)	Framework[c] Density (g/cc)	Dimensions of Main Channel Ways (nm)[b]
Group I, S_4R				
Phillipsite	$(K,Na,Ca)_{1-2}(Si,Al)_8O_{16} \cdot 6\ H_2O$	$(K,Na)_{10}[(AlO_2)_{10}(SiO_2)_{22}] \cdot 20H_2O$	1.58	0.42×0.44 0.28×0.48
Paulingite	$(K_2,Ca,Na_2,Ba)_5Al_{10}Si_{32}O_{84} \cdot 34\text{–}44H_2O$	$(K_2CaNa_2Ba)_{76}(AlO_2)_{152}(SiO_2)_{520} \cdot 700H_2O$	1.54	0.39
Laumontite	$CaAl_2Si_4O_{12} \cdot 4H_2O$	$Ca_4[(AlO_2)_8(SiO_2)_{16}] \cdot 16H_2O$	1.77	0.46×0.63
Group II, S_6R				
Erionite	$(K_2,Ca,Na_2)_2Al_4Si_{14}O_{36} \cdot 15H_2O$	$(K_2,Ca,Na_2)_{4.5}[(AlO_2)_9(SiO_2)_{27}] \cdot 27H_2O$	1.51	0.36×0.52
Group IV, D_6R				
Chabazite	$CaAl_2Si_4O_{12} \cdot 6H_2O$	$Ca_2[(AlO_2)_4(SiO_2)_8] \cdot 13H_2O$	1.45	0.37×0.42
Faujasite	$(Na_2Ca)Al_2Si_4O_{12} \cdot 8H_2O$	$(Na_2Ca)_{29.5}[(AlO_2)_{59}(SiO_2)_{133}] \cdot 235H_2O$	1.27	0.74
Group V, T_5O_{10}				
Natrolite	$Na_2Al_2Si_3O_{10} \cdot 2H_2O$	$Na_{16}[(AlO_2)_{16}(SiO_2)_{24}] \cdot 16H_2O$	1.76	0.26×0.39
Edingtonite	$BaAl_2Si_3O_{10} \cdot 4H_2O$	$Ba_2[(AlO_2)_4(SiO_2)_6] \cdot 8H_2O$	1.68	0.35×0.39
Group VI, T_8O_{16}				
Mordenite	$(CaNa_2K_2)Al_2Si_{10}O_{24} \cdot 7H_2O$	$Na_8[(AlO_2)_8(SiO_2)_{40}] \cdot 20H_2O$	1.70	0.64×0.70 0.29×0.57
Ferrierite	$(Na,K)_2MgAl_3Si_{15}O_{36}(OH) \cdot 9H_2O$	$Na_{1.5}Mg_2[(AlO_2)_{5.5}(SiO_2)_{30.5}] \cdot 18H_2O$	1.76	0.43×0.55 0.37×0.48

[a]Group designations after Breck (1974), see Fig. 2.18.

[b]After Breck (1974) as presented in Flanigen (1977), pp. 23–24, Table 2.2.

[c]Density and channel-way dimensions are based on unit cell of hydrated zeolite.

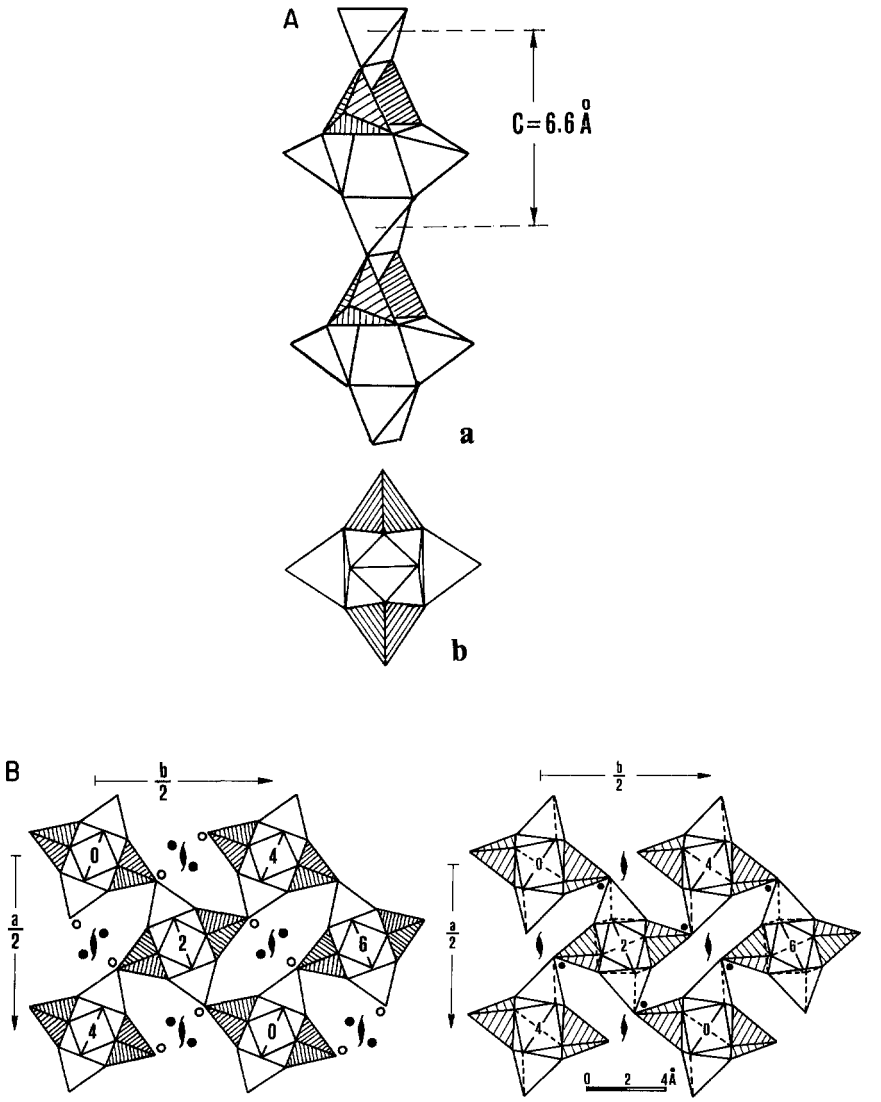


Fig. 2.17 Schematic representation of the structure of the zeolite natrolite [$Na_2Al_2Si_3O_{10} \cdot 2H_2O$]. (**A**) The ($SiO_4$, AlO_4) chains, viewed parallel to *c* (along the chain length) and down *c*. The striped tetrahedra are AlO_4. (**B**) The structure of natrolite and dehydrated natrolite. Solid circles are Na^{+1}, open circles are H_2O, ⧫ = axis of symmetry; a/2 and b/2 indicate vector direction in the crystal structures. Note the rotation of tetrahedra and shift of the Na^{+1} positions in the dehydrated structure. Dehydration changes the configuration of the open areas between chains.

whose length parallels that of the fiber axis. If only Si^{+4} ions were present in each tetrahedron of the natrolite framework, it would be electrically neutral. However, Al^{+3} substitutes for Si^{+4} at two (shaded in Fig. 2.17A) out of the five possible T sites, creating a net negative charge that is balanced by other cations. In natrolite, Na^{+1} and H_2O molecules occupy special positions related to the framework. The location of the cations in relation to the framework is illustrated in the crystal structure viewed perpendicular to the fiber axis (Fig. 2.17B). Also included in this figure is the structure of dehydrated natrolite, to illustrate the effect on the framework configuration of dehydration and removal of the H_2O molecules. Note the changed position of the Na ions and the shift and rotation of tetrahedral chains from their positions in natrolite.

Natrolite is a typical example of the zeolitic framework structures. Based on the ratio of the tetrahedral cations—that is, Al^{+3}:Si^{+4}—and the structure, a variety of elements and molecular species can reside in the openings and channelways created by the zeolitic framework. The dimensions of the main channelway and the density differences of the frameworks for different groups of zeolites are shown in Table 2.7. The ions and molecules within the openings have little or no effect on the stability or general configuration of the tetrahedral frameworks. As long as charge balance is maintained, cations and molecules substitute or exchange without significantly altering the three-dimensional structure of the zeolite.

Cations and loosely bound molecules are easily exchanged in many zeolites. A zeolite with one composition placed in a new medium exchanges with the new cations and molecular species and, on return to the original medium, can revert to the original composition. Such chemical activity is analogous to that proposed for enzymes: zeolites undergo exchange of ions and molecules, acting as catalysts, but the reaction does not affect the basic composition and structure (the cage or aluminosilicate framework) of these inorganic materials. The size and continuity of the openings, which are dictated by the ring structure arrangement, affects the dimensions and charges of those species that can be exchanged, and the rate of exchange. Further, the composition of a zeolite reflects that of the last solution to which it was exposed.

Fibrous Zeolites

The term fibrous, as applied to zeolites, does not necessarily indicate flexibility. Flexibility, however, is one of the physical properties of cotton stone found on the Isle of Skye, Scotland. This locality provides a feathery sample of mesolite, ($Na_2Ca_2Al_6Si_9O_{30} \cdot 8H_2O$), whose composition and structure place it in the same group as natrolite. The similarity between appearance of this sample and that of the mountain flax variety of palygorskite emphasizes the difficulty of identifying fibrous minerals based on morphology alone.

Mordenite [$(Ca,Na_2,K_2)Al_2Si_{10}O_{24} \cdot 7H_2O$], one of the most common zeolites from saline sedimentary localities, occurs as small hemispheric fibrous concretions (fans). The structure of the mineral is a complicated array of

chainlike stacks of six silicate tetrahedral rings cross-linked with AlO_4 tetrahedra in groups of four. Rewriting the formula as $Na_8[(AlO_2)_8(SiO_2)_{40}] \cdot 28H_2O$ may help in visualizing the structure.

Erionite $[(K_2,Ca,Na_2)_2Al_4Si_{14}O_{36} \cdot 15H_2]$, another relatively common sedimentary zeolite, is found in either acicular or fibrous habits. A scanning electron microscope photograph of erionite from Shoshone, California, shown in Fig. 2.18A, is accompanied by a stereodiagram of the erionite structure (Fig. 2.18B). The basic framework structure of this mineral may be considered as six double-silicate tetrahedral rings linked by six double-tetrahedral rings. This three-dimensional array of rings creates cages and a series of cavities with dimensions ranging from 1.5×0.6 nm to 0.36×0.52 nm. The principal cations in natural erionite are K^{+1} and Ca^{+2}, with K^{+1} not generally involved in exchange. Needlelike crystals up to 100 micrometers in length are known. Erionite commonly cleaves into crystallites with diameters of less than 1 micrometer. Erionite needles, identified in soils and dusts in the Kurdish town of Karain, Turkey, were implicated as the fibrous mineral responsible for the high rate of the cancer, mesothelioma, found in the area (Baris et al., 1975).

Humpton and Ormsby (1976) presented scanning electron microscope photographs that show the range of morphologies adopted by the many members of the zeolite group of minerals. For more detail on the many intricate structures of natural and synthetic zeolites, see Breck (1974), Sand and Mumpton (1977), Flanigen (1977), or Barrer (1978).

The zeolites are generally thought of as having three-dimensional rather than sheet or chain structures. The existence of tetrahedral ring linkages that produce chainlike substructures characteristic of the natural zeolitic species found as needles or fibers reinforces the earlier statement: fibers can be constructed from any number of basic units that grow in a preferential direction.

ISOLATED TETRAHEDRA SILICATES

Not all silicate minerals that form fibers have structures based on rings, sheets, or chains of linked tetrahedra. Several species whose structures are based on isolated tetrahedra commonly occur in acicular or fibrous form.

The Olivine Mineral Group

The olivine mineral group is an example of an isolated tetrahedral structural species. The group has a compositional range that can be expressed as the ideal formula $(Mg,Fe^{+2},Ca,Mn,Co,Ni)_2(SiO_4)$. The chemistry and associations of cations bonded to the silicate tetrahedra parallel those outlined for the pyroxene minerals. Within the olivines, the most important mineral series ranges in composition from fosterite (Mg_2SiO_4) to fayalite ($Fe^{+2}{}_2SiO_4$). Fosterites are common minerals, typically occurring in solidified lavas such as those found in Hawaii or the lunar basalts. Fayalitic members of the group are rare; they tend to occur in certain granites and metamorphic rocks. The

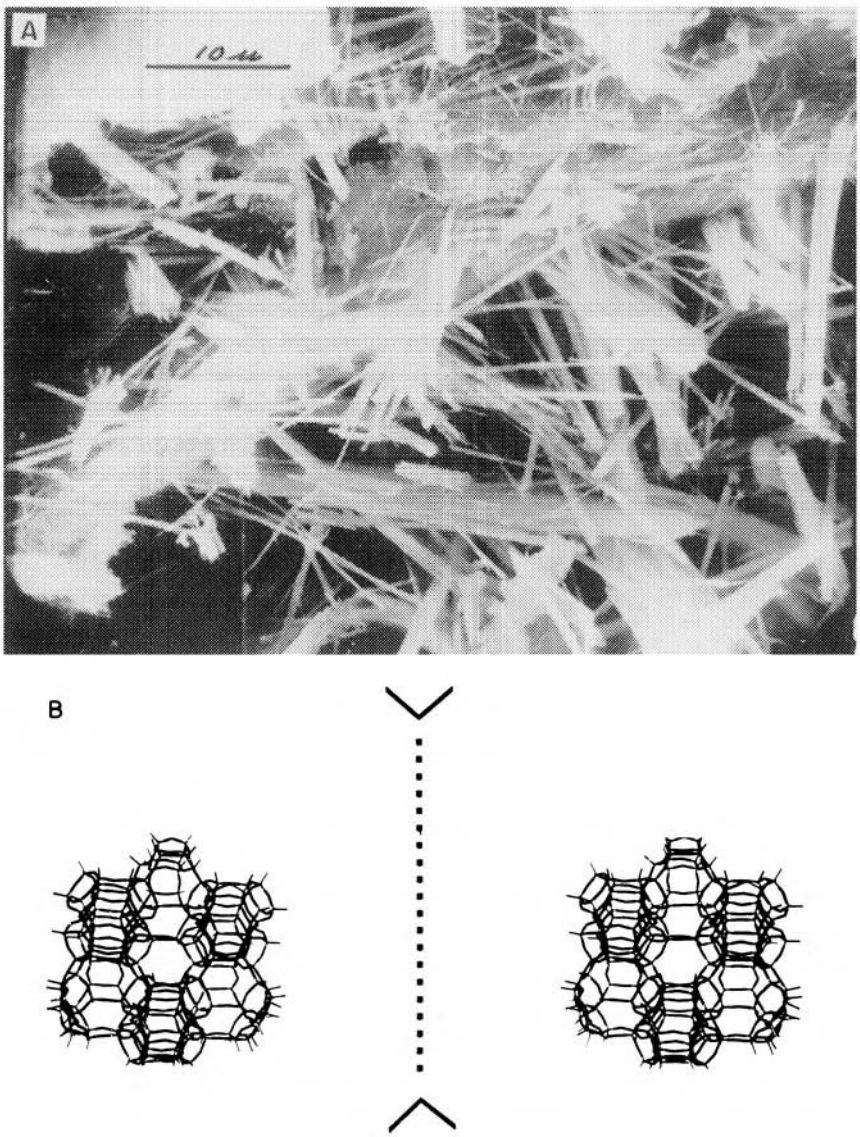


Fig. 2.18 The fibrous zeolite erionite $[(K_2, Ca, Na_2)_2Al_4Si_{14}O_{36} \cdot 15H_2O$. (**A**) Photograph from Shoshone, California. (**B**) Stereoscopic view of the framework of erionite. The view is parallel to the *c*-axis of the crystal and shows the stacking of the six-unit rings. The framework consists of double six-rings, D6R and S6R units, which are in parallel planes perpendicular to the *c*-axis (hexagonal). The length of the *c*-axis is 1.5 nm or 6 times the 0.25 nm spacing of a single six-ring. The internal diameters of the main cavities are 1.51 × 0.63 nm and the aperture between cavities is 0.25 nm (too small to permit diffusion of most molecular species). Six eight-rings form apertures that open into any single cavity; these have dimensions of 0.36 × 0.52 nm, and each aperture is common to two cavities. The position for stereoscopic viewing is indicated.

olivines exhibit a wide range of crystal habits as well as compositions (Deer et al. 1A, 1982). Grown under equilibrium conditions olivine crystals are predominantly equant in form, but they also occur in tabular, acicular, dendritic, and spherulitic habits. Blander et al. (1956) and Donaldson (1976) undertook experiments that varied the rates of cooling and the composition of a melt. The results appear to explain the diverse morphologies observed.

Olivine minerals are very susceptible to alteration when exposed to environments different from those of the lavas and other rocks in which they crystallized. Changes in temperature, pressure, or chemistry, and especially exposure to hydrothermal solutions, usually lead to alteration of olivine to a hydrous mineral. Commonly, partly altered olivine crystals are surrounded by halos (reaction rims) containing fibrous pyroxenes, amphiboles, and serpentines. The process, known as serpentinization, produces lizardite, antigorite, or chrysotile from the original olivine (Deer et al. 1A, 1982). In southern Quebec, for example, two distinct episodes of serpentinization have been identified (Laurent, 1975). In the first stage, fosteritic olivine was changed to lizardite, while the second stage produced fibrous chrysotile in veins cross-cutting the host rocks. Today, export-grade chrysotile is mined in this locality. The lizardite is partially fibrous and partially lamellar in form.

The Humite and Epidote Mineral Groups

The humite and epidote groups of minerals also have a structural motif based on isolated tetrahedra. The latter mineral group is characterized by pairs of corner-sharing tetrahedra as well as chains of AlO_6 and $AlO_4(OH)_2$ (Deer et al. 1, 1962; 1B, 1986; Ribbe, 1980). The epidotes are common minerals with acicular habits in metamorphic rocks. They are often mistaken for other species with prismatic morphologies, such as the pyroxenes or amphiboles. Alteration products of the humite and epidote mineral groups are the serpentine minerals and the chlorites.

The Tourmaline Mineral Group

Good quality natural fibers are often obtained from the tourmaline mineral group. Chemically the tourmalines are borosilicates, rather than silicates or aluminosilicates. The tourmalines have the general formula $AB_3C_6(BO_3)_3Si_6O_{18}(OH,F)_4$, where A = Ca^{+2}, K^{+1}, Na^{+1}; B = Al^{+3}, Fe^{+2}, Fe^{+3}, Li^{+1}, Mg^{+2}, Mn^{+2}; and C = Al^{+3}, Cr^{+3}, Fe^{+3}, V^{+3}. Slender acicular crystals with a wide range of compositions, the tourmalines exhibit a wide range of colors. They are common minerals in granitic and metamorphic rocks, although the amounts are generally less than 1 percent of the total volume of the host rock.

Fibers of tourmalines up to 8 inches long have been described from the Alps (Dietrich et al., 1966). Novad and Zak (1970) described shorter and thinner (diameter < 1 micrometer) tourmaline fibers from the Ural mountains. With high birefringence and pleochroism, tourmaline is readily identified by optical examination. It is distinguished from other fibrous silicates

by the high concentration of boron on chemical analysis (Deer et al, 1B, 1986).

In his recent book, Dietrich (1985) described the common habits of tourmaline as being acicular, filiform, asbestiform, and chalcedonylike, and as whiskers. This last term indicates that tourmaline composition fibers have been synthesized. The wide range of forms for minerals in this group probably accounts for some of the early confusion when samples of tourmaline were equated with asbestos. Schorl, now known to be $NaFe^{+2}Al_6(BO_3)_3Si_6O_{18}(OH)_4$, usually occurs as dark green or black acicular crystals. Based on their appearance alone, schorl could easily be mistaken for an amphibole.

SILICA MINERALS THAT ARE FIBROUS

SiO_2 is one of the most abundant compounds in nature. It forms a number of minerals and several varieties whose names are quite familiar; agate, carnelian, sard, amethyst, chalcedony, flint, and chert. All are composed of SiO_2 with only small or trace amounts of other elements or compounds included during crystallization. In many cases it is the additional components that impart the peculiar color, optical, or physical properties to these minerals. The names are familiar because since ancient times these minerals were used or commonly set in jewelry. All of the names are varieties of the mineral quartz, the stable form of SiO_2, formed at ordinary temperatures and pressures. SiO_2 also forms several polymorphs, which are mentioned below.

Quartz

The structure of quartz is based on the $(SiO_4)^{-4}$, silicate tetrahedron. Each of the oxygen ions in a tetrahedron is shared by two silicon ions generating a three-dimensional network in which the silicon ions, or tetrahedral groups, appear to have a helical arrangement (Fig. 2.19A). The view of the quartz structure perpendicular to the helices (Fig. 2.19B) shows the hexagonal and rhombohedral symmetry that characterizes the large single crystals of this mineral.

Chalcedony

Chalcedony is a variety of quartz composed of fibrils that are not separable. The fibrils may have variable thickness, and lengths, from a few to hundreds of microns, and may be twisted (Fig. 2.19C). The fiber axis, usually perpendicular to the free or growing surface, is easily detected in the crystalline material consisting of tightly packed, parallel or subparallel fibrils. The range of color, and the mechanisms of inclusion of impurities, and especially of water and $(OH)^{-1}$ in chalcedony, have been described and discussed by many authors, most recently by Frondel (1978, 1982).

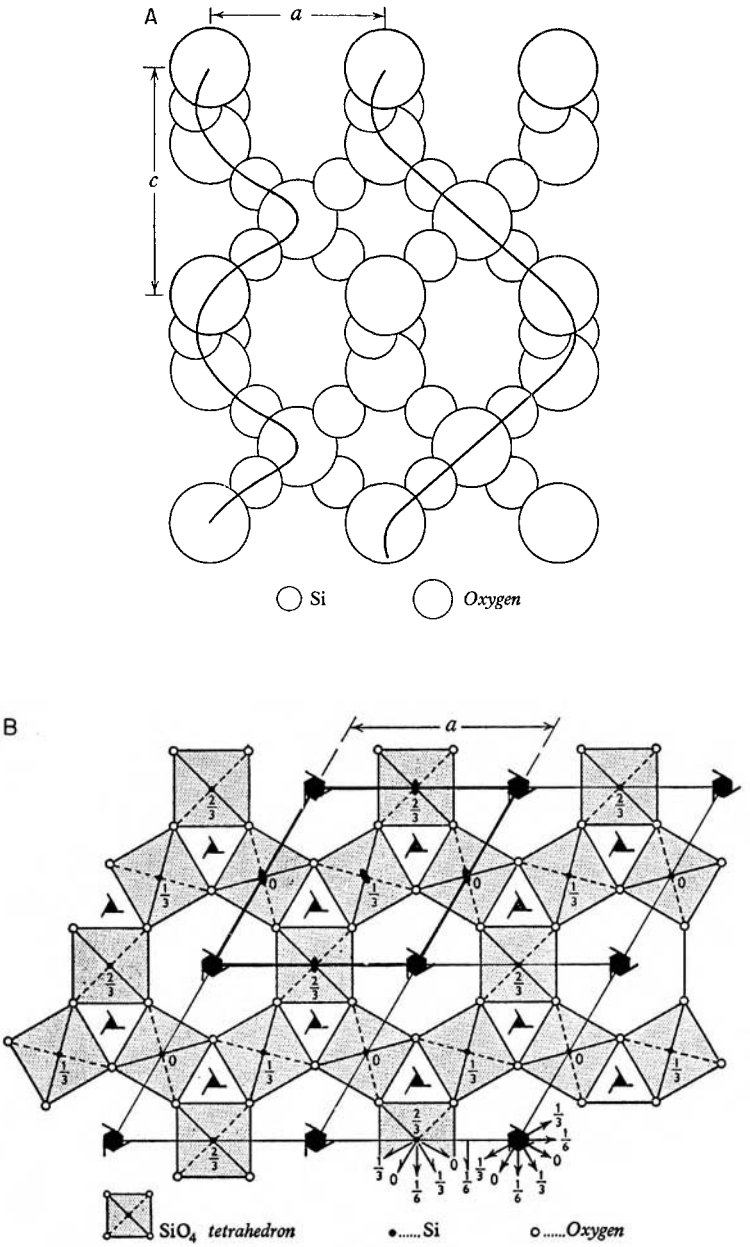
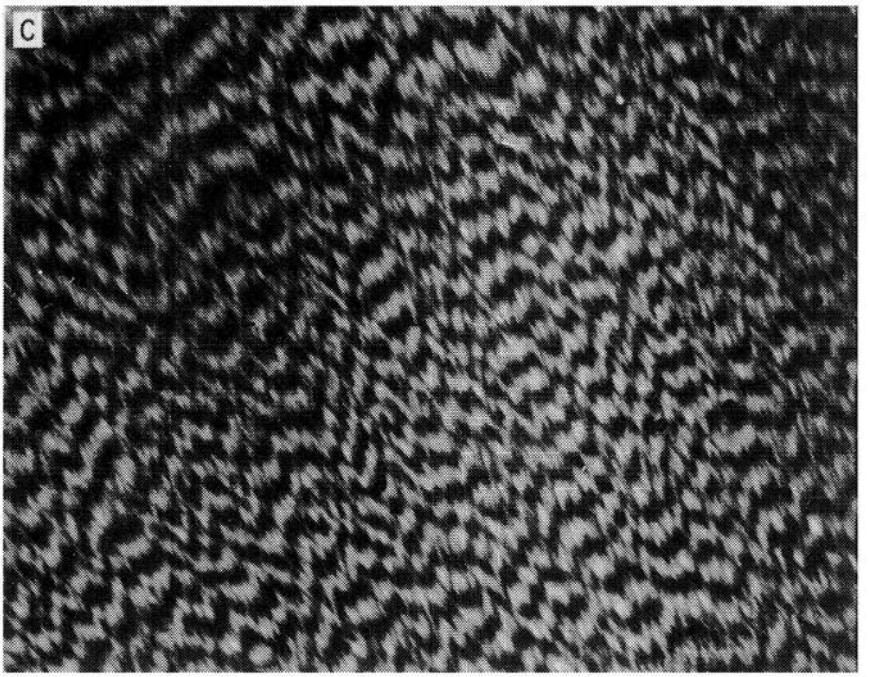


Fig. 2.19 Quartz. (**A**) Structure of B quartz, on (1120) projection, showing the helical arrangement of Si-O-Si-O ... Unit cell size is indicated by *a* and *c* vectors. (**B**) Structure projected on (0001), illustrating the hexagonal 6_2 and rhombohedral 3_2 disposition of the SiO_2 tetrahedra in three dimensions. (**C**) Chalcedony, a fibrous variety of quartz at 120X magnification. Bundles of twisted fibrils of SiO_2 in parallel alignment display an alternating black-and-white pattern along their length. The pattern indicates the irregular but twisted nature of the SiO_2 bundles.



The optical character of chalcedony is distinct from that expected for the normally uniaxial mineral, quartz, and signals the fibrous nature of a particular sample. The direction of fiber elongation is often parallel to the [1120] crystallographic direction of the quartz structure (Fig. 2.19A), but other fiber directions have also been determined within a single sample (Frondel, 1985). The presence of helically twisted fibers are suspected from the variations in extinction and birefringence noted along the fiber length (Fig. 2.19C). More detailed information on the optical or other physical and chemical properties of quartz and its many varieties can be found in volume 3 of Palache et al. (1962) and in Frondel (1985).

Flint

Flint and chert, on microscopic examination, show spherulitic or fan-shaped areas of fibrous quartz, or perhaps more appropriately, chalcedony. The fibers, as well as the calcified remains of living creatures that are often included in flints, are held together by a quartz cement. Flint is, in effect, silicified chalcedony, that is, an aggregate of quartz fibrils bound in random fashion by a fine-grained matrix of granular quartz. The patterns observed on fractured surfaces of flint are the result of crenulated and interlocking units of subparallel bundles of fibers. The microcrystalline granular interstitial quartz in flint may have originally been silica gel (an amorphous material).

The common gray, brown, or black flint result from admixed iron oxides or organic compounds. Pure quartz is usually colorless and transparent. The conchoidal fracture typical of flint was a boon to primitive humans, who desired clean, smooth, sharp edges that were not susceptible to uniform wear. This physical attribute and the densities of flint reflect the patterns of aggregation of its fibrous constituents.

Other Fibrous Varieties of Quartz

Particles of Fe_2O_3, Al_2O_3, H_2O, opal, and other metallic salts, gases, or voids may be included in the crystalline mass as fibrous quartz grows. The result is attractive, usually colored minerals that are known by different names. For example, agate is a subvariety of chalcedony. The distinct banding typical of agates is the result of small compositional changes during growth that produce successive layers of different colors and degrees of translucency. Iris, or rainbow agate, has exceedingly small bands, at least 6800 to the centimeter, that run perpendicular to the fiber axis. They produce distinctive diffraction effects (Frondel, 1978, 1985).

Tiger's eye is a yellow and brown-banded gemstone, and Hawk's eye is similar but with blue bands. Both come from South Africa and result from silicification of cross-fiber veins of crocidolite. Cut *en cabachon,* and parallel to the fiber length, Tiger's eye and Hawk's eye exhibit variations in sheen and color that arise from the not-quite-parallel arrangement of the intimately associated asbestos and quartz.

Clear crystals of quartz, some of which are many inches in length, can contain embedded within them needles of the mineral rutile (TiO_2) and of tourmaline. Such materials are referred to as rutilated or tourmalinated quartz (Dietrich, 1985).

SiO_2 Polymorphs

Several polymorphs of SiO_2 are known in addition to quartz. These have structures generally similar to those described for the silicate and aluminosilicate minerals, except that the chemistry is simpler: it is all SiO_2. Which silica polymorph is stable depends on the temperature and pressure during the material's formation. The structures adopted by tridymite and cristobalite, two of the ten known polymorphs of SiO_2, can be likened to layer silicates with simple linkages between silicate tetrahedra. Tridymite and cristobalite each has more than one possible arrangement, analogous to the layering of the aluminosilicates. The configuration adopted by a particular sample is probably somewhat fortuitous. Once formed the structure may persist (metastably) to room temperature. Tridymite often occurs as thin plates and as needles in fan-shaped or spheroidal aggregates. Long, thin crystals of cristobalite and tridymite are found in the cavities formed in volcanic rocks.

Another very well known fibrous variety of silica is the gem called opal. Opal is actually a hydrated form of cristobalite whose fiery primary colors come from the diffraction of light by aligned water and silica fibers. Lus-

satite is a rare variety of fibrous hydrated cristobalite. These mineraloids have been known for a long time (Palanche et al., 1962).

As must be obvious, we have only touched on the natural occurrences of crystalline fibrous SiO_2. For example, SiO_2, usually quartz, often replaces fibrous minerals of another composition as rock masses are altered. SiO_2 also occurs in fibrous form within some plants (phytoliths) and in the soil. To summarize, in addition to the usual and common occurrences of the mineral quartz and its varieties, several silica polymorphs occur as fibers in a variety of biologic and geologic environments.

FIBERS OF NONSILICATE MINERALS

From every chemical group mentioned in *Dana's System of Mineralogy* there are minerals that form as fibers. We began with the most commonly encountered minerals, the silicate and aluminosilicate groups, and now briefly mention a few from other chemical classes.

Native sulfur (S) in several polymorphs and many of the metallic elements (tellurium, arsenic, gold) can be found in spherulitic masses or as fibers formed through sublimation from the gases escaping near volcanic vents. Minerals that contain sulfur, such as the ore minerals sphalerite and wurtzite (polymorphs of ZnS), or livingstonite, $HgSb_4S_8$, are also occasionally found as fibers and spheroidal aggregates. Of the fifty-eight entries in Appendix 1 under sulfate (SO_4), another naturally occurring complex of S, some common minerals, such as gypsum ($CaSO_4 \cdot 2H_2O$), occur occasionally as fibers. Other sulfate minerals, such as uranopilite [$(VO_2)_6(SO_4)(OH)_{10} \cdot 12H_2O$], are rare but usually occur in fibrous form. Several species of sulfates occur frequently or only in acicular form or as fibrous crusts.

Natural fibrous materials are identified somewhat by chance. For example, there are seven vanadate and seven vanadium oxysalt minerals on the list of fibrous minerals. These species are composed of a rare element, vanadium, but the fibrous samples may have attracted attention because they are often brightly colored. Vanadinite [$Pb_5(VO_4)_3Cl$] for example, is bright orange-red. Further, the list of natural mineral fibers we have compiled contains seventy-seven phosphate species. So many phosphates are listed because detailed descriptions of these mostly quite rare minerals were readily available (Nriagu and Moore, 1984).

Only one phosphide mineral appears on the list. The tabulation contains twenty-six arsenate species but not a single arsenide. The fibrous minerals recorded reflect the limitations imposed by natural circumstances, and especially the opportunities for elements to be juxtaposed geochemically and able to produce a particular mineral compound. Oxygen containing compounds form by far the most prevalent natural fibers, but simple hydroxide and carbonate compounds are also prominent on the list. There are more oxyhalides and water-containing minerals than pure chloride minerals, al-

though one might encounter fibrous NaCl much more readily than some of the other less common element associations. The message, however, is clear: the chemical range of fibrous natural compounds is vast, and few of these compounds have been studied in sufficient detail to provide more than a cursory view of the properties uniquely associated with fibrosity.

SYNTHETIC FIBERS

Under suitable conditions, virtually any inorganic compound can be synthesized in fibrous form. Thousands of fibers of different compositions have been produced experimentally, a few have become commercial, and at least one type, fiberglass, is as well known as asbestos. Synthesis of fibers that began with simple and common elements and compounds imitating those in nature has progressed to fibers from hitherto unknown chemical combinations. Indeed, fibers of less than 10 micrometers in diameter, and composed of more than one material, have been constructed. These side-by-side or sheath and core combinations of two inorganic compounds in fibrous array (Doremus et al., 1958; Grayson, 1983) provide materials with special, often astounding, chemical and physical properties. However, the most rapidly expanding market for inorganic fibers today is in the production of fiber-reinforced materials or *composites*.

The entire spectrum of inorganic fibers can be divided into two classes, based on differences in the crystallinity of the solids (Ray, 1978). Synthetic fibers have been known as man-made mineral fibers (*MMMF*) and man-made vitreous fibers (*MMVF*). But fibrous materials can be approached or divided in other ways. For example, in the *Concise Encyclopedia of Chemical Technology* (1985) the entry for chemical fibers includes both man-made and natural polymers, with the discussion centering on carbon-based compounds such as acetates, acrylics, and cellulose. Fibers of other inorganic compounds were not mentioned in the encyclopedia under this entry, but silica glass fibers were described under the heading "Optical Fibers."

A division based on crystallinity facilitates our discussions of both mineral and synthetic fibers by accentuating the morphology of the fibrous object rather than its source or composition. Further, although both amorphous and crystalline mineral fibers are known, most of these used in commerce—and certainly the best known—are crystalline. The opposite is true for synthetic or man-made inorganic fibers (*MMIF*). The fibers used in commerce are predominantly amorphous.

MMVF are synthetic fibers with glasslike structures. The term usually refers to silicate-based glass fibers, because these compositions form the largest volume of fibers produced. However, in addition to fiberglass and fused silica (SiO_2), there are other amorphous fibers used in commerce: alumina (Al_2O_3) and silica combinations, rock and slag wool, as well as fibers with nonsilicate compositions such as carbon. Many of these amorphous fibers have proprictary names.

MMMF are synthetics that have crystalline rather than amorphous structures. Not surprizingly, early examples are reminiscent of the naturally occurring fibers: synthetic chrysotile (Jander and Wuhrer, 1938) and needles of amphibolelike composition and crystal structure (Shell et al., 1958). However, the bulk of the crystalline synthetic fibers, both in use and under investigation, do not have mineral equivalents; therefore, we chose to use the term whiskers to distinguish crystalline man-made inorganic fibers from their natural relatives.

Whiskers are synthetic crystalline fibers of variable size, but with diameters of usually less than 25 microns. An upper limit in diameter exists because the physical and chemical properties approach those of the bulk material as the diameter of fibrous sample increases. Since the purpose of synthesis is to take advantage of some characteristic property of the material in fibrous form, such as enhanced strength for small volume, the optimum material has a small diameter. For similar reasons the aspect ratio of useful whiskers is often well over 100. Whiskers can be single crystals, but many are polycrystalline aggregates of fibrils with preferred orientations. The compositions and crystal structures of the compounds synthesized as crystalline fibers also have the broadest possible variety (Brenner, 1958).

The fiber-containing materials called composites are the products of materials engineering. Aerospace applications, which require durability over an extreme temperature range and high strength with light weight have fueled investigations of composites. Markedly enhanced strength under a broad range of stress conditions, greater resistance to wear and abrasion, and the ability to be cast or molded to suit a particular function are the attributes of these multicomponent materials; they have applications in many areas.

Composites are synthetic materials created from at least two phases or compounds. The two phases may be interbonded, but the purpose is to provide high-performance materials. Strictly speaking, individual fibers composed of two components, such as the sheath and core variety mentioned earlier, are composites (Slayter, 1952). Fiber-reinforced bulk materials are the more typical composite. Fibers (either natural or synthetic) are mixed within a matrix, usually to maximize strength and durability. Optimally, the dual system has advantages—the composite is more than an additive improvement over the reactions of the individual components, that is, the new material is "greater than the sum of the parts." Rebar, or steel-rod-reinforced concrete, is a macro example of the genre; another product, inorganic fiber-reinforced paper, is closer to the scale of our interests. There are fiber-reinforced plastics (Schwartz and Schwartz, 1968), fiber-reinforced ceramics (Rauch et al., 1968), and intercalated graphite composites (Pietronero and Tosatti, 1981).

Manufacture of inorganic materials as fibers is now common. Industry has developed fibers to respond to a range of technological demands. In the process the new fibrous materials have often provided impetus for innovation and development of new uses. The study of synthetic fibers is a rapidly expanding area of research. A variety of sources such as the *Journal of*

Crystal Growth, Journal of Solid State Chemistry, and *Carbon,* as well as national and international societies, such as the American Association for Crystal Growth, provide outlets for information on the new compounds, and about the methods of synthesis. However, much of the information is contained in technical reports that have limited circulation within industrial laboratories (see chapter 5 in McCreight et al., 1965). In many cases the synthetic materials are proprietary and patented. Appendix 2, a listing of synthetic fibers, was compiled to illustrate the chemical range of synthetic compounds. It includes recent references but is certainly not complete. It is presented merely to document the range and variety of inorganic synthetic fibers. In the concluding pages of this chapter we briefly summarize some crystallochemical data and methods of synthesis of glass fibers, whiskers, and carbon-based fibers as three types of fibrous synthetics to compare with mineral fibers.

MMVF OR GLASS FIBERS

Glass fibers, also called fibrous glass or fiberglass, were first commercially synthesized in the 1930s and have become one of the most versatile and widely disseminated materials in our culture.

The formation of a glass takes place when a liquid of any composition, cooled to room temperature, solidifies and retains a random liquid structure. Freezing-in of the random structure is facilitated by a rapid downshift of temperature when the liquid contains a high proportion of species known as *glass formers*. The common oxides of the high ionic charge elements, such as silicon, aluminum, and phosphorus, are well-known glass formers.

The lack of periodicity in glasses can be detected using polarizing microscopy. Other methods such as light scattering, x-ray, and electron diffraction are necessary for detailed analyses of glasses. Broad, indistinct bands recorded by diffraction techniques stand in sharp contrast to the discrete spots typical of the three-dimensional order of crystalline solids. These experimental results leave much room for interpretation. Small amounts of cations such as Ca^{+2}, Mg^{+2}, and Na^{+1} added to the glass-forming liquids usually aid in forming small molecular clusters that modify the random anionic network. Their presence changes not only the chemistry but also the properties of the glass in the direction of more commercially desirable properties. For example, trace additions can increase the resistance of the glass to acid dissolution.

The fibrous glass used for insulation materials does not require starting materials of high purity. Beach sand, which consists largely of the mineral quartz, is easily obtainable and quite inexpensive. Alternatively, silicate slags or waste rock from mining can be melted and processed to create the products called rock-, slag-, and mineral-wool. Such materials are used for insulation. Where specific properties are desired, such as resistance to ultra-

high heat, chemical attack, or the ability to be woven or molded, the glass composition must be closely controlled.

E glass, patented in 1943, combines the highly desirable properties of good chemical and heat stability, and good electrical resistance with high strength. Continuous textile fibers made of glass have been widely employed for electrical insulation (Gagin, 1980). The actual composition of E glass and other varieties used for producing textiles are compared with the compositions of fibrous insulation materials in Table 2.8. The composition of a particular glass may be deliberately modified not only to tailor the glass to the application but also to assist in production.

Production of Glass Fibers

Spinning is one of the commercial processes for producing fibrous glass. Streams of molten glass fall on rapidly rotating wheels and spin off as droplets. The droplets on settling develop glass tails or fibers that are accumulated, spray treated, and annealed. The diameters and lengths of the fibers formed by this process are variable. In fact, a single fiber may vary in thicknesses along its length. An alternative, and inexpensive process for wool insulation materials is breaking up the molten fluid into droplets in a high-velocity gas stream. Glass wools are, therefore, a mixture of fibers and beads.

Nature produces fibers of essentially identical composition by a similar process. During volcanic eruptions molten magma spewed into the atmosphere as a result of the explosion forms fibers before it settles to earth. Called Pele's hair, the natural fibers have diameters ranging from less than 1 to at least 300 micrometers. The site of concentration of volcanic glass fibers varies with the winds moving around the crater. The composition of the glass fibers in Hawaii, where Pele's hair is common, reflect the composition of the magma: about 50 percent SiO_2 with the remainder consisting

Table 2.8 The Composition in Weight Percent of Fibrous Glasses

				Continuous Textile	
	E Glass	Glass Insulation	Glass Wool	1951	1959
SiO_2	55.2	62.8	50	54.0	54.5
Al_2O_3	14.7	5	10	13.5	14.0
B_2O_3	7.2	6		10.5	8.0
CaO	18.7	7	25	16.0	17.4
MgO	3.3	3	14	5.0	5.0
$Na_2O + K_2O$	0.5	15		0.5	0.5
Fe_2O_3	0.3	0.5	1	0.2	0.35
TiO_2				0.3	0.5
SO_3				0.1	0.1
F	0.3	0.7		0.2	0.2

Sources: Data on E glass composition are from Loewenstein (1973), Table vi/i; glass insulation and wool composition data come from Mohr and Rowe (1978), Table 5-1; continuous textile fiber composition data are from Gagin (1980).

principally of CaO, MgO, Al_2O_3, and FeO (compare glass wool composition in Table 2.8).

Continuous textile fibers are usually made by drawing molten glass though a bushing with many fine holes. In Fig. 2.20 glass marbles of controlled composition are fed into the melting pot, and primary filaments of glass are pulled into the jet flame. Typically, uniform-diameter fibers of between 4 and 20 micrometers are drawn at speeds in excess of 5000 feet per minute.

The surfaces of glass fibers for textiles need protection from abrasion and chemical attack to preserve high strength and flexibility during use. Different composition materials to form a coating or "size," are usually sprayed onto the drawn fibers during the manufacture (Fig. 2.20). Such coatings are distinct from the finish, which is a surface treatment for fibers after they have been made into yarn by combining many fibers and woven into fabric. Sizings are often organic compounds that are added to fibers to act as a film to prevent the filaments from abraiding one another, to lubricate filament movement, or to aid the subsequent dyeing of the fiber or textile (Mettes, 1969). In any case they provide an interface between the inorganic glass fiber, with its large surface area, and the surroundings.

To produce composites, a binder rather than a size is usually required. A variety of high-temperature, high-strength compounds now available facilitate compatability of the fibers with matrix compounds. Insulation fibrous glass has been paired with phenol formaldehyde resins and a mineral oil lubricant. The binder may be up to 12 percent by weight of the final product (Barnhart, 1976). The composite compositions are discretely different from those of textiles in which fiber coatings are usually less than 0.5 percent of the total.

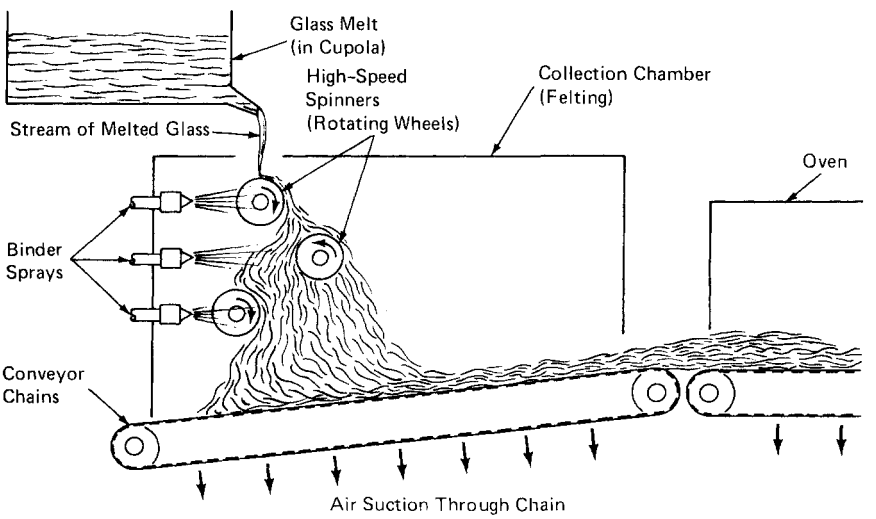


Fig. 2.20 The production of fibrous glass.

Glass Fiber Size

Glass fibers are produced commercially in a wide range of sizes. For control in producing uniform smaller sizes, primary filaments of about 1 millimeter in diameter are reduced to long, fine fibrils by a flame attenuation process. Fibers of 1 micrometer or less represented about 1 percent of the world production during the 1970s (Hill, 1978). Continuous-filament (drawn textile) fibers have a narrower diameter range than the fibers in insulation wools (Fig. 2.21). Although the mean diameter of the wool fibers in such a sample

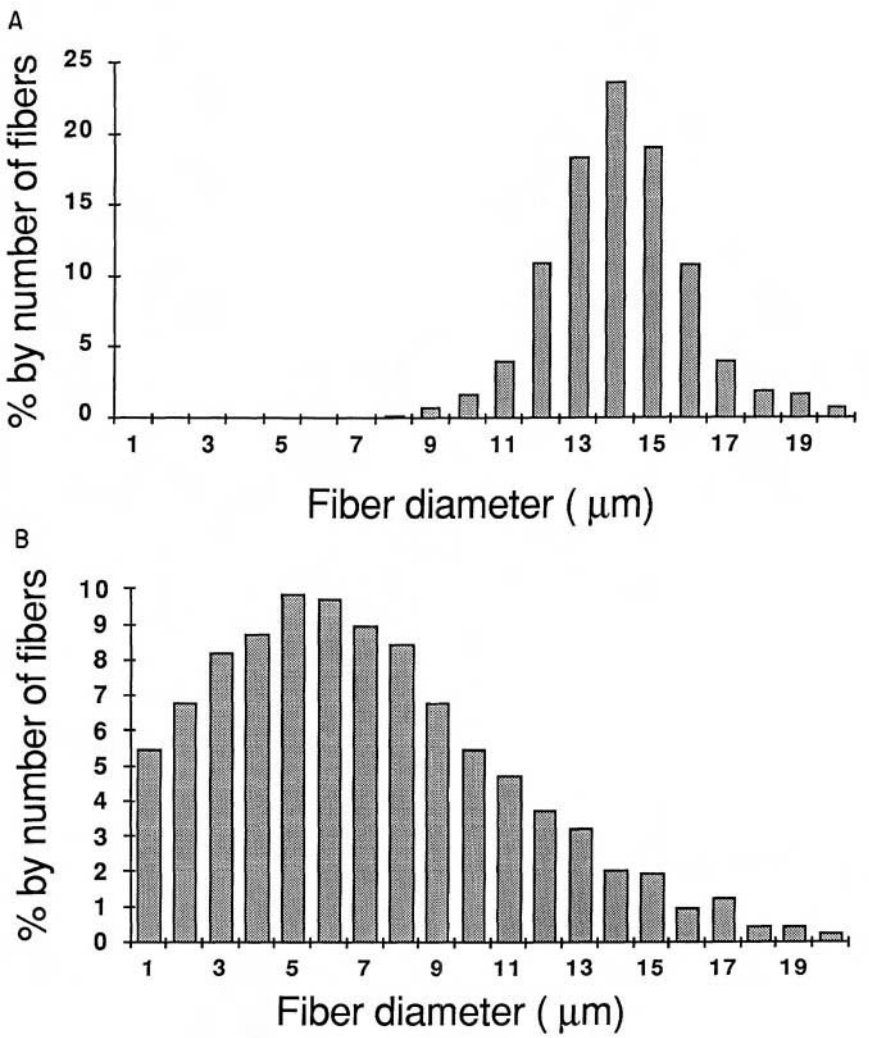


Fig. 2.21 Typical distribution of fiber diameters in continuous filament materials and insulation wools. (**A**) Continuous filament glass. The mean diameter is 14.1 micrometers, with standard deviation of 1.9 micrometers. (**B**) Glass fiber wool. Mean diameter is 7.0 micrometers, with a standard deviation of 4.0 micrometers.

is 7 micrometers, note that data on fibers of less than 1 micrometer diameter are not presented and presumably have not been recorded. Fiber length is extremely variable and is determined by the production methods.

The principal distinguishing features of glass fibers reflect the vitreous state or lack of crystallinity of these materials. Glass fibers should also, exhibit distinctive fracture patterns, and would be expected to break across the fiber, decreasing the fiber length while the diameter remains the same. Observation of circular cross section and bulbous regions along the fiber length, in contradistinction to the steplike irregularities common in crystalline materials, indicates that the fiber is a glass. As an anhydrous silicate, glass fibers are not likely to change their composition or physical properties on application of heat, although any sizing or finish materials can exfoliate. If the temperature reaches the softening region of the glass composition, however, the dimensions of the fibers could change.

WHISKERS

Early investigations into the growth of crystalline fibers (Joffee et al., 1924; Ewald and Polanyi, 1925) showed the relative ease with which this special morphology could be obtained from a variety of elements and compounds. The first thorough systematic study dates from 1954, when Gyulai investigated the fibrous properties of NaCl; but it was the utility of metallic whiskers in the transmission of electric signals that spurred investigations (Herring and Galt, 1952) on to large-scale industrial methods of growth. More than seventy-five elements and alloy compositions capable of forming whiskers are listed in Appendix 2; only a few have made the transition from laboratory to commercial production.

Of the 273 varieties of whiskers included in Appendix 2, most are single-crystal whiskers. Polycrystal fibers and aggregates composed of fibrils are also known and have been produced. Stellate or spherulitic aggregates are common, although they are mostly unplanned—the result of rapid growth during experimental synthesis studies and in manufacturing.

Appendix 2 was compiled and formatted by composition paralleling the presentation for the fibrous minerals. The list, in contrast with that of the minerals, shows a predominance of simple chemical compounds that combine two or three elements. One-third of the recorded synthetic fibers are of elements or binary alloys. Another third are compounds such as sulfides, phosphides, and halides that do not contain oxygen (Table 2.9). Only three synthetic fibrous silicate compounds are listed, although undoubtedly other experimental silicate combinations have been made but not recorded by us.

The differences between the two lists is not surprising. Metallurgists and chemists are interested in combinations of chemical elements other than those available in nature or those of relatively simple composition and structure. Syntheses of new compounds, regardless of morphology, seem to become more complicated as each new component is added. The detailed physical

Table 2.9 Compilation of the Numbers of Fibrous Synthetics and Fibrous Minerals, as Recorded in Appendices 1 and 2

Fibrous Material Composition	Number of Species	
	Synthetics	Minerals
Elements	35	4
Alloys	39	0
Sulfides	19	16
Sulfates	4	57
Sulfosalts	1	18
Selenides	10	0
Selenates	1	3
Tellurides	12	0
Phosphides	22	1
Phosphates	9	77
Arsenate	0	26
Vanadate	0	14
Halides	27	8
Oxides	37	13
Hydrides	1	0
Hydroxides	0	8
Nitrides, azides	12	0
Nitrates	0	3
Carbides	19	0
Carbonates	1	29
Borides	7	0
Borates	1	15
Iodates/tungstates	4	4
Silicides	10	0
Silicates	3	92
Other oxysalts	7	0
Total	281	388

and chemical information required to perform controlled syntheses vary inversely with the number of elements included. Finally, although many elements and compounds have been studied and phase diagrams prepared (e.g. *Phase Diagrams for Ceramists,* 1933–) the synthesis of fibers of most compounds remains more an art than a science.

Synthetics and mineral fibers have other parallels. A few synthesized fibers show a higher level or secondary ordering of the crystalline structure, such as that described for chrysotile. Composed entirely of carbon, graphite fibers are synthetic fibers with such a secondary structure (see the following section). Tubular fibers of other compositions, such as aluminum silicate polymers, have also been synthesized (Farmer et al., 1977).

Because every element and compound probably can, under special conditions of temperature and pressure, be made to crystallize in a fibrous form, the methods used to produce synthetic fibers offer some insight into the generation of mineral fibers.

Whisker Growth

All of the various methods of producing whiskers may be characterized as "one-dimensional growth." The term refers to conditions that are constrained in such a way as to promote growth in one crystallographic direction. If the basic units, or crystal structure, of the phase to be made as a whisker are anisotropic, the direction of growth is influenced and possibly enhanced along certain directions by chemical affinities that lower the nucleation energy. A well-known example is polymerization.

Preferential growth in a given crystallographic direction can be enhanced. Varying the level of saturation or changing temperature or pressure may enhance growth of a crystalline solid on one crystal face or in one crystallographic direction. Alternatively, growth on a particular face may be retarded or poisoned. Elements or compounds that impede or prevent the development of certain crystal faces can be added to the crystallizing medium. Conditions forbidding growth can also be produced by dense nucleation in one plane, followed by free growth perpendicular to, or inclined, to the plane. The result of these conditions is that only special sites continue to be available for further nucleation and growth.

Restricting the supply of solution or vapor of the required composition during crystallization is an easy and effective means of promoting unidirectional growth. A simple method of producing whiskers is to partially submerge a porous ceramic plate in a saturated solution. Whiskers grow on the upper surface of the plate as the supply of new material from the saturated solution moves by capillary action through the pores to the tip of the whisker, where it evaporates. Electrolysis, a method of separating, transporting, and aggregating specific charged species at a site has also been utilized to produce some whiskers.

The usual method for attaining a single-crystal whisker is by taking advantage of a crystalline species that has a screw axis or develops a screw dislocation on a crystal face (Fig. 2.22). The dislocation provides ever-present growth steps and kinks on the face, or perpendicular to the screw axis, thus facilitating accretion of new material and the elongation and growth of the fibril or fiber. Screw dislocations have been detected in some whiskers, and it has been suggested (Evans, 1972) that the helical elongation through screw dislocations is the exclusive cause of whisker growth.

Whiskers of some compounds are commonly synthesized by vapor condensation methods. These methods take advantage of substances that do not decompose on heating but produce appreciable vapor below their melting temperature. The aluminum oxides, and the carbides and nitrides of silicon, for example, can all be grown as fibers by a direct evaporation–condensation process. In a stable gaseous environment, the material needed for growth is transported to the cooler portion of the container and the growing surface of the whisker using transportation agents, such as volatile oxides. In this process, known as the VLS (vapor–liquid–solid) mechanism, vapor of appropriate composition is made to condense on a suitable substrate, which

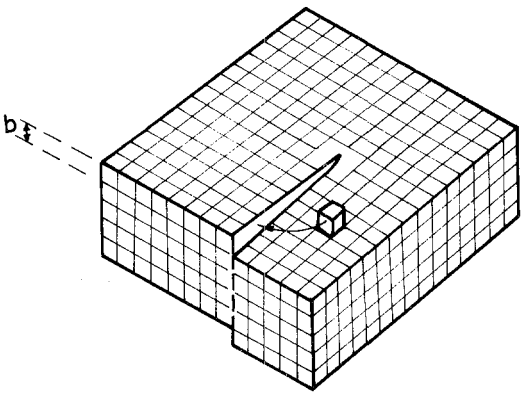


Fig. 2.22 Continuous crystal growth around a central screw dislocation axis. The small blocks are unit cells of the crystalline material and are usually well organized. The displacement site acts as a site for nucleation.

has similar atomic arrangement, distribution and size. Gold and crystalline seeds of the chemical compound forming the whisker, for example, are common substrates. Any impurities in the drop of liquid evaporate into the vapor at the interface as crystallization of the solid proceeds (Fig. 2.23). Subsequent whisker growth is ensured by the continuous condensation of the vapor at the tip of the fiber. Whiskers grown by the VLS method may not exhibit a central screw dislocation, except when such dislocations are inherent in the substrate surface (Evans, 1972).

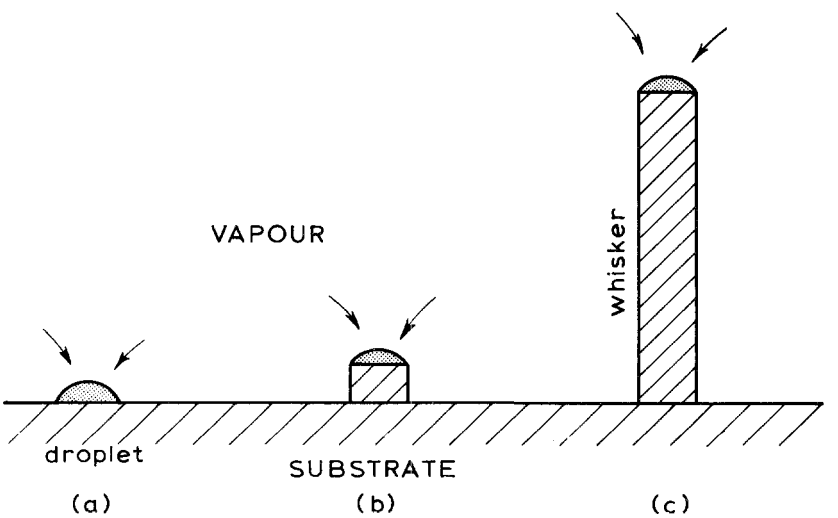


Fig. 2.23 The VLS mechanism of unidirectional growth of a fiber. Vapor condenses on a substrate and continues to localize at the site, providing the necessary material for whisker growth.

The growth of whiskers requires a dynamic system that balances a number of factors. Knowledge of the phase and physical chemistry, including the crystallography, of the compound, are basic information necessary in designing a system of growth that can be monitored and maintained. Not surprisingly, once the special conditions required for production of whiskers are discovered, they become jealously guarded information that can be patented. The compendium by Wilke (1973) contains the most complete description of the diverse methods of crystalline compound synthesis we have encountered. For an overview of whisker technology in English, see Evans (1972) and Levitt (1970).

CARBON AND GRAPHITE FIBERS

The element carbon occurs naturally in several forms, some amorphous (e.g., lampblack), and others crystalline (graphite, diamond). Collectively these solids represent an extraordinary range of stability and physicochemical properties for a single composition. Synthesis of fibers composed of carbon has increased rapidly since the 1960s. The early experiments used vapor deposition. Carbon compounds were grown on fibrous templates, such as silicate glass fibers or tungsten wires, using pyrolitic techniques in which carbon whiskers were generated by cracking ethane (C_2H_6). Today, carbon fibers are produced industrially through thermal degradation of synthetic organic fibers such as rayon. It is estimated that in 1982, 1200 tons of carbon fiber was produced (Fitzer, 1985). The strong, light, stable C fibers are primarily employed in making composites and are used for military, aerospace, industrial, medical, and sporting goods applications. The diversity of uses for the composites and the availability of inexpensive carbon sources such as petroleum pitch have resulted in the generation of many types of carbon fibers.

The fibrous carbon product depends on the source and quality of the starting materials and the method of synthesis. Fig. 2.24 illustrates the production system starting with either polyacrylonitrile fibers (PAN) or petroleum pitch. The materials are first spun into oriented fibers, then heat set to fix their fibrillar alignment; next they are further heat treated, or carbonized, at a specified temperature between 500 and 1400°C, to drive out noncarbon elements such as hydrogen and nitrogen. Further heat treatment, usually above 2000°C, graphitizes or initiates crystallization of the pure C and increases the tensile strength of the fibers. As with the system generating glass fibers there is postformation surface treatment of the carbon fibers to facilitate bonding or association with other materials such as resins, metals, and ceramics in the production of composites.

The crystalline form of carbon known as graphite, is composed of stacked hexagonal networks of C atoms. The generalized structure of such a network is identical to that presented in Fig. 2.1 as the ideal array for silicate sheets. The graphite sheet is simpler in that only one atom, C, is located at the

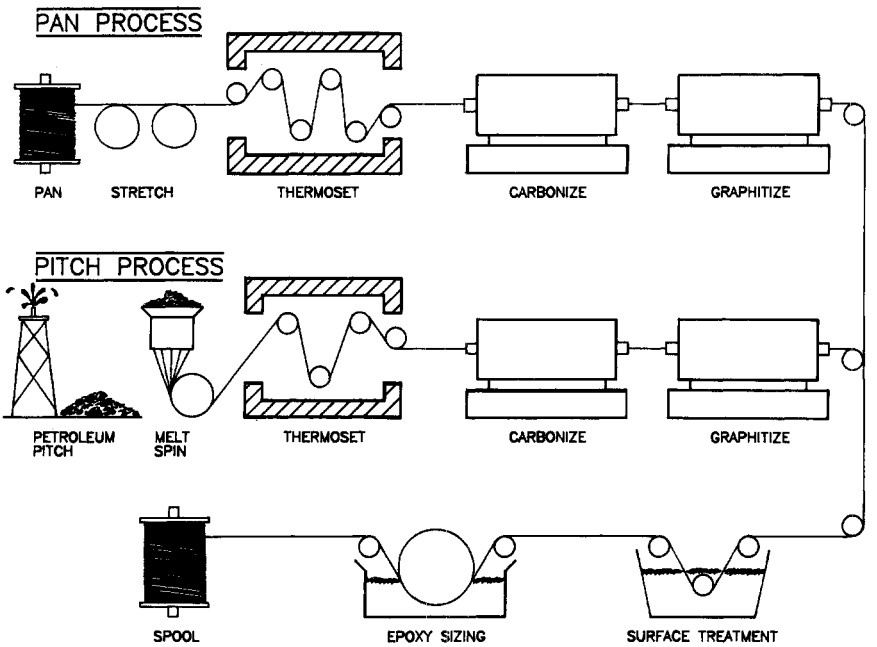


Fig. 2.24 The production process for C fibers. Starting with pitch or polyacrylonitrile the fluids are spun into oriented fibers, thermoset, carbonized, and graphitized to carbon fibers. Surface treatment improves bonding to resin matrix.

hexagonal nodes. Carbon bonds within the hexagonal sheet are exceedingly short (0.142 nm) and strong. Indeed these carbon–carbon bonds are among the strongest known, whereas bonds between the sheets are long (0.342 nm) and very weak (Bernal, 1924). The sheet-to-sheet bonds are so weak that adjacent hexagonal nets do not necessarily superpose. The variations in bond strength are expressed in the characteristic ease of separation of flakes from crystals of graphite directly analogous to that described for talc, micas, and other sheet silicates.

The graphite lattice may show stacking faults or defects within the sheets, and, possibly, bending of the sheets (Fig. 2.25). Omission of a carbon atom (voids), or inclusions of noncarbon elements or molecules, disrupts the orderly configuration and inhibits crystallization of carbon as graphite. These "impurities" act as sites of local strain that directly influence crystallite size, distribution, and orientation within a sample, and in turn affect the physical and chemical characteristics of the material, especially its strength.

Graphite is midway between a semiconductor and a metal in electrical characteristics. The resistivity is very sensitive to impurities, and therefore to crystal perfection, and is directional, being two to three times greater in the basal plane than perpendicular to the plane. Properties measured in the hexagonal plane are independent of the direction within the plane, probably

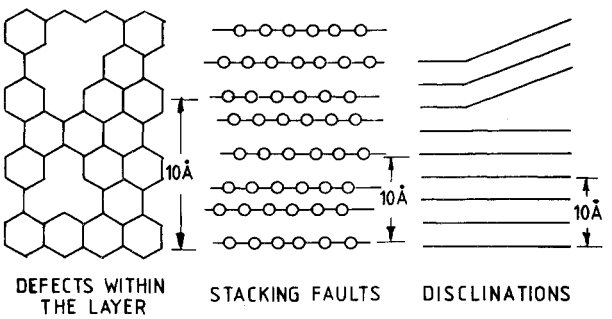


Fig. 2.25 Schematic diagram of lattice defects in carbon fibers.

because disorientation between component layers does not affect transmission.

Carbon Fibers

Carbon fibers are mosaics, that is, they ordinarily contain more than one structural array of the C–C bonds. Within a fiber there might be areas of graphitic crystallites randomly associated with ribbons or single sheets of hexagonal carbon arrays separated by disordered carbon atoms, which is an example of amorponous structure. It has been suggested that such a random aggregation is responsible for the extraordinary strength of some carbon fibers (see Table 1.2). The variations in structure could minimize the ease of crack propagation and contribute to the isotropic character noted in optical and other coefficients measured on carbon materials. Fig. 2.26 illustrates several carbon structures that might be present in a graphitized carbon fiber.

Carbon fibers have been produced with a range of stiffness, strength, and density—physical differences that appear to be related to variations in the

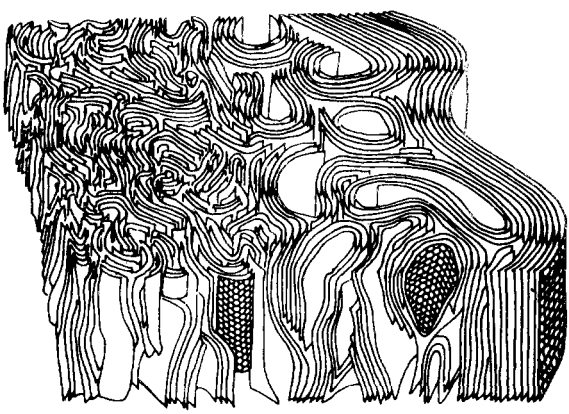


Fig. 2.26 The three-dimensional Johnson model of PAN-based high-temperature carbon fibers.

distribution and ordering of the carbon atoms (or phases) in the body or at the surface of the fibers. The structural order and any lattice defects reflect the starting materials and the specific temperature treatment. To obtain a particular fiber type reproducibly, uniform source materials and strictly controlled pyrolysis are needed. Many carbon-based fibers exist, with a plethora of names. In spite of attempts to regularize the nomenclature (Fitzer, 1985), some confusion will continue as some investigators call the materials carbon fibers and others use the term graphite fibers. The proportion of crystalline or graphite content of carbon-based fibers could be evaluated through quantitative measurements of the physical properties of the fibers.

Surface properties of the carbon fibers can be changed from hydrophobic to hydrophilic by heating fibers in air or adding a coating of pyrolytic C. These treatments are thought to increase the number of pits or flaws on the surfaces of fibers, endowing the fiber with its own surface microtexture. Alternatively, during production C fibers may be preimpregnated (prepregs) to accommodate a specific resin or other application. Because carbon is extremely susceptible to oxydation in air, the preparation of fibers for optimum use would normally include coating or some mechanism to minimize access to oxygen. Surface treatments can increase the strength of a particular fiber sample by up to 50 percent and also increase its durability (Kalnin and Jager, 1985).

Graphite Whiskers

Graphite whiskers are really a polycrystalline material in which the normally planar sheets of carbon atoms curl back onto themselves to form scrolls (Fig. 2.27), reminiscent of the fibrils of chrysotile. The elongation direction of the whisker and the axis of the scroll are in the planar hexagonal sheet so that the sides or surfaces of the graphite whisker are equivalent to the basal plane of the graphite crystal. Graphite whiskers have been made with diameters ranging from 0.01 to 200 micrometers and lengths up to 5 cm, with a continuous C sheet along the entire length of the whisker. The hexagonal carbon plane gives graphite whiskers a perfect surface layer with no edges or steps for stress initiation. Imperfections between layers (stacking faults or twinning) are thought to be relatively unimportant to the structural integrity of these scrolled whiskers.

The theoretical mechanical strength of perfect carbon fibers is between 14 and 20 $\times$ 10^6 psi, while the Young's modulus for graphite whiskers was calculated as 145 $\times$ 10^6. Diamond (the most dense crystalline C modification at 3.5 g/cc, compared with graphite at 2 to 2.22 g/cc) has a Young's

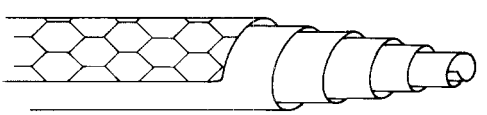


Fig. 2.27 The scroll structure proposed for graphite whiskers.

modulus of 174×10^6. Tensile strength of 2.8×10^6 psi, and a Young's modulus of 102×10^6 have been measured on graphite whiskers (Bacon, 1960). It has been postulated that failure under tension is caused by portions of the scroll pulling out of the sheath, presumably because of the low shear strength between the layers (Bacon, 1958). Graphite fibers are extraordinarily flexible, and may be kinked and straightened many times with no reduction in their strength.

Graphite and carbon fibers, although widely used in a variety of mechanical situations, have certain obvious drawbacks. They have high oxidation susceptibility, high thermal conductivity, and without the scrolled secondary structure graphite fibers may show poor abrasion resistance and markedly different directional strength. However, because graphite is unusually inert, these detractions have not prevented the use of carbon-based fibers in medical applications (Bokros, 1977). Carbon-fiber-reinforced carbon composites are biocompatible and have been manufactured and tested as artificial replacements for heart valves, artificial joints such as hips, and structural supports for use in the healing of torn ligaments, especially in the hand. The normal tendon is a ropey aggregate composed of the biomolecule, collagen, which is also fibrilar in structure. Replacing the tendon with carbon fibers allows growth of new collagen, aligned parallel to the C fibers, and hopefully the successful reconstitution of normal biological tissue. In other medical applications unidirectional orientation is not required and, in fact, is inappropriate (Jenkins and McKibben, 1980). A structure with multidirectional strength and resiliency is needed as a substitute for many biological tissues. It is entirely possible that a composite, carbon fibers in a carbon matrix, or a triphasic C composite (Robinson, 1986) could be constructed for these medical applications. Carbon and graphite fibers and composites are some of the most actively investigated fibrous materials.

This brief summary of the composition and structural characteristics of glass fibers, whiskers, and carbon and graphite fibers illustrates the ranges of synthetic inorganic fibrous materials. The purposes of the construction of these materials is to capitalize on the physical and chemical advantages of the fibrous morphology, size, and state.

SUMMARY

We have recorded 388 minerals (Appendix 1) that occur, at least occasionally, as fibers; some minerals are found only in fibrous form. This number includes more than 92 silicate and aluminosilicate species, most of them common rock-forming minerals. This list, only a fraction of the 3000 minerals known, probably represents only a sampling of naturally occurring fibers.

The composition range of mineral fibers is circumscribed by the natural associations of elements and compounds and fortuitous mechanisms of growth. The existence of so many different species is testimony to the relative ease

of formation and stability of the fibrous form. The compositions that form fibers naturally were and are the primary candidates for synthetic fibrous materials. However, synthetic fibers can be created from virtually any inorganic compound. Several methods, customized for the particular compound, produce fibers efficiently and economically; Appendix 2 lists more than 200 such compounds.

The structural variety of the compounds that form fibers is as diverse as their chemistries. From glasses (fiberglass), and partially crystalline materials (carbon), to special three-dimensional arrays, including polymers, the small, elongate solids may have aspect ratios up to 5000. From our research and compilation (Appendices 1, 2) we noted many mineral and synthetic compounds that have structures characterized by basic linear units. Amphiboles, the major mineral group mined as asbestos, are characterized as double-chain structures. Many of the minerals in Appendix 1 are polymorphic (di- or trimorphs), and where one member of a mineral series has been described as fibrous the others in the same series are likely to be able to grow as fibers as well. Probably all compounds with similar structures and compositions, mineral or synthetic, can form fibers, even though they are not presently listed. It is also clear that fibrous formation is not confined to compounds with linear structural units; indeed the variety of crystalline structure patterns is remarkably diverse.

Perhaps the most intriguing fibrous structure is that of chrysotile, the common asbestos mineral, formed from scrolled fibrils with diameters of about 200 A. The impetus for the natural formation of such a distinctive fiber appears to involve water, its dissociated species (H^+ and $(OH)^-$), and a unique crystal chemistry that fortuitously disposes ions along normally planar sheets. The specific opportunities for generating such fibers, especially for aluminosilicates, are not particularly rare because clays (e.g., halloysite, palygorskite) as well as serpentine minerals abound. However, the same structure is adopted by graphite whiskers, suggesting that the mechanism for producing fibers by secondary coiling must be more general and not confined to solids that contain water.

Scrolled-form fibers, capillary whiskers, and the cage–framework zeolitic fibers offer not only large surface area, but sites for intrafibrillar reactions. These additional sites for adhesion are advantageous for special applications such as the use of fibers in filtration and in the construction of composites. In fact, the synthetic composites most resemble bone, the tissue in which strength and resiliency are essential. It is not surprising that fibers will continue to be much used in our technologically oriented society.

In discussing fibers we adopted a very general definition to accommodate the range of objects called fibers. Needlelike or acicular objects, usually the result of fracture, and often more specifically of cleavage of larger solid samples, have also been labeled fibers. Distinction between fragments and fibers, especially of the asbestos minerals, is probably basic to understanding the reactions of these materials in biological environments because the surface properties are distinctive for each fibrous particle.

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3

Health Effects of Inorganic Fibers

HISTORICAL HIGHLIGHTS AND PERSPECTIVES

It has become fashionable to start discussions of disease related to fibrous inorganic materials by referring to Pliny the Younger (A.D. 61–114), who commented in a letter on the sickness of slaves who worked with asbestos. His observation was forgotten, as evidenced by the fact that during the Middle Ages, Paracelsus (1493–1541) as well as Agricola (1494–1556) wrote extensively on "miner's disease" without mentioning asbestos. Later, Zenker (1867) coined the word *pneumo(no)coniosis* to describe the diseases endemic to coal and iron miners. Differential diagnosis of the pulmonary disorders, tuberculosis, silicosis, pneumonia, and other lung disease was attempted thereafter, although the varieties were often confused even by experienced physicians.

The industry that provided asbestos to modern society started at about this same time (in the 1870s). The first indication of pulmonary disorder in an asbestos worker came in an autopsy report of fibrosis by Dr. Montague-Murray at Charing Cross Hospital, London, in 1899–1900 (Peters and Peters, 1980). By 1902 asbestos was included in the list of dusts considered injurious by the Lady Inspector of Factories, Adelaide Anderson (Oliver, 1902). Auribault (1906) appears to have been the first to note high mortality in workers in an asbestos mill and weaving establishment, but he attributed their illness to calcium carbonate dust rather than asbestos. Scarpa (1908) believed the pulmonary disease of 30 asbestos workers was caused by tuberculosis, and Fahr (1914), who published the case of a female asbestos worker who died of "pleuro-pneumonia . . . with a large number of crystals in pulmonary tissue of a peculiar nature," was clearly somewhat mystified at the presence of nonbiological materials. It was Cooke (1924, 1927, 1929) who first defined asbestos as a specific etiologic agent in pulmonary fibrosis. He described extensive fibrosis with thickened pleura and adhesions to the chest wall and pericardium in asbestos workers and noted the presence of abundant mineral matter ("curious bodies"), but also tubercular lesions. The term *asbestosis* was used in the 1927 publication. Pancoast and Pendergrass (1925) argued that the fibrosis seen in asbestos workers was a result of ad-

mixed silica and an expression of "asbestosilicosis," signifying uncertain etiology of the observed symptoms, a view that survivied into the 1930s (Lynch and Smith, 1935).

After numerous reports from countries around the world (Simson, 1928; Seiler, 1928; Wood and Gloyne, 1930), pulmonary disease was linked with asbestos, and the medical community generally came to accept the pathogenicity of the fibrous mineral material. Soon after a report by Merewether and Price (1930), who attempted to estimate the dust exposure of a group of asbestos workers, a conference between employers and inspectors in asbestos textile factories in England (Employers-Inspectors, Report, 1931) established asbestosis as a compensable occupational disease in Great Britain. In the United States New York was the first state (1935) to include asbestosis in worker's compensation legislation (Peters and Peters, 1980).

It was observed at about this time that pulmonary tumors developed concurrently with asbestosis in humans (Lynch and Smith, 1935; Gloyne, 1936), but the relationship between fibrosing disease and the carcinogenic properties of mineral dusts seemed absurd to the medical/scientific community of that era. Early papers from Germany suggesting a cause and effect relationship between asbestos and lung cancer (Hornig, 1938) were treated with some skepticism in the United States, and a contemporary textbook (Lanza, 1938) asserted that "no definite conclusion can be drawn on the relation between the two diseases" (asbestosis and lung cancer).

Animal experiments were undertaken to test the relationship: 235 guinea pigs exposed to asbestos dusts were found to have asbestosis but no cancer (Vorwald and Karr, 1938), whereas only two pulmonary carcinomas were reported among ten surviving mice after 240 days of exposure to asbestos dust (Nordman and Sorge, 1941). One fortuitous but often cited "animal experiment" was that of pulmonary asbestosis reported in a dog who served for ten years as a "ratter" in an asbestos factory. The animal died of alveolar fibrosis and collapse as a result of "diffuse distribution of asbestos in the lungs" (Schuster, 1931).

Some epidemiological studies (Merewether, 1949; Gloyne, 1951) suggested that the percentage of lung cancer among asbestos workers (9.7 to 14.2 percent) was higher than that expected in the general population (0.7 to 2.4 percent). In the first large-scale prospective epidemiological study on any population, Doll related asbestos exposure to cancer (Doll, 1955). He demonstrated that asbestos textile workers with one or more years of exposure before 1933, the year asbestos industry regulations took effect, had an incidence of lung cancer ten times greater than expected. Although the relationship between smoking and lung cancer had recently become established, smoking histories were not routinely recorded. Therefore, the confounding effect of smoking in this population could not be taken into consideration. The estimate of elevated risk of cancer with asbestos exposure was explicit, however, and indicative of future research efforts. Other researchers found asbestosis but no cancer among asbestos miners, (in Finland, Wegelius, 1947) or only a very low incidence. Braun and Truan (1958)

reported only nine cases of lung cancer among 4000 to 6000 Thetford mines (Quebec, Canada) workers exposed to asbestos, and Cartier (1955), discussing 40 autopsies carried out on 128 cases of asbestosis in Canada, stated that only 6 deaths were caused by bronchial carcinoma. The incidence of cancer in these studies was about that expected in the general population, although the statistical methodology and completeness of the human data were severely criticized (Hueper, 1955a and b). Opinions differed on the relationship of asbestos exposure to the etiology of cancer, and animal experiments appeared not to support the link between cancer and asbestos dust inhalation.

Over the next decade many more epidemiological studies were undertaken in which attempts were made to research the possible contribution of smoking as well as asbestos exposure to the incidence of lung cancer (Mancuso and Coulter, 1964; Elwood and Cochrane, 1964; Selikoff et al., 1964a and b, 1965). These, as well as experimental studies (Wagner, 1962; Smith et al., 1965; Gross et al., 1967), reinforced the hypothesis that cancer and asbestos exposure were related. The early discoveries of tumors in the tissues lining the pulmonary and abdominal cavities (pleural and peritoneal tissues) in asbestos-exposed workers in Germany (Wedler, 1943; Weiss, 1953) was forcefully recalled in perhaps the most important and damning report from the Cape Province of South Africa: Wagner et al. (1960) reported pleural mesothelioma related to generalized asbestos exposure. This paper documented the occurrence of a special form of cancer not only in miners but in their families and possibly in others living adjacent to the crocidolite mining locality. The study of Selikoff on disease in asbestos insulation workers in the United States (Selikoff et al., 1964a; Selikoff, 1965), indicated the possibility that the general public might be at risk. This produced a feeling of a "widening spectrum of asbestos malignancy" (Selikoff et al., 1964b). All of these findings were discussed in great detail at a 1964 conference in New York City on the biological effects of asbestos. The proposition that asbestos inhalation could result in cancer of the lung and diffuse malignant mesothelioma of the pleura and peritoneum met with little opposition (Whipple, 1965).

In recognition of several possible pathologic effects of asbestos dust, there was an effort to define the qualitative and quantitative aspects of the hazard. The biomedical scientists of the 1960s appreciated that asbestos was mined at several geographic/geologic sites in different parts of the world. Testing the carcinogenicity of asbestos required large quantities of standardized materials for animal experiments. Therefore, in 1965 the Union Internationale Contre le Cancer (IUCC) set about providing the samples. Five of the most common commercial asbestos materials were obtained: amosite and crocidolite from South Africa, anthophyllite from Finland, and two samples of chrysotile, one from Rhodesia and the other from Canada (note that no tremolite or actinolite were selected). Literally tons of asbestos was prepared for distribution to all qualified investigators who wrote to the Medical Research Council Pneumonicosis Unit in Penarth, Wales (Timbrell et al., 1968). Much

of the information identifying the specific hazards of asbestos stems from animal (in vivo) or other biological systems (in vitro) experiments using these UICC materials.

The biomedical investigators did not realize that the UICC materials labeled "asbestos" were not well characterized or uniform, nor did most of these researchers at that time appreciate the differences between the minerals. The samples varied, not only mineralogically, but with geographic source, including the possibility that two aliquots of a sample might differ. Dusts generated from the samples were mixtures containing a variety of fiber sizes, if not several minerals. Further, the two samples designated "chrysotile" from separate localities each had its own unique chemical and physical properties.

The conflicting reports from the experiments in the complicated biological systems employed to test the materials are not surprising. In general, the chrysotile samples were found to be relatively more biologically active in vitro than the amphibole-asbestos samples (McNab and Harrington, 1967). However, in whole animal (in vivo) experiments, usually inhalation studies, the amphiboles gave a pathologic response equal to that of chrysotile. The experimental results, unfortunately, conflicted with views of the medical community who thought that of all the asbestos varieties, crocidolite (riebeckite-asbestos) was the most potent carcinogen while chrysotile seemed relatively benign (Wagner et al., 1974).

The differences in pathogenicity determined for the five UICC samples constructed for experimentation, alerted researchers and physicians to the variety of fibrous minerals. Man-made fibers, offered as substitutes for asbestos in many applications, began to be included in the laboratory testing procedures, epidemiological data collection broadened to include fibrous glass factories. The man-made vitreous fibers were relatively purer, and questions of fiber diameter, length, and composition as the salient features in the gestation of disease began to be investigated.

Suggestions for mechanisms of disease induction began with the unique feature of the inhaled particles—their fibrous morphology. Inorganic materials had been noted in the lymph nodes, spleen, and sputum of humans suffering from asbestosis (Stewart et al., 1931), an indication that inhalation of asbestos dust was followed by transport of fibers from the pulmonary cavity to many sites within the body. The size of the fibers in relation to the anatomy and physiology of the pulmonary tree, the possibility of their penetration into cells, and the finding of encapsulated asbestos or ferruginous bodies within the lung tissues focused attention on the physical and chemical attributes of the materials as well as on the biologic responses. The burden of inhaled or ingested fibrous inorganic (foreign) materials stimulated biological defense mechanisms. In some individuals these responses seemed successful in combating both debilitating pnemoconioses and cancer. Asbestos workers in high dust areas with large lung burdens, as measured by the number of asbestos bodies in lung tissues, did not necessarily contract lung cancer or mesothelioma (Gold, in Langer et al., 1979). The expected

dose-response relationship between incidence of cancer and degree of exposure was not observed. Understanding of the effects of the inorganic fibers on the human body would require more study. Not only the availability and transport of the fibers into the pulmonary or gastrointestinal tracts, but the cellular as well as the micro- and molecular-level responses would need to be elucidated. These areas continue to be investigated.

Epidemiological studies encompassing miners as well as those who work on asbestos products (Selikoff and Hammond, 1978) and other fibers (Enterline and Henderson, 1975) continue to be undertaken. Groups of workers needed to be tracked over longer time spans. The pneumoconioses are slowly progressive and cumulative diseases. Lung cancer and mesothelioma, have long latencies, usually around twenty years, before definitive symptoms allow adequate diagnosis. To determine the hazards related to inhalation of fibers, the documentation of occupational exposure and responses needed quantitation and study. Concomitant with general appreciation of the variety of potential health effects, concerted efforts were made to reduce the number of fibers in the workplace. Many countries promulgated regulations (Simpson, 1979).

When a high incidence of mesothelioma was reported (Baris et al., 1978) from an area in Anatolia, Turkey, that had no mining, manufacturing, or asbestos in the vicinity, another fibrous mineral, erionite, was suggested as the culprit. This reaffirmed the opinion that the fibrous morphology was the primary detrimental feature of the inorganic materials. The erionite fibers were part of the environment, and exposure was inadvertent and casual. The Turkish occurrence of mesothelioma appeared to extend the possible risk of contracting cancer to other fibers and, most important, to an unsuspecting general population. This, together with the pervasive distribution of asbestos as insulation in public buildings, for example, galvanized public policymakers and governments worldwide into action. They immediately set about lowering, if not excluding, asbestos from the environment of the workplace, the home, and schools (Sawyer and Spooner, 1978; Simpson, 1979, 1983).

The complexity of the questions that now surround the disease potential of fibrous inorganic materials has increased markedly (Bogovski et al., 1973; Lemen and Dement, 1979; Doll and Peto, 1985). Experimental procedures have been honed: methods of detection and identification of fibrous particulates in air and tissues have been investigated (Siegrist and Wylie, 1980; McCrone, 1978; Marconi et al., 1984). The biomedical community, originally focused on a "simple" trauma resulting from asbestos exposure (Cooper, 1971), has since identified the range of fibrous materials and substitutes (Levin, 1980) and a cascade of effects (World Symposium on Asbestos, 1982; Breslow, 1984). Over the past 25 years international attention, focused particularly on asbestos as a fibrous material and health hazard, has produced a flood of information. New investigative approaches involving and crossing several disciplines have been explored. To place these contributions in context, we present some basic medical background, anatomy and physiology, and include a fraction of what is known and actively under in-

vestigation on cell biological reactions to fibrous inorganic materials. We also review the symptoms and diagnostic features that characterize the diseases ascribed to asbestos exposure that may also relate to inhalation and ingestion of other fibrous materials.

In the process of reviewing the available data on the reactions of fibrous materials in the biological environment, and specifically the medical implications, one is impressed that the information is usually limited or imprecise. Although the etiology of a disease may be suggestive, its mechanisms of induction remain elusive. The variability of the human metabolism, conditions, and experience confound precise conclusions applicable to all cases. Statistically, the hazards connected with occupational exposure to fibrous inorganic materials, especially asbestos, are documented: high-dose and long-term exposure result in high risk of contracting debilitating pneumoconiosis, with some indication of an increased risk of lung cancer and mesothelioma. But the effects of low doses over the long term are difficult to determine. The drive to substitute other materials for asbestos in manufactured products is underway. Zero risk, however, will be unattainable: asbestos minerals are normal and highly disseminated constituents of the earth's surface and the substitutes are other inorganic fibers.

New sets of questions have been generated along with the popular belief that asbestos is so hazardous that it must be irradicated. The estimation of relative risk from asbestos or other fibrous materials requires judgment and decisions by members of our society. These decisions should be rational, and generally appreciated and understood as they affect each one of us. If this volume provides even a modicum of the information needed to allay some of the fears now generated by the mere mention of the term *asbestos* or that all fibrous inorganic materials are asbestos, and therefore dangerous, it will be successful. It is important that the general population has been alerted but sad that many are unable or unwilling to consider the confusing aspects of these potential health problems. The legal and economic considerations related to the present and future use of fibrous materials have enormous implications (World Symposium on Asbestos, 1982).

THE RESPIRATORY SYSTEM: STRUCTURE AND FUNCTION

The lung is an organ that participates in gas exchange. The tissues and structures unique to the human lung provide for oxygen to be taken up from ambient air and absorbed into the blood while carbon dioxide is released from the blood into the atmosphere. A human being inhales about ten cubic meters (10 m^3) of air a day.

The upper respiratory tract begins at the nose and mouth. Air passes into the larynx at the base of the tongue (Fig. 3.1). The opening of the larynx is guarded by a valve, the epiglottis, which closes during swallowing to prevent the passage of material into the lungs. At the lower end of the larynx are the vocal cords, situated behind the thyroid cartilage, also known as the

Adam's apple. The trachea starts at this juncture and extends downward behind the sternum (breast bone), where it branches into two bronchi behind the upper portion of the heart. One branch enters the right lung and the other the left. Upon entering the lungs the bronchi further subdivide into smaller branches, the bronchioles, which open into the alveolar ducts and then into the alveoli or air sacs. At this point the air is in close proximity to the pulmonary capillary blood (Fig. 3.2). The surface area of the gas exchange portion of the lung is approximately 90 square meters (90 m^2). The pulmonary capillary blood volume is approximately 100 milliliters, and it circulates through the capillary bed in approximately 0.75 of a second in a person at rest, resulting in pulmonary capillary blood flow of approximately 4.5 liters per minute.

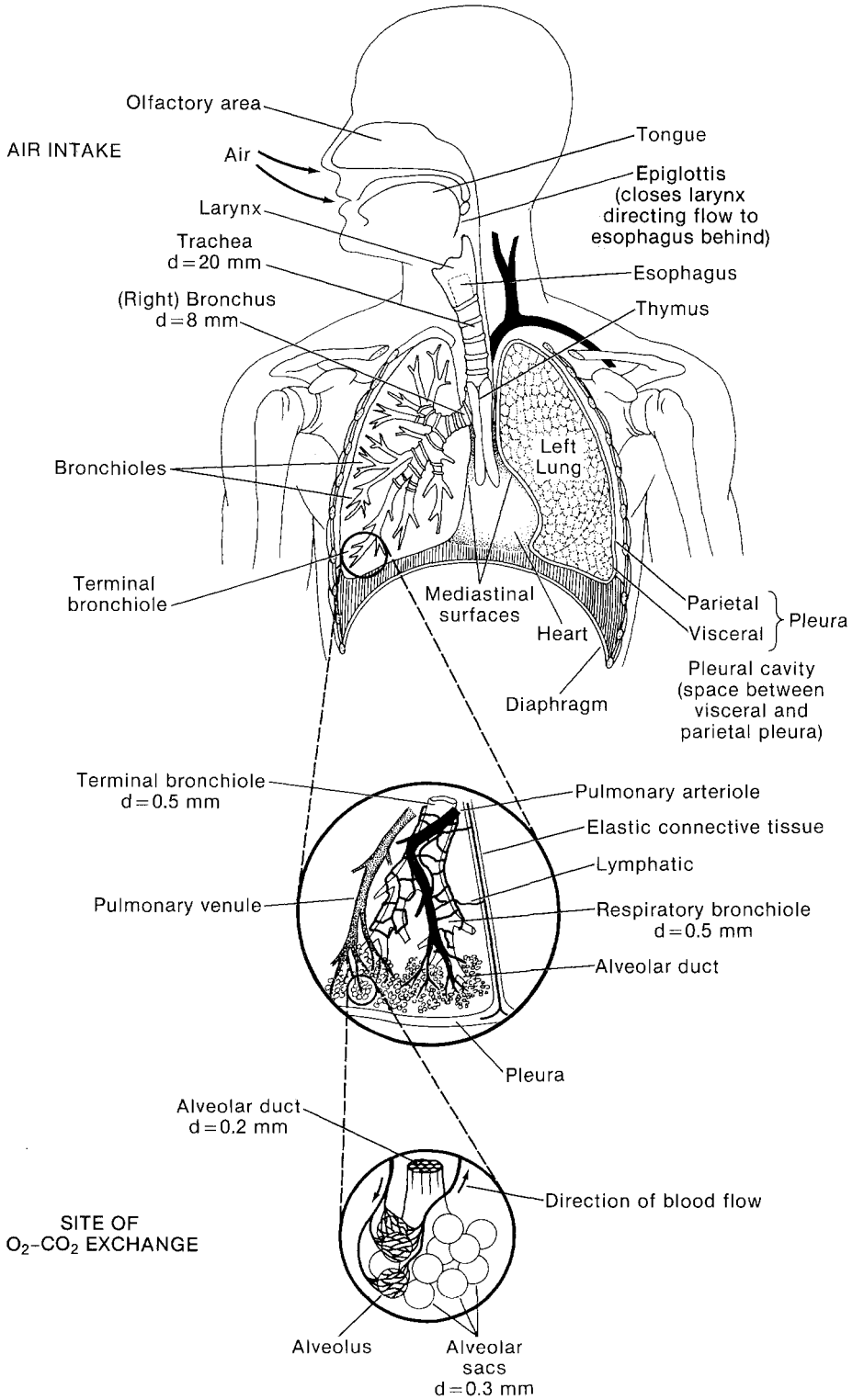
In addition to the oxygen and carbon dioxide exchanged here, this area of the lung is necessarily exposed to other gases (carbon monoxide, nitrogen, etc.) to fluid droplets and to particulates in the ambient air. The air in the lung is essentially saturated with water vapor as it passes through the nasal scrubber to the bronchi, bronchioles, and ducts to the air sacs.

Beginning at the larynx, the respiratory tract pathways are almost completely surrounded by rings of cartilage. Cartilage is a relatively firm tissue composed predominantly of the protein collagen and mucopolysaccharides; it is quite similar to other connective and matrix tissues. The toughness of the tissue and the rings prevent the airways from collapsing when pressure in the lungs is less than the pressure outside. As the bronchi divide into smaller and smaller branches, the rings reduce, eventually disappearing at the bronchioles (diameter about five micrometers). This is considered the end of the conducting airways in the respiratory tract. The respiratory unit consists of the respiratory bronchioles, alveolar ducts, and alveoli (see Fig. 3.1).

The complex functions of the lung and pulmonary system are accomplished through a series of specialized cells (more than forty types have been identified), tissues, and structures. Standard medical texts such as *Gray's Anatomy* (Warwick and Williams, 1973) and *Functional Anatomy of the Lung* (Nagaishi, 1972) should be consulted for details, but for our purposes, we describe four features that ensure optimum lung function, before discussing the diseases that affect the system.

The first is transport. The air, with its variable components, requires the inspiratory activity of the respiratory muscles—namely, the diaphragm and intercostals (the muscle between the ribs). The action of these muscles is under both voluntary and involuntary central nervous system control; thus, gas flow can be adjusted to maintain a steady state of gas exchange. Air must also be provided to the upper airway for speech.

During normal quiet breathing, expiration is largely passive, the lung behaving essentially as a self-deflating balloon with elastic recoil. If it lacks elasticity there is instability of the airways and poor expiratory rates that lead to a pathologic accumulation of air in tissues of the lung, overdistension and stretching of the air sacs, with rupture of alveolar walls, and formation


Olfactory area
AIR INTAKE
Air
Larynx
Trachea
d = 20 mm
(Right) Bronchus
d = 8 mm
Bronchioles
Terminal
bronchiole
Tongue
Epiglottis
(closes larynx
directing flow to
esophagus behind)
Esophagus
Thymus
Left
Lung
Mediastinal
surfaces
Heart
Diaphragm
Parietal
Visceral
Pleura
Pleural cavity
(space between
visceral and
parietal pleura)
Terminal bronchiole
d = 0.5 mm
Pulmonary venule
Pulmonary arteriole
Elastic connective tissue
Lymphatic
Respiratory bronchiole
d = 0.5 mm
Alveolar duct
Pleura
Alveolar duct
d = 0.2 mm
Direction of blood flow
SITE OF
O_2-CO_2 EXCHANGE
Alveolus
Alveolar
sacs
d = 0.3 mm

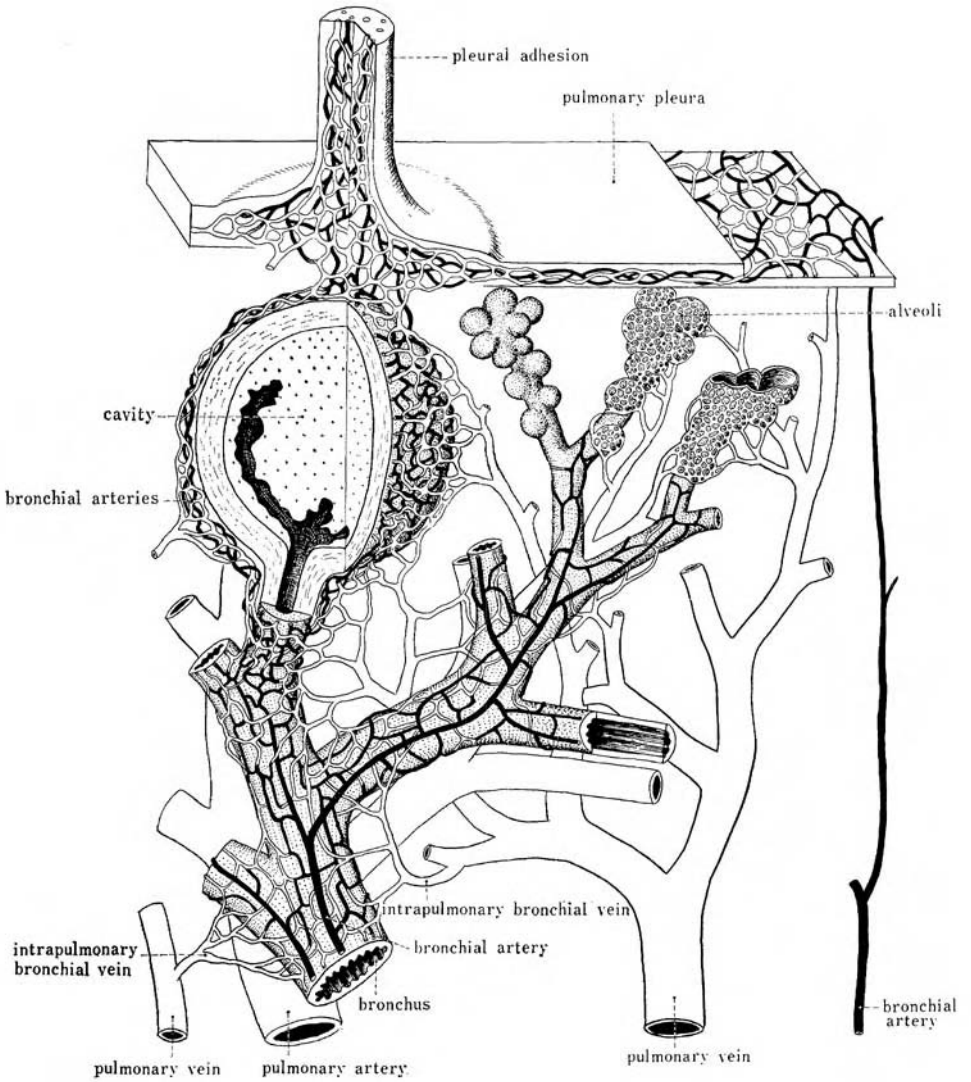


Fig. 3.2 The blood–gas exchange system at the bronchioles and alveolar portions of the pulmonary system.

Fig. 3.1 Schematic diagram of the human respiratory system. The gross anatomy of the lung, the covering membranes (pleura), airways and air sacs (alveoli) are shown. The average diameter of portions of the air flow system are indicated: trachea, 20 mm; bronchus, 8 mm; terminal and respiratory bronchioles, 0.5 mm; alveolar duct, 0.2 mm; alveolar sacs, 0.3 mm.

of areas of emphysema. The result of the changes in the tissue is reduction in recoil and in the surface area for gas exchange at the alveolar wall. In contrast, the fibrosing lung disorders, such as asbestosis, increase elastic recoil. Although the increased elastic recoil increases the expiratory flow rate, scar formation increases stiffness of the lung, hindering lung expansion. Scaring effectively reduces lung volume, and greater muscular effort is required to inflate the lung during inspiration.

The second factor is motion. The lung in the upper trunk (thoracic cavity) is encased by a lining membrane known as the visceral pleura. In fact, this is a dual membrane; one membrane covers the lung and a second membrane lines the chest wall (the parietal pleura, see Fig. 3.1). Characteristics of the pleura are discussed later, but we mention this important tissue here because the movements of the lung are facilitated by the juxtaposition of the visceral and parietal pleura and the thin layer of fluid between them.

Structure is the third factor ensuring optimum lung function. Airways and air sacs have to remain open for adequate gas exchange to occur. Any narrowing or obstruction not only imposes mechanical problems in getting air in and out, but also impairs mixing of gas and its transport to distal air spaces as well as the ultimate function of the lung: exchange with capillary blood. Surfactant, a substance that reduces surface tension, lines the alveolar walls, and the walls of the respiratory and terminal bronchioles. When it is stretched, the surface tension rises; under compression the tension falls to zero. Constriction or contraction, scar formation, or anything that diminishes the alveolar volume diminishes the volume of gas retained in the lung in the interphase portion of breathing (inspiration to expiration), and ultimately leads to defective oxygenation of capillary blood.

The fourth factor is protection. To protect the respiratory tract and exchange, mechanisms exist to expell harmful components from the system. The upper passages of the respiratory system, the bronchi, are lined with ciliated columnar cells. The cilia act as beaters, transporting particles on a blanket of mucus upward toward the larynx, where they can be expelled by coughing or can be swallowed. In addition, a system of lymphatic vessels, found throughout the lung and pleura, removes a variety of materials from the small air spaces, transporting them through ducts into lymph nodes, nonlung structures within the chest cavity. The lymphatic system, including the cells in the lymphatics, is outlined and discussed later.

Another form of protection for the lung is the localized sequestering of foreign materials as "ferruginous bodies" within the parenchymal tissues. Protein coats adventitious particulate matter that may be deposited in the lung tissues. The coating can also contain considerable amounts of iron (as part of the protein species, ferritin), which is easily detected on examination of stained tissue sections with the electron or perhaps the light microscope (Fig. 3.3). It is thought that the encapsulation effectively isolates and immobilizes the foreign particle. Adult humans, especially those who have lived in cities or in dusty environments, may exhibit several hundred thousand ferruginous bodies when sections of lung tissue are submitted to his-

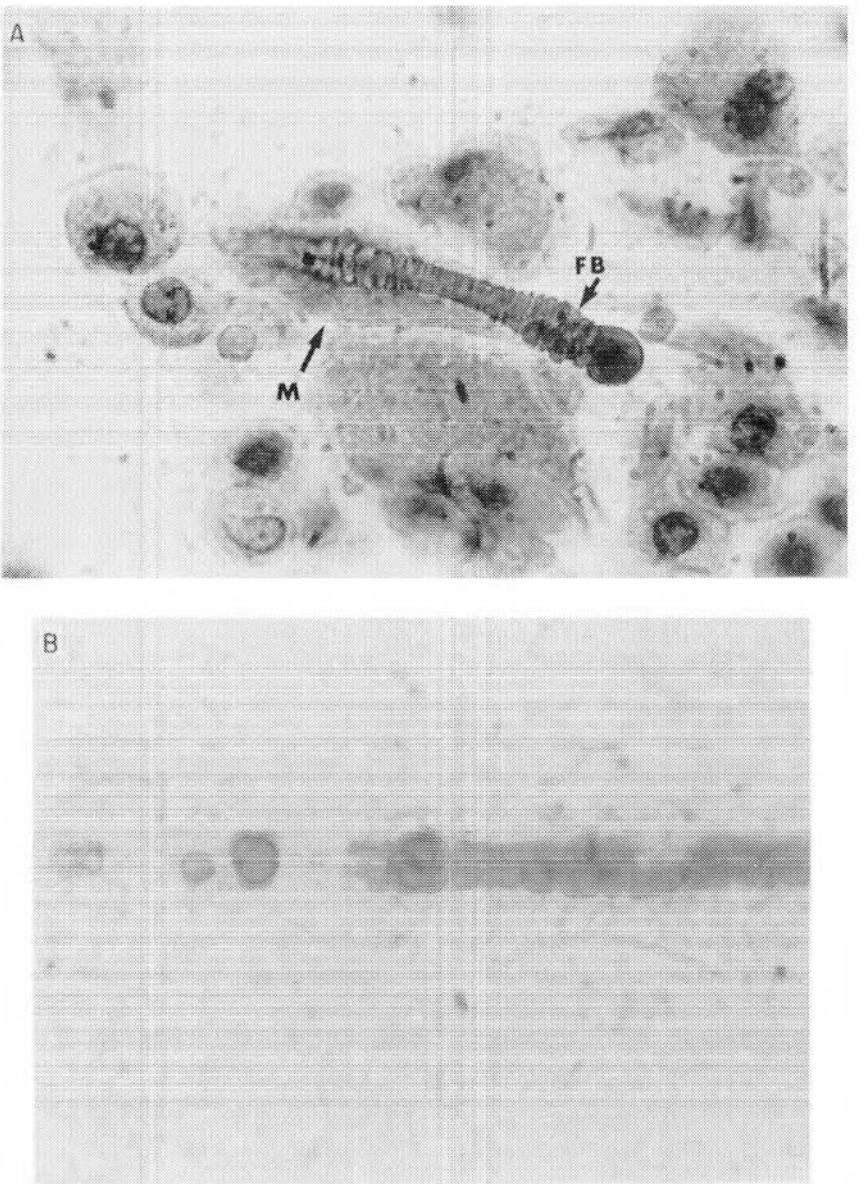


Fig. 3.3 Asbestos or ferruginous bodies. (**A**) Ferruginous body (FB, short arrow) within macrophage cytoplasm (M, long arrow); ferruginous body lies within alveolus among other inflammatory cells. Photographed under oil, original magnification X1000. (**B**) Ferriginous body, as seen on filter; prepared from human lung tissue. Photographed under oil, original magnification X1000.

tological examination. The presence of these bodies does not usually impose any difficulty, nor does it necessarily indicate a pathological condition, that is, the onset of disease. The bodies are one of the natural responses of the system to trauma.

THE PLEURA: STRUCTURE AND FUNCTION

The lung is covered by a lining membrane attached directly to its external surface, known as the *visceral pleura*. A second, similar membrane, forming an internal lining for the thoracic cage, is the *parietal pleura*. The visceral pleura functions as an external barrier, which is relatively impermeable to gases, specifically water-insoluble gases such as nitrogen. Nitrogen, which constitutes approximately 80 percent of the air in the lung, is poorly absorbed by blood and serves as the filling, maintaining the air spaces in a state of inflation. The visceral pleura retains air within the lung parenchyma and prevents leakage into the potential space between the visceral and parietal pleura known as the *pleural cavity*. Leaks, commonly known as *pneumothoraces,* are associated with varying degrees of lung collapse. The visceral pleura is rich in lymphatic drainage channels.

Normally, the space between the visceral and parietal pleura is only a potential space. More accurately, it is a surface covered with a thin film of fluid, to lubricate movement of the lung. Both pleura are relatively flexible and passive, and do not limit the inflation or deflation of the lungs during the breathing cycle.

The pleural tissue is a typical connective tissue that consists mostly of matrix: the fibrous proteins (collagen, elastin), and mucopolysaccharides, and a few scattered mesothelial cells, capillaries, venules, and ducts. Anatomists have defined several layers (Fig. 3.4) for each of the pleura. Layers 3 and 5 in Fig. 3.4 contain an abundance of fibrous protein, especially elastin. Both the interstitial (Layer 4) and mesothelial (1 and 2) layers contain capillaries of the vascular system and lymphatic channels. The matrix (ground substance) gives the pleura structural integrity and is responsible for its mechanical properties such as elasticity and distensibility.

Under normal conditions the layers prevent passage of fluid between the lung and pleural cavity and maintain the inflation of the lung by means of negative pressure, in addition to aiding the motion of the lung. Accumulation of fluid within the pleural space, known as a pleural effusion, is common in certain diseases. It may occur along with a generalized excess fluid accumulation in the body, as during congestive heart failure, in association with tumors affecting the lung surface and pleural cavity, or with inflammatory disease in the lung from infections such as pneumonia. Fluid accumulated in the pleural cavity is usually drained by the lymphatics, a process enhanced by respiratory movements.

Although a good deal is known about the permeability of the pleura to proteins, the transport and reactions of the tissue to particulates such as fi-

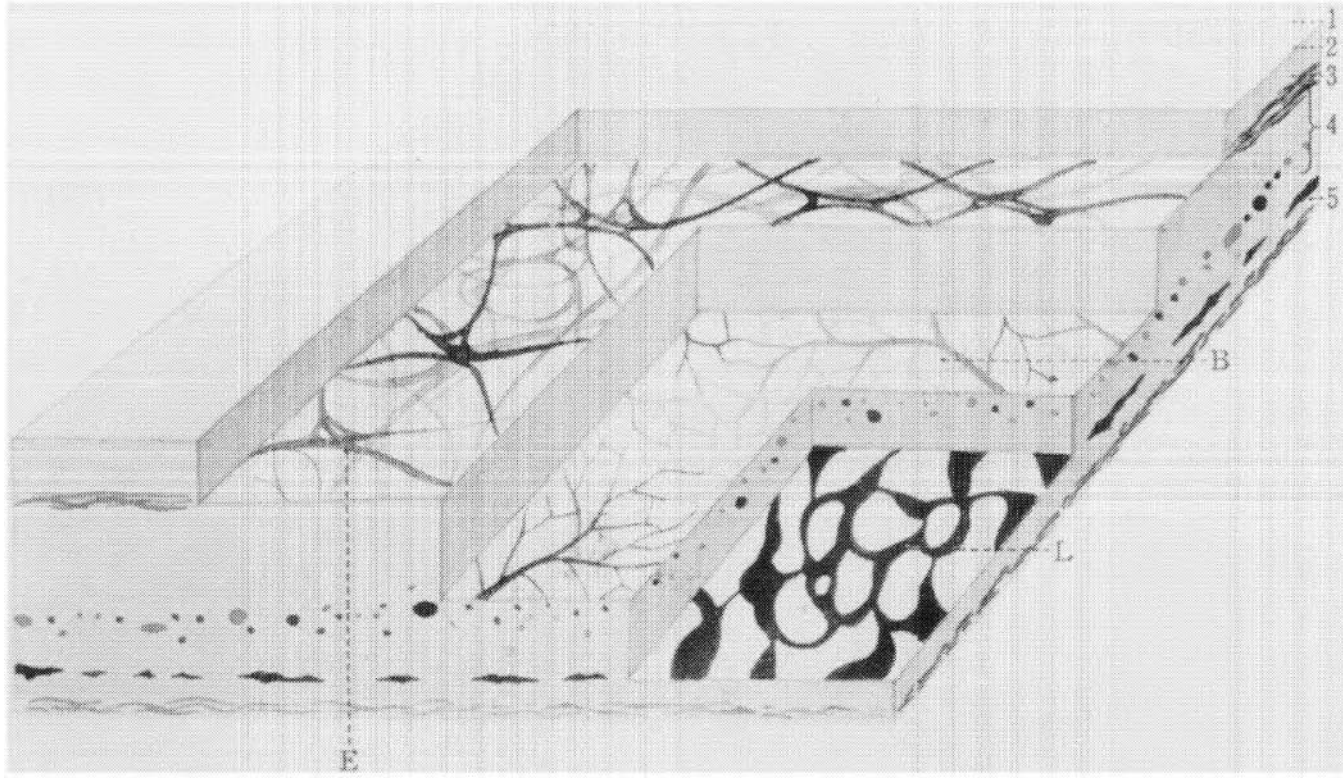


Fig. 3.4 The structure of the pulmonary pleura: 1, mesothelial layer; 2, submesothelial layer; 3, external elastic layer; 4, interstitial layer; 5, internal elastic layer; B, blood capillary net; E, elastic fiber net; L, lymph vessel net.

brous materials need to be further investigated. As will be discussed later, however, asbestos and other fibrous materials are clearly associated with effusions and scarring of these tissues. Scar formation is the localized, and usually enhanced, production of fibrous protein (collagen) that causes general thickening of the pleura or formation of plaques, islands of fibrous proteins within the pleura. Scarring can also result in adhesions between the two pleural layers. Fibrous scar tissue usually causes contraction and loss of tissue flexibility. The areas of plaque can subsequently calcify (deposition of calcium phosphate within the fibrous nodes), totally disrupting the elasticity and tissue viability. All of these changes ultimately impede normal movement of the underlying lung and function.

The tissues of the pleura are considered to be relatively inert, functioning mainly as support structures or frameworks for the ducts and capillaries. The mesothelial cells in these tissues are sparse and their metabolic activities, especially as producers of fibrous proteins required to maintain healthy tissue, have not been fully explored. The mechanisms that lead to increased protein production (i.e., plaque formation) remain under study.

LYMPHATIC SYSTEM: STRUCTURE AND FUNCTION

The lymphatic system is a circulatory system that functions throughout the body to drain and remove fluids accumulating within tissue space. The fluids derive from leakage of the blood or vascular system, particularly from the capillaries. Accumulation of fluid within tissues characteristically distends and may deform the organ and impair function. Water accumulation, or lung edema, is associated with stiffness of lung tissue and rapid, shallow breathing. Fluid in the air spaces impairs gas exchange. The lymphatic system serves an important function in ameliorating such fluid accumulation, in health as well as in disease.

The fluid in the lung tissues may drain either toward the pleura or toward the center of the thoracic cavity (Fig. 3.5). The pleural fluid returns through the lymphatics to the central thoracic cavity, where a duct opens into the venous circulation. Thus, the fluid transported from lung tissue is returned to the systemic blood circulation by the lymphatics. Alternatively, fluid can be transported directly by and into the central lymphatic system.

Much of the fluid movement in the lymphatics is passive, depending on the effects of inflation and deflation of the relatively compliant vessels during breathing. The cyclic motion of breathing acts as a continual external pumping mechanism. A capillary net of small lymph vessels and ducts composed of connective tissues contains smooth muscle. However, the lymphatic system also contains solid structures or lymph nodes, situated at intervals throughout the lymphatic channels (Fig. 3.5B, and indicated on Fig. 3.5A as black dots of different sizes). The nodes are normally tiny at the periphery of the lung, gradually increasing toward the central thoracic structures. Small bronchial lymph nodes grade into larger nodes around the major

bronchi and especially at branch points. In the space between the two lungs, where the heart and esophagus are located, the largest lymphoid nodular tissue—the mediastinal nodes—are found. These nodes can increase in size; they are particularly prominent in some lymphatic disorders.

Lymphoid tissue with its associated cells, lymphocytes, is also found at lymphoepithelial junctions where the cells may be directly exposed to the gases, fluids, and particulates within the airways (Fig. 3.5B). In the bronchus, for example, the associated lymphoid tissue could mount a local response to particulates without involving the generalized, whole body immune system. Lymphocytes are located in the nodes but also distributed throughout the lung tissue itself, either as small focal accumulations or scattered. Pulmonary lymphocytes can be obtained for examination by surgically opening the thoracic duct to the exterior of the body, or individual cells can be extracted from the airways and air sacs of the lung through brochoalveolar lavage. With the latter technique, a fluid is introduced into small sections of the lung; subsequent aspiration of the fluid permits recovery of several types of cells. Lymphocytes are further discussed along with inflammation and the immune system in the section on Inflammation.

The lymphatic system, lined with epithelial cells, contains a highly proteinaceous (albumin) fluid with prominent electrolytes, which are characterized by the associated cations of Na^{+1}, K^{+1}, and Ca^{+2}. In health as well as most disease states lymphatic fluid contains no red cells or cells directly derived from the circulating blood system; in addition to the lymphoid cells, it does contain macrophages, another major cell type.

Derived from the lung tissue, macrophages are migratory cells capable of phagocytosing (engulfing) or consuming particulate matter. Macrophages transport the ingested materials through the lymphatic circulation toward the lymph nodes. Silica particles, for example, that entered the lung and reached the airways or sacs would be consumed by macrophages, transported through the lymphatic circulation, and deposited in the lymph nodes. Nodes with an accumulation of dense inorganic particles stand out as opaque spots on x-ray transmission photographs of the lung. The nodes may also be the site of subsequent calcification. The so-called egg-shell calcification observed on chest x-rays is characteristic and is used in diagnosing silicosis. Similar transport and deposition mechanisms have been postulated for other substances that enter the respiratory system.

Particulates can either cross into the lymphatics at the spaces in the tracheobronchial wall where epithelial cells directly overlay lymphoid tissue or pass through the endothelium of thin capillary walls in the air spaces. The transfer is a portion of a clearance mechanism that assists the lung in maintaining its normal function of gas exchange. Absorbtion and transport mechanisms of a variety of materials that enter the lymphatics continue to be studied. It was shown early in this century that water, dyes, proteins, bacteria, lipids, and particulates enter the lymphatic system relatively easily. The rates of transport and quantity vary with the size and chemistry of the material. Classic studies by Kihara (1924; 1950) and Nishikawa (1941) dem-

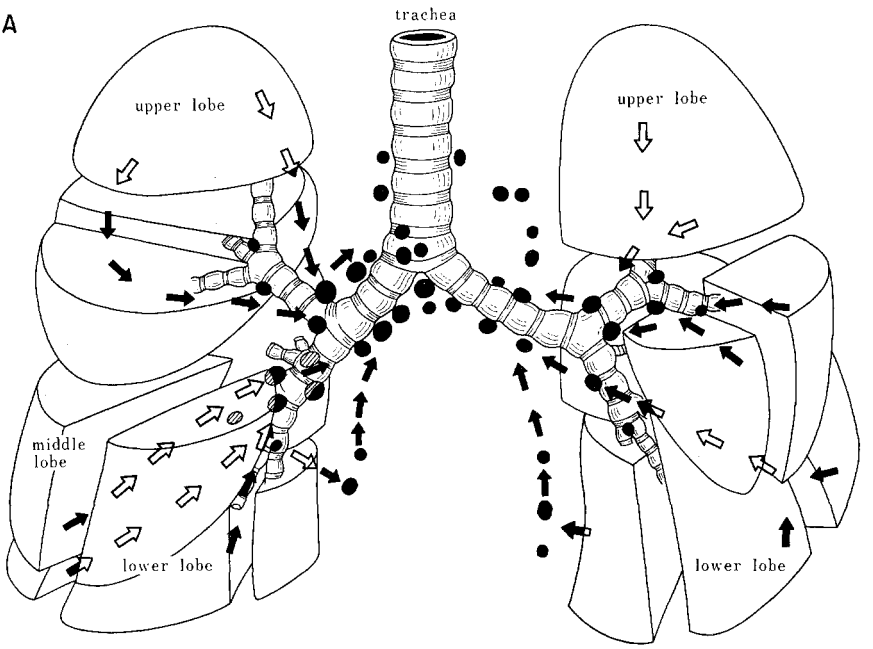
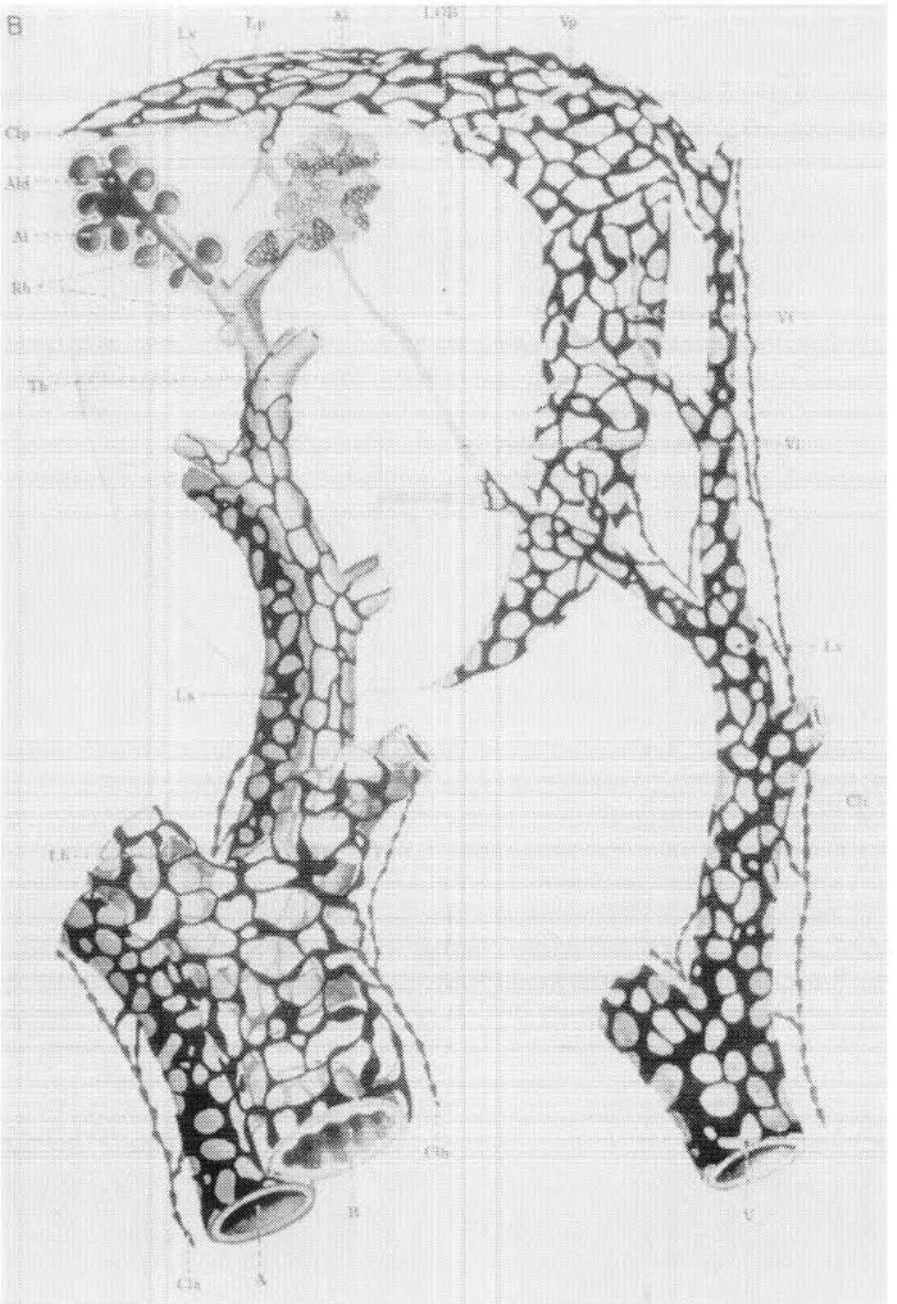


Fig. 3.5 The lymphatic flow system in the human lung. (**A**) Direction of efferent flow of lymph circulation and location of lymph nodes. Note the large size of the nodes at the mediastinum. (**B**) The capillary net of lymph vessels—periarterial, perivenial and peribronchial—and the collecting lymph ducts and nodes.

onstrated that inhaled charcoal powder absorbed by the tracheobronchial wall, for example, was transported through the lymphatics' extracellular fluid pathway to nodes where it accumulated. The powder was also found at the surfaces of the pleura. The black carbonaceous material appeared to cause little disturbance of the surfaces or scar formation and no functional impairment. The charcoal distribution mimicked the characteristic appearance of a coal worker's black lung.

The lymphatic system assumes great importance with respect to the migration and spread of cancer. Cancer cells from any organ ultimately invade the lymphatics. In the lung they are found first in the lymph nodes in the immediate area; migration through the lymphatic channels takes them to other intrathoracic nodes and it is merely a matter of time before the cells reach the central thoracic cavity. The spread of cancer documents the transport pathway. The same mechanisms that help clear particulates spread the cancer cells and complicate surgical resection, in some cases the preferred treatment for malignancy.

For more detailed information on the respiratory tract, the pleura, and the lymphatic system, consult *Gray's Anatomy* or other standard medical texts. A comprehensive review of the lung and its structure and function is presented in Nagaishi (1972).



FIBER INHALATION AND HEALTH EFFECTS

The aerodynamic behavior of a fibrous particle is neither simple nor well understood (Timbrell, 1965). However, once any fibrous particle is suspended in ambient air, there is always the opportunity for inhalation. Fibrous particulate aerodynamics may be related, as a first approximation, to fiber diameter (Timbrell, 1979).

Fibers less than 5 micrometers in diameter appear to be relatively easily suspended, and a small fraction may be inhaled and a smaller fraction transported in the pulmonary system to the alveolar spaces. Using radiolabeled compounds, it has been shown that thin, relatively straight fibers of crocidolite asbestos, with an average diameter of less than 0.25 micrometer, enter the respiratory tract, but about 75 percent of the particles were transported out again. They were ejected up the airways by the mucociliary escalator, and emerged in the sputum. This liquid suspension can be expectorated or swallowed; if swallowed, the fibers would subsequently be excreted following passage through the gastrointestinal tract (Morgan et al. 1977). Curled fibers, such as chrysotile, deposit in the upper airways, particularly at bronchial or bronchiolar bifurcations (Harris and Timbrell, 1977). There they come in contact with epithelial cells, and may be cleared through the mucocilliary elevator (Evans et al., 1973). The small particles, less than 3 micrometers in diameter and less than 10 micrometers in length, could also be transported to the lower lung and the alveolar sacs (Timbrell, 1965; Elmes, 1980), and presumably, along the lymphatic pathways to the nodes or the pleura, as described earlier. Wagner (1980) suggested that fine fibers, especially of crocidolite, might induce the formation of pleural plaques and mesothelioma, the cancer associated with asbestos exposure.

Fibers in the airways could induce metaplastic responses in local cell populations. Metaplasia is the change noted in the normal organizational structure of a cell, which often precedes abnormal or cancerous growth. The airways contain epithelial cells, two types of mucus-secreting glands, and in certain portions, the ciliated cells involved in the clearance of particulates. Metaplasia of the squamous (epithelial) cells is characterized by the cells becoming flattened and scaly. An increase in the number and size of the mucus-secreting glands in the respiratory tract has been noted in people suffering from diseases of the lung caused by particulates (pneumoconioses). The early symptoms of exposure to dusts (whether or not they contain fibrous particulates), are cough and increased sputum, the normal respiratory tract responses to injury. Construction workers and others engaged in dusty occupations often smoke, a habit that undoubtedly exacerbates the adverse respiratory reactions.

Continued lung injury from inhalation of particulates, whatever their source, size, or composition, produces inflammation (alveolitis, bronchitis), and perhaps eventually fibrosis, a pathological reaction that distorts the architecture of the airways (Lippman et al., 1971). Lung function is compro-

mised, and changes in rates of airway gas flow follow. The oxygenation level of the blood and the rate of exchange of CO_2—imperative to normal metabolism in the entire body—are reduced, resulting in general debilitation and perhaps pathologic responses in several organ systems. In addition, inhalation of asbestos can cause mesothelioma, or lung cancer (Becklake, 1982).

Inflammation—Alveolitis, Bronchiolitis, and Bronchitis

Particle deposition in the respiratory tract can initiate inflammatory responses. With repeated deposition, inflammation becomes chronic, and the site or sites of deposition become laden, not only with the particulates, but with several types of cells—fibroblasts, macrophages, leukocytes, and lymphocytes. These cells are normal constituents of the lung, an organ composed predominantly of connective tissue. Lung connective tissue forms the thin membrane that defines the functional alveolar–capillary unit. Inside this air sac and on the membrane are specialized cells required for gas exchange, maintenance, and repair (Fig. 3.6).

Macrophages

If the site of injury or deposition is the alveoli, alveolar macrophages (AM) scavenge and ingest the foreign particulate matter, serving anti-infection and clearance functions. Macrophages have a life span averaging 60 days and

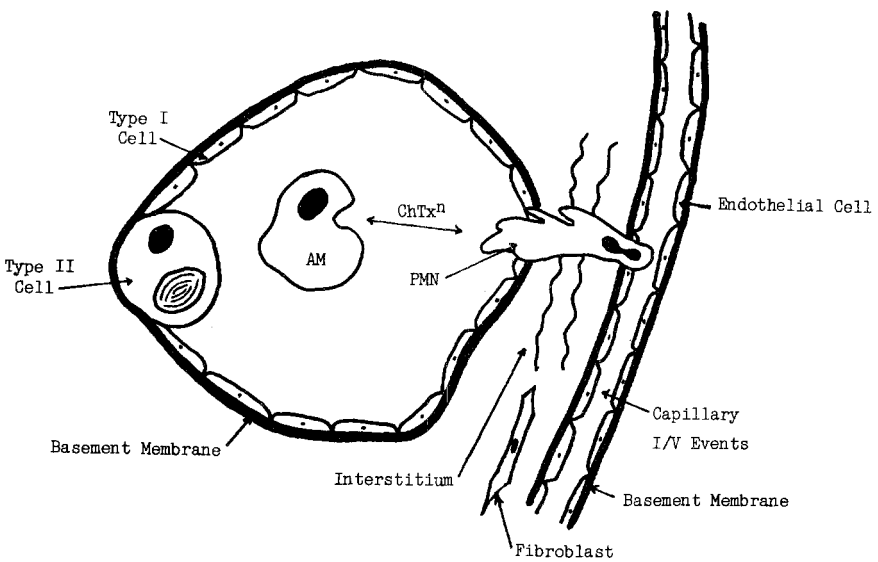


Fig. 3.6 Sketch of an alveolar–capillary unit showing alveolar spaces, cells, and a blood vessel. AM = alveolar macrophage, PMN = polymorphic nucleosite. Other cells indicated: Type I and II intraalveolus, a fibroblast in the interstitium, and endothelial cells lining the adjacent capillary. ChTx^n = chemotaxin.

appear to arise, for the most part, from mononuclear cells of the circulating blood that, in turn, are differentiated from bone marrow cells. There is some indication that macrophages are derived from pulmonary interstitial tissues per se, but local cell division of alveolar macrophages appears to occur infrequently (Furth, 1975). The specific factors influencing AM cell differentiation, especially as a response to injury by particulates, are as yet untested.

The scavenger function of AM is well documented by in vivo and in vitro studies. Fibers less than 5 micrometers in length may be completely engulfed by these cells, which average 10 micrometers in diameter. Longer fibers are often, but not always, encapsulated or coated with ferruginous proteins (ferritin, hemosiderin). The composition of these ferruginous bodies has been investigated by Davis (1970), and their formation and clinical significance have been studied by Churg and Warnock (1977).

Research over the past decade clearly indicates that AM have other functions: (1) release of chemicals that relate to tissue injury; (2) regulation of other cells that determine further tissue injury or postinjury repair; and (3) adaptive response to biologic and other materials to sustain the first two functions. These macrophage activities may contribute to the initiation and progression of fibrosis that characterize the disease called asbestosis. A few details of the experiments performed with macrophages will illustrate the direction of present research.

Because fibers of a certain size and composition are sequestered and essentially stored within a macrophage, their effects on the cell appear minimal. However, in tissue culture (in vitro) experiments, it was observed that lysosomal enzymes were released from the macrophages after phagocytosis of SiO_2 particles. These enzymes cause cell autolysis and can attack the matrix (connective tissue proteins, carbohydrates, and lipids), causing inflammation (Allison, 1977). Incomplete engulfment of fibers can also release enzymes and fibronectin, but in general, asbestos fibers are nontoxic for macrophages (Gee and Fick, 1981).

An immediate response to dust inhalation is the migration of polymorphonuclear leukocytes (PMNs) across epithelial–endothelial junctions to the alveolar space (see Fig. 3.6). Macrophages release a chemotactic factor that mobilizes and attracts PMNs from the pulmonary blood. However, the initial PMN accumulation clears rapidly.

Macrophage release of chemotactic factors also attracts fibroblasts, an effect that has been studied in animals and humans. The factors are sufficiently strong and specific that fibroblasts migrate up a concentration gradient (tested in artificial chambers) and can induce replication (in vivo experiments). Thus, fibroblasts—the primary source of structural proteins, notably collagen—can be mobilized by AM to the inflammatory sites and can also markedly increase in number in response to secretion of activated AMs. These factors, in addition to the other activities and secretions of the AM, are being characterized (Gee, 1984).

Macrophages may also secrete proteases, enzymes that attack other pro-

teins such as collagen and elastin (Nathan et al., 1980). In vitro exposure of rodent AMs to chrysotile and amosite diminished the release of one protease, elastase. Differential release of proteases could alter the balance of structural proteins deposited as basement membrane or, in the case of injury, in the formation of scar tissue. Alternatively since proteases affect the dissolution of proteins in the lung parenchymal tissue, different resorbtion could ultimately change the function of these tissues.

Alveolar macrophages generate oxidizing free radicals during phagocytosis of many materials. The activity, which could cause local tissue damage, has been specifically demonstrated in vitro following cell ingestion of asbestos.

AMs are richly endowed with endoplasmic reticulum (ER). Following exposure to cigarette smoke hydrocarbons in the presence of asbestos, the ER synthesizes the enzyme aryl hydrocarbon hydroxylase. This enzyme converts biologically inactive hydrocarbons to metabolically active forms that, when excreted from the cell, react with the extracellular matrix materials.

What determines the type and extent of the responses of AM delineated here is not clear. These data do suggest that AMs are important cells, not only in clearing particulate materials but in some associated tissue responses.

Polymorphonuclear Leukocytes (PMNs)

Neutrophils, eosiniphils, and basophils—the PMNs—make up the major portion of the white cells of circulating blood and can be mobilized into the lung air spaces by a factor secreted by AMs.

Using the broncholavage technique, asbestos-exposed workers in France with no detectable pulmonary disorder (as judged by x-ray and respiratory function tests) did not show PMN migration (Bignon et al., 1978). In contrast, individuals with active clinical disease (fibrosing alveolitis), regardless of the cause, had an excess of PMNs in the lavage fluid. Intratracheal instillation of crocidolite (in sheep) in large doses did mobilize PMNs.

What is the reason for the migration of PMNs? One theory holds that PMNs play a major role in inflammation and fibrosis—the repair process. Collagenase, a protease found in the lavage fluid of patients with idiopathic (of unknown cause) fibrosing alveolitis and presumably in asbestos-induced alveolitis, appears to be derived from PMNs (Gee, 1984). The collagenase initiates the degradation of collagen, which can subsequently be digested by other proteolytic enzymes. The PMNs therefore initiate the sequence of events by providing the collagenase.

PMNs also produce oxygen-derived free radicals when exposed in vitro to chrysotile or crocidolite. The highly reactive superoxides could injure other cells or attack extracellular matrix molecules. Hyaluronic acid (part of the mucopolysaccharide molecule) is a particularly vulnerable matrix species, but the specific reaction mechanisms have not been elucidated.

PMNs seem to be able to initiate degradation of two matrix tissue components, reactions that could compromise the viability and function of the lung structures.

Lymphocytes

Lymphocytes, mentioned in the description of the lymphatic system and its role in clearing particulates, have been the subject of much recent inquiry because of interest in the immune system (Golub, 1981).

Lymphocytes are of two general types. Those derived initially from the thymus gland, which atrophies at birth (T cells), and those derived from the bone marrow (B cells). Although both types have complicated subsets, it is the B cells that generate antibodies, material of very specific character that identifies and aids in the destruction of foreign (and occasionally host) proteins. T cells, widely distributed after birth, have a variety of functions, one of which is to promote B cell function and thereby enhance antibody formation. T cells also recognize foreign antigenic material, proteins made by the body during previous exposures. T cells, which persist for years, provide an immune memory system through recall of the exposure to antigens. Complex reactions that regulate the immune system occur between T cells and between T cells and macrophages.

Lymphocytes generate antibodies against inhaled materials. The immune system–generated antigen–antibody complexes found in the lavage fluid in spontaneous fibrosing alveolitis patients can cause adverse tissue reactions. The antibodies and other small fragments produced by lymphocytes may, by acting on AMs and PMNs, stimulate these cells to release enzymes or other factors that destroy normal tissue components and lead to fibrosis. The biochemical sequence, set in motion by lymphocyte activities, can create fibrous scar tissue as part of the normal physiologic defense mechanisms of the system. Unfortunately, the buildup of scar tissue interferes with lung function.

Lymphocytes are also found in another type of inflammation known as a granuloma. A granuloma is a tumorlike mass or nodule containing macrophages, lymphocytes, actively growing fibroblasts, and capillary buds. Granulomas may develop in response to chronic inflammation associated with infection. They are common in hypersensitivity-induced pneumonitis (inflammation of lung tissue). The mass is an effective mechanism that localizes or destroys a variety of invasive lower organisms such as bacteria, including tubercle bacillus, or parasites (schistosomes).

Chemotactic factors are also produced by lymphocytes. These factors attract circulating mononuclear cells in peripheral blood, which when localized, may differentiate into macrophages and perhaps other types of cells.

Fibrosis

Fibroblasts

All connective tissues (fascia and membranes) and a large portion of the structural elements of organs such as the lung are generated through the action of a group of cells that can be labeled *fibroblasts*. Fibroblasts are the

cells that create fibrous proteins and mucopolysaccharides, the major components of connective tissue matrix in which the cells reside. Collagen is the most prominent of the fibrous proteins produced. It forms about 65 percent of normal lung connective tissue. At least five distinct types of collagen have been identified. Other fibrous proteins—elastin, reticulin, and keratin, each a family of biomolecules—are also produced by fibroblastic cells.

The fibrillar proteins, like any polymer, can cross-link to form large aggregates. Elastin, as indicated by the name, has some elastic properties desirable in the recoil of lung parenchymal tissue. Collagen forms ropelike structures. Tendons are examples of a tissue composed entirely of cross-linked collagen; their function and reactions illustrate that, although some distensibility may exist, it is minimal. Collagen typically cross-links over time, decreasing the volume occupied by the molecules and stiffening the tissue. Further, collagen is the molecular species on which calcification occurs, both normally (bone) and pathologically.

In scar tissue formation, production and deposition of fibrous proteins is abnormal, above that found in the normal connective tissues. In lung fibrosis the relative volume of collagen and elastin are altered. Fibroblasts increase the production of certain types of collagen, and the effect is to change the flexibility and distensibility of the tissues. Fibrosis at the alveoli results in the loss of air space, through occlusion or contracture, diminishing not only the gas volume but the surface area available for gas exchange. Disruption of the capillary bed by fibrosis lowers the diffusion of gases. Fibrosing alveolitis is but one example; fibrosis in any part of the bronchoalveolar system has concomitantly debilitating results. Fibrosis of the pleura is discussed separately later.

Fibroblasts have another and apparently contradictory capability—namely, the secretion of collagenase, the enzyme that initiates the dissolution of collagen. Mechanisms controlling the creation, extrusion, and deposition of fibrous extracellular components, and the synthesis of dissolution enzymes, are incompletely known. Each of these areas continues to be investigated (Furthmayr, 1982).

Finally, fibroblasts respond to chemotoxins derived from other cells, macrophages and lymphocytes, that could increase fibrous protein production or collagenase activity. For example, some fibrotic lungs show a 2.5-fold increase in collagen (Madri and Furthmayr, 1980).

Fibronectin

Fibronectin is a glycoprotein that has assumed some importance in recent studies of lung cell behavior (Pearlstein et al., 1980). As a surface component of many types of cells, it is partly responsible for cell–cell and cell–matrix interactions. With a binding site for collagen, fibronectin can function as an organizing protein of normal tissue matrix. The molecule is found in elevated amounts in the fibrosed regions of the lung in diseases such as silicosis. Studies of the actions of fibronectin offer promise for increasing our understanding of lung injury and repair.

This sketchy overview of the inflammatory and repair activities at the cell and biochemical levels summarizes the data collected from in vitro and in vivo research. Much more information is required before fibrous materials as pathogens can be assessed or understood. Cell biology research has indicated the variety of roles played by the cells in the lung and their participation in pathological fibrosis. Cells obtained through bronchoalveolar lavage are used in detecting and monitoring disease and evaluating therapy.

Asbestosis

> Asbestosis is a chronic lung disease resulting from the inhalation of asbestos fibers and characterized by diffuse interstitial fibrosis, frequently associated with pleural fibrosis (thickening) or pleural calcification. The characteristic x-ray changes of asbestos are small, irregular opacities in the lower and middle lung fields, often accompanied by pleural thickening and pleural calcifications.
>
> The pulmonary fibrotic changes develop slowly over the years, often progressively even without further exposure, and their radiographic detection is a direct correlate of their extent and profusion. In some cases minor fibrosis with considerable respiratory impairment and disability can be present without equivalent x-ray changes. Conversely, extensive radiographic findings may be present with little functional impairment.
>
> Commonly found in asbestosis are bilateral end-inspiratory pulmonary rales at the lung bases, dyspnea, finger clubbing, and cyanosis, but any or all of these symptom can be absent in any one case. Pulmonary hypertension is frequently associated with advanced asbestosis, and the resultant *cor pulmonale* (right-sided heart failure) may be the cause of death (Lemen et al., 1980, p. 2).

Asbestosis, as defined here, is a parenchymal disease affecting the essential or functional elements of the lung, and not a pleural disease. Asbestosis is another in the group of disorders termed *fibrosing alveolitis,* which consist essentially of the fibrosing of lung tissues that produce disabling symptoms and can cause death. *Alveolitis* indicates the inflammatory reaction at the alveoli (the air sacs at the ends of the bronchioles), and emphasizes the site of the disease. *Fibrosing* indicates the progressive nature of the pathology, that is, fibrosis continues after the original trauma, whatever it may have been, has disappeared.

The clinical aspects of asbestosis are well defined and predictable. First, the lung tissue changes to scar tissue as inflammation, initiated by the cells normally in the tissue or air spaces, is expressed as an increase of inelastic collagen. The fibrosed or scar tissue renders the lung tissue stiff and narrows the airways. Mechanical constraints become obvious as the patient expends more effort to breathe.

In the early stages of the disease, fibrotic lesions can be found in the bronchioles and alveolar ducts of the pulmonary tree. If exposure to asbestos is not documented in the patient's life history, laboratory examination (tissue analysis), to demonstrate of the presence of asbestos fibers and ferruginous bodies is necessary. However, the demonstration of these bodies in the ab-

sence of fibrosis is insufficient evidence to justify the diagnosis of asbestosis (Craighead et al., 1982). Biopsy and tissue analysis (histology), in association with sequential radiographic analysis, is necessary for accurate diagnosis only when an appropriate clinical picture of fibrosing alveolitis and exposure history are unknown.

In moderate to advanced stages of asbestosis the patient complains of shortness of breath (dyspnea). Because of poor gas exchange through narrowed airways and disorganized fibrosed lung tissue, oxygenation of the blood is defective. If the oxygen essential for the variety of metabolic events throughout the body is insufficient, the biological feedback system continues to demand more from the decreased supply in the blood. An effect of severe hypoxia is increased work for the heart. Ultimately the organ cannot respond and the patient succumbs to heart failure.

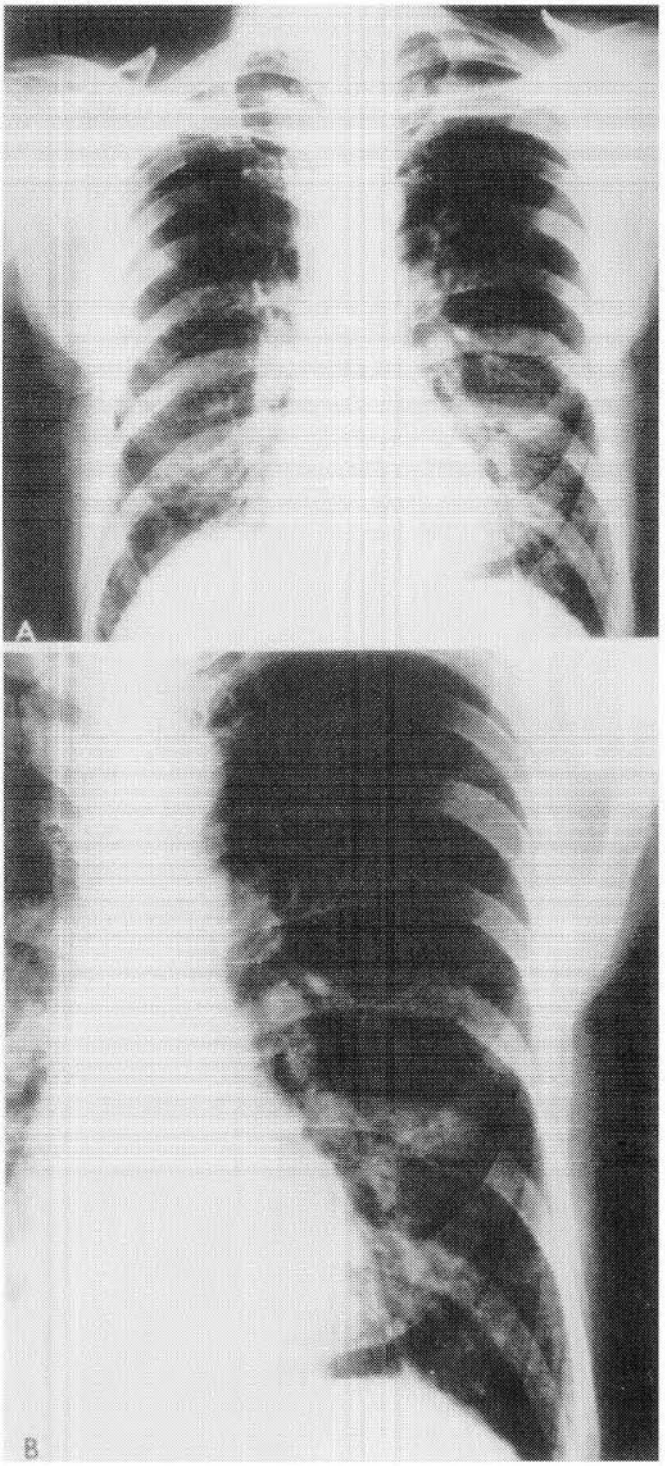
Parenchymal asbestosis can be characterized in the earliest stages through the noninvasive technique of x-radiography. Diffuse irregular or rounded opacities are seen on a chest x-ray film. The first changes noted on the films are fine, pinpoint mottling, or, if the nodules are less discrete, an homogeneous veiling of the whole field giving the appearance of ground glass (Seaton, 1984). The opacities are typically located in the lower lobes. More advanced interstitial fibrosis can be expressed as a linear or criss-cross pattern. As the fibrosis becomes more extensive the sharp borders of the heart and pulmonary vessels take on a "shaggy" outline, and the organs are gradually obscured. Continued fibrosis can increase the linear features and the general hypotranslucency.

Etiology

Wagner (1963) hypothesized that asbestosis might be induced as follows: mineral fibers reaching the alveolar sacs in the lower lobes of the lung attract macrophages. If the load becomes too great or the fiber size is too large for the macrophages to handle, the cells die and the lumen is occluded. The occlusion, a localized trauma, induces a local "normal" tissue response, resulting in the formation of scar tissue. Scar tissue compromises the normal action of the lung, decreasing its flexibility and the transmission of gases. The scar then becomes the site of additional trauma, and the sequence repeats, ensuring continuance of body defense mechanisms, the cascade of cell–biochemical reactions, long after the initial exposure.

Widespread fibrosis in the lung causes tissue and airway disruption and can create air-filled cavities or cysts of various sizes. Commonly, cavities are filled with secretions, appearing radiographically as multiple sausage-shaped opacities. In the late stages opacity spreads throughout both the upper and lower lobes of the lungs (Fig. 3.7).

Fibrotic changes occur in the pleura. As in the parenchyma, however, the early stages of pleural fibrosis may be small and localized, becoming bilateral and extensive over time. The radiological manifestations of asbestosis are frequently nonspecific, that is, the fibrosis detected on x-ray examination occurs in many other diseases. If a pleural change can be detected radiologi-


A
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cally, especially if it is bilateral and symmetrical, the diagnosis of asbestosis is often made. Calcified pleural plaques, especially if detected overlying the hemidiaphragms and anterior, lateral, and mediastinal pleural surfaces, are often cited as indicators of exposure to asbestos fibers, although they do not themselves confirm a clinical diagnosis of asbestosis without a history of exposure. Plaques have been reported with exposure to other dusts, particularly calcimine, mica, tremolite, bakelite, and talc. Pleural calcification can also be the result of another type of injury, such as the reaction to tuberculous empyema (accumulation of pus).

Involvement of the pleura, i.e. formation of pleural plaques (fibrotic masses on the pleura) may accompany asbestosis or occur independently, that is, as lesions with no obvious causal relationship (Whitwell, 1978). Pleural plaques only occasionally cause symptoms, as when they restrict the motion of the lung by thickening the membrane (pleura) around the lung or disrupting tissue viability by calcifying.

Pleural effusions, fluid occurring between the parietal pleura and the visceral pleura, which is often transient and quickly absorbed, may or may not be induced by exposure to asbestos; they are therefore also not strictly a part of asbestosis but can be associated as a symptom. Other symptoms include pleurisy (inflammation of the pleura), pain, and breathlessness.

Complete documentation of the health status of an individual thought to have asbestosis requires recording of the personal medical history and a physical examination. Details of any occupational exposure to asbestos and the levels of exposure are mandatory. Any history of smoking should be detailed. Chest x-rays, usually taken annually, are read using the Union International Contra Cancer/International Labor Organization (UICC/ILO) guidelines. Physiological tests, including lung volume and diffusing capacity, are performed to quantify the functional limits and grade the degree of respiratory system involvement. Therefore, the disease is assessed through four criteria: type of exposure, level of exposure, analysis of the chest x-ray, and finally, measurement of lung function. The final criterion includes the ventilatory capacity, in particular, and estimation of oxygen diffusion from the air in the alveoli to the venous capillary blood that bathes them.

In the most recent and comprehensive review of the diagnostics for differentiating asbestosis from the other pneumoconioses in pathologic terms, Craighead et al. (1982) suggested that clinical symptoms alone are insufficient but justify the diagnosis when combined with an occupational exposure history. A somewhat different tack pursued by pathologists, which could enhance understanding of the disease, was suggested by Craighead and Mossman (1982). The usual direct examination of autopsy material could provide an estimation of the lung burden. The amount and the precise miner-

Fig. 3.7 Chest x-rays of a patient showing early evidence of asbestosis (in the lower lung). **(B)** Close-up of the base of left lung in **(A)** showing the diffuse and linear opacities.

alogical nature, as well as location, of all the fibrous material in the lung could be related to the pathogenesis of asbestos-related disease. Such basic information is essential not only for accurate determination of the cause of death, but for documenting the pathogenic mechanisms operating in a specific patient. These data, together with the clinical manifestations, might define the initiation as well as the cellular and biochemical pathways of disease. In the meantime such analyses can aid in treatment.

Severe asbestosis leading to cor pulmonale is rarely seen today (Gaensler et al., 1985), and presumably the opportunity for contracting such a disease will continue to decline with the imposition of controls limiting occupational exposure. The characteristic irregular pleural opacities seen on x-rays and many noncalcified plaques detected on autopsy and documented in patients with asbestos-related disease (Whitwell et al., 1977) may also be found in casually exposed and even in presumably nonexposed individuals because the lung tissue acts as a filter, entrapping the many varieties of particulates (Lippman et al., 1980). The presence of plaques is usual and unsymptomatic, not necessarily related to fibrosing disease except for certain individuals exposed in dust-filled environments. Many aspects of the etiology of the fibrosing diseases remain to be investigated, but immunological mechanisms have been cited as among the most important.

Pleural Disease

The pleura are connective tissue membranes composed of matrix, mesothelial cells, and fibroblasts. There are two types of pleural responses: benign responses, such as thickening of the matrix, formation of plaques (which may calcify) or effusions, and fluid accumulation in the interpleural spaces between the visceral and parietal pleurae; and neoplastic disease, or the malignancy known as mesothelioma.

In asbestos workers two forms of benign pleural disease have been described (Bogovski et al., 1973). The first and most common finding, largely asymptomatic, is the bilateral thickening of visceral and parietal pleurae. Increase in membrane thickness, especially in certain areas on the parietal pleura, is relatively easily detected on a standard chest x-ray film (see Fig. 3.7). Pleural thickening, however, does not generally parallel parenchymal lung fibrosis. Adhesions between the two pleural membranes are common at the bases of the lung lobes, and occasionally these lesions become calcified, enhancing their visibility on the films. Calcification is a general but poorly understood response to tissue injury throughout the body. These lesions are quite common and usually occur without detrimental effect to normal metabolism or activity of the lung. The calcified areas may spontaneously resorb (disappear) over time.

Pleural Plaques

Another and also quite common observation is the occurrence of pleural plaques. When it is bilateral, the occurrence has been cited as evidence of

exposure to asbestos (Bohlig and Gilson, 1973). There is some indication that asbestos-exposed workers with plaques may be at increased risk of subsequently (about five years) developing asbestosis (Davis, 1984). However, at this time, little direct correlation exists between plaque formation and number of plaques and the incidence of mesothelioma or lung cancer (Whitwell, 1978).

The prevalence of plaques appears to vary with the type of fiber exposure. Plaques have been described in anthophyllite miners, their families, and others dwelling in Paakkila, Finland (Hillerdal, 1980). In the United States plaque formation is common with chrysotile exposure (Selikoff and Lee, 1979). Erionite, the fibrous zeolite, is assumed to be the cause of plaques described in the population of the Cappodocian villages in Turkey, where mesothelioma has also been described (Baris et al., 1979).

In many autopsies on patients who succumb to a variety of disorders, pleural plaques are noted. They are present without associated disease, and seemingly have little effect on organ function. Jacob and Bohlig called them "epidemiological fossils," indicating exposure but not disease (Jacob and Bohlig, 1955). Largely acellular, bundles of collagen are only sometimes calcified. Gaensler suggested an inverse clinical relationship between pulmonary fibrosis and plaque formation: heavy exposure gives rise to severe asbestosis but little plaque formation. When plaques developed without asbestosis they were often detectable on x-ray films and did not change much over the years (Gaensler et al., 1985). Rosen et al. (1972) documented ferruginous bodies in the pulmonary tissue of eighty-six people living in an urban area, but no mesothelioma. Little is known beyond the descriptions of the occurrences of pleural plaques, presumably resulting in humans from inhalation of several types of inorganic materials, especially fibers. These observations parallel implantation experiments in animals (Davis, 1972) in which many materials instilled into the pleura form plaques (Stanton and Wrench, 1972).

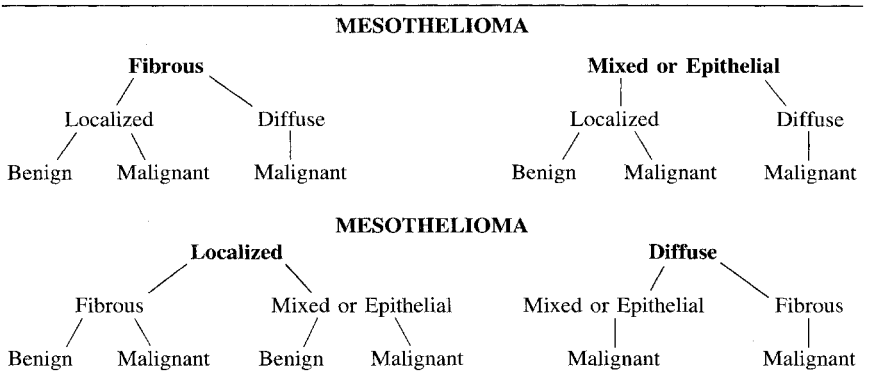
Pleural Effusions

Less common, although the precise incidence is uncertain, is the development of serosanguinous pleural effusions—that is, the accumulation of fluid often containing blood in the space between the parietal and visceral pleural membranes. The effusions usually resolve spontaneously, and no definite link with malignancy exists (Hillerdal, 1981). Some effusions cause pain, but many are asymptomatic and totally benign, although restriction of lung motion because of fluid accumulation has been reported (Gaensler and Kaplan, 1971). Fibers have been detected in the effusions, but no cause and effect relationship has been demonstrated.

Mesothelioma

A mesothelioma is a tumor of the mesoderm. Several types have been described, and some are malignant (Antman, 1981). Table 3.1 presents the

Table 3.1 Mesothelioma Classification Schemes



Source: From Carter and Eggleston (1980).

Armed Forces Institute of Pathology (AFIP) classification, based on histologic examination of the affected tissues. The observation of diffuse or localized tumors, coupled with the histology, shows that all diffuse mesotheliomas are malignant whereas localized tumors are usually fibrous (proteinaceous) and benign. Hillerdal (1983) surveyed published reports and concluded that the benign tumors bear no relation to the malignant tumors. Three distinct histological varieties of malignant mesothelioma are now recognized—epithelial, connective tissue, and mixed (Davis, 1984)—and despite earlier published information, metastasis to lymph nodes, bone, kidneys, and other sites have been observed.

Etiology

Malignant mesothelioma, described more than 100 years ago, is a comparatively rare tumor that occurs in the pleura and peritoneum, membranes that surround the lungs, line the thoracic cavity, surround the gut, and line the abdominal cavity. The survival time of mesothelioma patients is often less than a year, in spite of chemotherapy and radiotherapy. Combined therapy and surgical resection in cases of early diagnosis, a treatment currently being tested, has produced a few long-term (more than five years) survivors (Antman, et al., 1980; Antman et al., 1983), usually in cases with peritoneal rather than pleural involvement.

Designation of intrathoracic or abdominal tumors as mesotheliomas is not straightforward. A mesothelial mesothelioma may be difficult to distinguish from a peripheral bronchogenic carcinoma partly because of the nature of the clinical course of the diseases as well as their similar location. Mesothelioma spreads extensively on the pleura, is usually unresectable, and responds poorly to chemotherapy or radiation. In all of these respects it is identical to peripheral carcinoma of the lung parenchyma, which may spread to the pleura. The diagnostic distinction, perhaps somewhat academic (Gaensler et al., 1985), must go beyond clinical evaluation to tissue examination.

The morphological features of pleural mesothelioma have been investi-

gated by electron microscopic examination of the mesothelial cells (Wang, 1973). Characteristically, the cells contain many bushy microvilli and show greater complexity than the cells in adenocarcinomas (epithelial cell carcinoma). Mesothelial cells have also been shown to lack mucus, lamellar inclusions (Stoebner et al., 1979; Bohlen and Horning, 1980) and rootlets, but unfortunately there are no organelles specific to mesothelioma cells. Ultramicroscopy would therefore be beneficial in confirming the diagnosis, but such an expensive, time-consuming technique is rarely employed.

The difficulties of adequate and reproducible diagnosis have interfered with determination of the incidence of mesothelioma. McDonald studied 11,000 Canadian chrysotile miners and, in 1980, reported that of the 4547 deaths in this group between 1910 and 1975, only 11 were recorded as resulting from mesothelioma (McDonald et al. 1980). At other sites, especially shipyards, mills, and manufacturing plants, other authors had reported higher incidences among individuals exposed to asbestos (e.g., Elmes et al., 1965; Newhouse and Thompson, 1965). Selikoff reported 15 mesotheliomas out of 199 deaths in 689 asbestos production and textile workers exposed between 1959 to 1971, although only 4 such deaths had been recorded before 1966 (Selikoff et al., 1972).

The histological variability of mesotheliomas, now documented, was not known in the early 1960s; this has led to disagreement among authorities on the criteria for adequate diagnosis. There was even disagreement over the accuracy of standard stain tests to designate the nature of the cells involved. Needle biopsies, the usual technique for obtaining tissue samples, provide minimal amounts of tissue for examination and frequently contain cells of pleural effusions. The UICC convened expert reference panels to advise the medical community on mesothelioma (Whipple, 1965), and collaborative communication has greatly decreased the difficulties of diagnosis. The less than 50 percent agreement among experienced pathologists (and much less among those who encounter the disease infrequently) recorded by McCaughey and Oldham (1973) has been greatly improved, especially with autopsy. Table 3.2 summarizes data on deaths from peritoneal and pleural cancer (and asbestosis) in the United States (from Vital Statistics, U.S.A.) since 1968. Unfortunately the statistics are coded to organ not histological types. Annual totals for 1980 (male plus female) of 357 pleural, 123 peritoneal, and 447 retroperitoneal are a fraction (0.9 percent) of the deaths reported from lung cancer (103,844).

The initial connection between asbestos and mesothelioma was made by Wagner et al. (1960), when all but one patient in a study of mesothelioma-related deaths were found to be miners, workers, members of their families, or others living in the area of South Africa where the amphibole-asbestos crocidolite was mined. A comparable occupational exposure to crocidolite has been documented in Australia, with similar results (Armstrong et al., 1984). Mann and his associates (1966) documented three cases of mesothelioma among fifty-four patients dying of pulmonary asbestosis, and in two of the patients the mesotheliomas were peritoneal rather than pleural.

Table 3.2 Mortality from Asbestosis, Pleural, Peritoneal, Retroperitoneal, and Lung Cancers in the United States between 1968 and 1982

	501 Asbestosis 515.2[a]			163 Pleural 163.0			158.0 Peritoneal 158.9			158 Retroperitoneal 158.0			162 Lung 162		
Date	M&F	M	F	M&F	M	F	M&F	M	F	M&F	M	F	M&F	M	F
1982	106	99	7	401	281	120	151	78	73	389	207	182	111,393	79,228	32,165
1981	103	96	7	351	265	86	136	76	60	391	206	185	106,561	76,764	29,797
1980	101	96	5	357	260	97	123	51	72	447	239	208	103,844	75,535	28,309
1979	89	86	3	340	257	83	135	55	80	415	225	190	98,451	72,803	25,648
1978	72	64	8	348	249	99	246	107	139	427	203	224	95,086	71,006	24,080
1977	55	54	1	325	242	83	297	115	182	465	265	200	90,510	68,481	22,029
1976	54	53	1	303	210	93	279	115	164	486	259	227	86,412	65,910	20,502
1975	45	43	2	315	210	105	276	128	148	492	267	225	82,040	63,413	18,627
1974	35	32	3	289	202	87	267	107	160	487	254	233	78,873	61,611	17,262
1973	42	42	0	272	180	92	281	111	170	471	257	214	74,933	59,187	15,746
1972	58	56	2	272	200	72	262	92	170	476	262	214	72,610	57,668	14,942
1971	33	30	3	315	227	88	250	92	158	511	259	252	68,617	54,931	13,686
1970	26	25	1	298	214	84	300	115	185	558	294	264	65,168	52,801	12,367
1969	34	31	3	287	177	110							62,203	50,841	11,362
1968	29	26	3	289	186	103							59,410	48,871	10,539

Source: Data from *Vital Statistics of the United States*, Vol. II, Part A.

[a]Numbers following disease are from the eighth (1968–1977) or ninth (1978–1982) revision of the International Classification of Diseases, World Health Organization.

McDonald and his associates (1973) in Canada found that only 20 percent of mesothelioma cases had a documented history of significant exposure to asbestos, although Selikoff (1977) reported that 7.2 percent of the asbestos workers (in the United States) had the disease. Newhouse and Berry (1979) contended that mesothelioma was often misdiagnosed and stressed the difficulty of reconstructing reliable data on dust levels, especially when the time elapsed since exposure is more than 20 years.

Perhaps a fiber count, or the number of fibers per gram of tissue, is a more accurate test of exposure. Whitwell and his associates, after sampling cases of malignant mesothelioma, lung cancer, and asbestosis, estimated the fiber range as 20,000 to several million. For mesothelioma cases with asbestosis, 3×10^6 fibers per gram (f/g) of tissue was found, whereas for mesothelioma without asbestosis only 100,000 f/g was found (Whitwell et al., 1977). Fiber counts on tissue from asbestosis cases without mesothelioma range from one up to several hundred million (Davis, 1984). The expected relationship of dose to incidence of mesothelioma (or lung cancer) was not obtained.

The Turkish town of Karain, with a population of about 600, reported 36 mesothelioma cases between 1969 and 1974 (Baris et al., 1981), and the nearby village, Turzkoy, recorded 30 of 67 deaths between 1978 and 1980 resulting from mesothelioma (Artvinli and Baris, 1982). These extraordinarily high incidences, implying a devastating epidemic, were related to exposure not to asbestos but to the fibrous zeolite erionite, although the fiber levels in air samples from the environment were less than 0.01 f/cm^3 (Baris et al., 1981). If the diagnoses and exposure levels were correct, several factors in the induction of this disease, in addition to the fibrous habit, had to be considered.

Recently the variety of nonasbestos-related malignant mesotheliomas have been documented; as yet, however, none has been associated with exposure to man-made fibers (Brown, 1983), although other respiratory disease and lung cancer have been (Saracci, 1985). Peterson et al. (1984) lists radiation therapy, the oils on the fibers, silica dust, organic polymers, virus particles, tuberculosis, chronic inflammation, and possibly a range of fibrous mineral and man-made fibers (silicon carbides, e.g.) as potential factors causing mesothelioma. Wright et al. (1984) suggested that the incidence of mesothelioma attributed to asbestos exposure might be somewhat overstated; a bias toward seeing asbestos as the causative agent when any asbestos exposure has been recorded in the patient's records. McDonald and McDonald (1977) had proposed that mesothelioma resulting from asbestos exposure may account for up to 66 percent of reported cases, and these cases were clearly related to hazardous occupational exposure to crocidolite; they estimated, however, that of the remaining cases at least 10 to 15 percent were caused by environmental or possibly casual exposure.

It appears that factors other than dose may play important roles in inducing this cancer in individuals including those exposed to fibrous materials. In-

terestingly, cigarette smoking (or use of tobacco) is not a cofactor in mesothelioma as it is believed to be in lung cancer. Of the 1000 mesotheliomas reported each year in the United States, the actual number attributable to asbestos exposure is unclear. The level and mode of exposure to fibrous materials leading to mesothelioma remains under discussion.

Many investigators have commented on the long interval between occupational exposure and onset of the disease (20 to 40 years). For occupational exposure, the shortest latency period recorded was 13.3 years from the start of employment (mining, manufacturing, dockyard, and insulation workers) to the first onset of symptoms (Browne, 1983). But mesothelioma has also been reported in children with no known exposure to asbestos (Grundy and Miller, 1972). Browne, reviewing the epidemiology of mesothelioma, stated that "no childhood case has ever been shown, on the basis of post-mortem lung studies, to have any probability of being related to asbestos" (Browne, 1983).

Alternative hypotheses to fibrous materials exposure for induction might well be entertained in view of the possibilities of idiopathic etiology of childhood mesothelioma, the latency of onset, difficulty of accurate diagnosis, and uncommon occurrence of mesotheliomas in occupational situations, much less in the general population except in the dusty areas of Turkey.

Pleural Reactions to Fibrous Materials

We have described some of the pathologies in the pleura ascribed to exposure to asbestos and other fibrous materials. If the fibers are the specific agents that initiate and promulgate the pleural disease, by what method do they do so? The initial hypothesis following studies of the Finnish amphibole asbestos (anthophyllite) area where pleural plaques were widespread was that short, straight, needlelike fibers (possibly cleavage fragments) might be able to penetrate lung tissues because of their "needling" characteristics aided by the propulsive effects of repetitive cyclic breathing. Intrinsically reasonable, this hypothesis is supported by the evidence that (1) asbestos fibers can be found in subpleural locations even in the absence of parenchymal asbestosis and (2) pleural plaques are much more common than overt pulmonary asbestosis in every clinical study of asbestos workers. However, chrysotile has been found in pleural tissues. With the occurrence of the "curly" asbestos, a mechanism based on a straight morphology and mechanics is inadequate, at least in this simple form.

Another route for transport to the pleura is lymphovascular. Experimental demonstration that asbestos and glass fibers accumulated in the central (mediastinal) lymph nodes after intrapleural injection led to the suggestion that some retrogressive movement may occur from the pleura to nodes. Second, if fibrous materials can be bloodborne they might be relatively easily moved from the lung to subcutaneous tissues to the pleura. However, a major consideration in disease induction is the cellular reactions in the pleura. The normal pleura, with its monolayer of mesothelial cells and tight intercellular junctions, has phagocytic capacities and a potential for vigorous fibrous pro-

tein synthesis. Rat mesothelial cells in culture exposed to dusts produce collagen (Bignon et al., 1979). Fibrous dusts initially produce granulomata and subsequently intense fibrosis. Of the asbestos fibers, chrysotile seems to be the most fibrogenic, but the degree was lessened by leaching most of the magnesium from the mineral species with oxalic acid. The formation of plaques, presumably also the result of pleural cell actions, is benign.

Parietal plaques are often found without adjacent fibrosis in the visceral pleura. Second, the distribution of pleural plaques, although localized, do not necessarily conform to maximum deposition of fibrous materials, that is, at junctions or apices of the structures within the thoracic cavity. And further, asbestos bodies (collagen-coated asbestos fibers) are not seen in mesothelial tumors (Gaensler et al., 1985). Hypotheses on the relationship of dose to disease and specific mechanisms of disease rather than benign reaction have not yet been fully investigated. Finally, "the pathogenesis of lesions cannot be defined at present, in part because plaques occur only in human beings and experimental models have not been developed" (Craighead and Mossman, 1982). The research to elucidate the mechanisms of disease, specifically mesothelioma, and the possible induction by fibrous materials needs to be intensified (Brand, 1976; Gaensler et al., 1985).

Lung Cancers

The distinction between various types of cancer found in the lung requires pathological examination (Yesner, 1978a and b). There are five major and seven minor separate categories (Yesner and Van Hoff, 1979) based on cell type, but more than 50 percent of these occur as combined forms. The range of cells involved may be from stem cells to highly differentiated adeno or squamous cells. If the carcinoma is confined to squamous cell, either small-cell (oat or lymphocyte types) or large-cell adenocarcinoma, one can confidently describe it, but usually the affected tissue contains more than one cell type in close proximity to each other.

Subpleural lung cancer usually begins in the segmented portions of the lung (Yesner, 1978a and b). The cancer can be localized in the bronchi or found in all portions of lung tissue. Induction and growth of the five major forms of lung cancer have been associated with specific traumas. For example, smokers more often contract squamous or small cell carcinomas and, in general, the greater the insult, the more malignant the tumor is. Exposure to other suspected carcinogens such as fibrous materials are at the early stages of evaluation.

Bronchogenic Carincoma

Bronchogenic carcinoma (Table 3.3) is a thoracic neoplastic disease that has been associated with the inhalation of inorganic mineral fibers; malignancy that arises in the bronchial epithelium. The carcinoma may be a squamous cell or adenocarcinoma, a small- or large-cell carcinoma, may or may not contain asbestos fibers, and may or may not be associated with asbestosis.

Table 3.3 Bronchogenic Carcinoma Classification and Approximate Incidence

	Approximate Incidence (%)
Squamous cell carcinoma	40
Well differentiated	6
Moderately differentiated	18
Poorly differentiated	16
Small cell carcinoma	20
Lymphocytelike (oat cell)	3
Polygonal (intermediate)	14
Other and combined	3
Adenocarcinoma	20
Well differentiated	6
Moderately differentiated	5
Poorly differentiated	6
Bronchioloalveolar	3
Large cell carcinoma	20
Large cell undifferentiated	19
Giant cell	1
Clear cell	0
Combined squamous cell and adenocarcinoma	1

Source: Data are from the Armed Forces Institute of Pathology. (Carter and Eggleston, 1980).

In 1955 Doll established a statistical relationship between asbestos exposure and lung cancer. Subsequently, Selikoff et al. (1968) and Enterline et al. (1975) in America, and McDonald and his associates (1973) in Canada, have confirmed these observations. However, authors who have distinguished between smoking and nonsmoking asbestos workers find only a slight increase in incidence of lung cancer in the latter but a spectacular increase (approximately 50 times) among asbestos workers who are heavy smokers. The effect is multiplicative rather than additive (Selikoff et al., 1968).

Experimental evidence suggests that asbestos fibers are an example of a cocarcinogenic agent or promotor (Mossman et al., 1981) aiding rather than initiating carcinogenesis. Huang (1979), Price-Jones et al. (1980), and Sincock and Seabright (1975) demonstrated that asbestos fibers inconsistently cause chromosomal aberrations. Craighead and Mossman (1982) suggested that fibers may carry polycyclic aromatic hydrocarbons to and through cell membranes, thus rendering the pulmonary epithelium more susceptible to the carcinogens in tobacco smoke, for example. Autrup et al. (1978) suggested that fibers may stimulate AM proliferation, which in turn might metabolize carcinogens to an active state.

Kannerstein and Churg (1972), in reviewing fifty cases of asbestos-associated lung carcinomas and comparing them with fifty cases with no known exposure to asbestos, determined the following distribution of cancer types: twenty squamous, twenty-five small-cell, twenty adenocarcinoma, fifteen large-cell, and twenty combined adenocarcinomata and squamous-cell carcinomata in both series. The only difference noted was that asbestos-associated tumors were localized in the lower lobe whereas the carcinomas not associated with asbestos were more commonly found in the upper lobes. These authors also noted pleural involvement for 50 percent of the asbestos-associated and 33 percent of nonasbestos-associated carcinomas. Although there seems to be little doubt that inhalation of asbestos contributes to the development of lung cancer, much remains to be learned about the relationship to mesothelioma (Whitwell et al., 1977).

Gastrointestinal Cancers

In one way or another some of the dust, from the home or work environment, usually ends up in the gastrointestinal (GI) tract. The original source may be direct (the fibers present in liquids or foods ingested) or indirect (inhaled fibers brought up from the bronchial tree on the mucociliary elevator and subsequently swallowed). All the fibers are transported down the throat (esophagus) into the digestive organs (stomach, intestines) and eventually excreted in the urine or feces (Selioff and Lee, 1979).

A complete description of the lengthy journey through GI tract is not warranted here. The major pathway—the spillback from the respiratory tract—has not been fully studied. The potential health reactions, cancers of the esophagus and stomach, have low incidence in the U.S. population—4.3 in 100,000 and 8.2 in 100,000, respectively, for 1975. Those with higher incidence, such as colorectal cancer (24.4 in 100,000), have a plethora of potential causative agents (Morgan et al., 1985). Even with severe exposure conditions, as suggested for some asbestos workers, little increase occurs (Selikoff and Lee, 1979), including taking into account the difficulty of distinguishing GI cancer from peritoneal mesothelioma and primary from secondary sites for some tumors.

Experimental investigations such as instillation of crocidolite, glass, or synthetic fibers in the trachea of guinea pigs produced fibriosis (especially when the fibers were greater than 10 microns in length) but no tumors, even after two years (Wright and Kushner, 1977). Inhalation studies on rats using high doses and long duration failed to demonstrate a related tumorogenesis (Wagner et al., 1974). Likewise, ingestion experiments to investigate the effects on the gastrointestinal tract in rats for periods up to one year failed to demonstrate even that the fibers were absorbed (Bolton and Davis, 1976). Animal experiments attempting to duplicate (or exceed) the hazards have not been successful in generating the pathologies described in humans and ascribed to asbestos exposure. In a recent evaluation of the more than 40 papers on epidemiology (cohort studies) in asbestos miners, and factory and

insulation workers, Morgan et al. (1985) concluded that previous results of statistically significant elevation of esophageal and somewhat elevated stomach or colorectal cancer in these groups may stem from diagnostic and investigator error.

In summary, very little evidence at this time supports the hypothesis that exposure of the gastrointestinal tract to asbestos and other fibrous materials results in distinctive malignancies. The cells in the gastrointestinal system, if they react to inorganic fibrous materials, may follow the biochemical cascades described for the respiratory tract cells and produce local fibrosis. The general opinion is that even large quantities of asbestos fibers (through occupational exposure) are unlikely to induce gastrointestinal cancer (Doll and Peto, 1985).

Mechanisms of Disease Induction

We outlined the gross and cellular anatomy of the lung as background for summarizing the mechanisms of disease induction associated with exposure to fibrous materials. Such an exercise is a bit premature, as even the normal biologic processes of fibrosis and cell differentiation or action are not fully understood (Gee and Lwebuga-Mukasa, 1984). We can briefly outline some of the experimental approaches that are yielding information at this time. It should be reiterated that the experimental approach received a tremendous impetus when UICC samples were made available in 1965.

Experimental Studies

It is the aim of many investigators to design a model system that will allow testing and observation of the biologic effects of traumatizing agent(s) under known and controlled conditions. Because the experiments are individually devised, the approaches are as varied as the investigators (and as numerous!). The lines of approach can be generalized as follows:

1. Live animal experiments. Fibrous materials are presented, either in the normal physiologic fashion—that is, inhaled or ingested—or inserted (instilled) intratracheally, interpleurally, intraperitoneally, or at some other site known to be affected when humans are exposed to dust-filled environments. This in vivo research, using whole live animals as the experimental system, allows observation of the progression of disease and symptoms. Standard histology/pathology techniques, as employed in human diagnosis, can also be performed on animal samples. Excised materials may become sources for in vitro studies.

Recreating the potentially injurious conditions with an animal permits detailed examination of specific target tissues as well as observation on other systems and portions of the body. Unfortunately, large numbers of animals must be treated and maintained to obtain statistically significant results, and direct translation to the human condition is, at best, uncertain.

2. Portions of human or animal organs, explants, or tissue with cells, or the cell populations themselves can be maintained in culture for extended

periods of time. These materials are the basis for in vitro experimentation. The samples, normally in a fluid medium, offer systems in which the reactions of cells or tissues to a variety of inorganic fibers are relatively easily observed (microscopically). Erythrocytes, red blood cells from normal humans or animals and bacteria are an example of the type of cells employed in these studies. Investigations in cell biology, including engineering of vesicles such as liposomes or microsomes, continue to create new experimental systems for toxicity testing.

Tissue and cell in vitro systems can usually be more completely defined and offer the most direct and controlled experimental procedures that can be employed for detecting and defining early reaction to foreign bodies and following the biological sequellae. The experiments can indicate the relative hazards and provide insight to mechanisms of action. We summarize a few of these studies to illustrate and highlight some of the results.

In Vivo Systems. Rats, other rodents, and baboons have been subjected to the following:

1. Inhalation of fibrous materials with evaluation of acute and chronic toxicity and carcinogenicity on the pulmonary system.
2. Ingestion of fibers in the diets or water, to test effects on the gastrointestinal tract.
3. Implantation or instillation of fibers intratracheally or intrapleurally.

Usually groups of animals are exposed for several weeks or months to different levels and perhaps different kinds of fibers. The animals are sacrificed sequentially to assess ongoing as well as any immediate posttrauma responses. The necessity of observing animals through their normal life span, especially in view of the latency of onset of cancers, was stressed by Wagner et al. (1973).

Using radioactive labeled UICC samples, the deposition and distribution of asbestiform fibers in the pulmonary cavity have been studied. For example, after thirty minutes of inhalation, the deposition of fibers in the respiratory track was shown to be proportional to the median aerodynamic particle diameter for the two UICC chrysotiles, amosite, anthophyllite, and crocidolite. The percentage of total deposited fiber in the lower respiratory tract varied inversely as the square root of the particle diameter (Morgan et al., 1975).

Most studies have found little pathology in the lungs of animals exposed for a few weeks to high doses of the asbestos but pulmonary fibrosis, and occasional malignant tumors do develop when the exposure and observation periods are increased (Middleton et al., 1975). This result suggests that tumorgenicity by asbestos exposure through inhalation has a latency period but is also dose related. The effect of episodic exposure is unknown.

Differences in clearance rates between several asbestiform samples (chrysotile, amosite, and crocidolite) were detected: chrysotile was cleared most rapidly, corcidolite was deposited and retained in larger amounts than amo-

site, and all the fibers showed a dose response. An ultrastructural study of the lungs of rats exposed to crocidolite for five to seven months showed fibrosis and activated macrophages (Miller et al., 1978).

Early studies (Schepers, 1955a and b, 1959) using rats for intratracheal instillation and inhalation suggested that glass wool was not fibrogenic in the lung. These fibers of average diameter (0.5 μm) and length (10 μm) produced an "inert dust reaction" whether the fibers were glass only or coated with phenol formaldehyde or a starch binder. In 1976 Gross reported a macrophage response but no increase in collagen production with glass fiber trauma, although the fibers were observed in the lymph nodes (Gross, 1976). Experiments conducted to compare the effects of long (>10 μm) and short (>5 μm) crocidolite, glass, or synthetic fibers by tracheal instillation concluded that the long fibers of each type and the asbestos materials were more effective in producing fibrosis. No tumors were found after two years of exposure (Wright and Kushner, 1977).

Stanton and Wrench (1972), using a somewhat different system of intrapleural (surgical) instillation, showed a high incidence of mesothelioma from fine fibrous glass with diameters ranging from 0.06 to 3 micrometers and lengths of 1 to 20 micrometers, similar in size to crocidolite fibers. The authors postulated that carcinogenicity was probably related more to morphology than to physicochemical properties of the materials.

Employing glass fibers for experimentation has several advantages if one wishes to test the morphology and size of particulates. They can be made with a specific diameter, from about 2.5 to 0.1 micrometers, and of relatively uniform length with various coatings. Theoretically, homogeneous and reproducible samples can be obtained. Using such materials in intrapleural implantation experiments, Stanton suggested that fibers longer than 8 micrometers and less than 1.5 micrometers in diameter were highly carcinogenic (Stanton et al., 1977).

Other researchers showed that many fibrous materials, in addition to asbestos and glass fibers, produced malignant neoplasms following intrapleural or peritoneal implantation (Wagner et al., 1976; Harrington, 1981), whereas intratracheal instillation initiated fibrosis. Bernstein et al. (1980), comparing different modes of instillation and fiber sizes, concluded that short fibers located in mononuclear phagocytes in the lung and regional lymph nodes, and long fibers incompletely engulfed by macrophages and not cleared to the lymph nodes produced a striking foreign-body reaction. Bertrand and Pezerat (1980) suggested that fibers less than 10 micrometers in length with high aspect ratio might be the most deterimental to health, and Walton (1982) concurred suggesting that the main carcinogenic effect of some materials may be produced by fibers below the size detectable by optical microscopy. No mechanism of carcinogenesis for either small or large fibers has been demonstrated.

These studies reinforce the stiking biologic and anatomic differences in the several components of the pulmonary system, each with its own potentially unique response (Lippman et al., 1980), and some of the difficulties

in interpreting the results of systemic exposure. Several points can be made. First, large doses are necessary to produce fibrosis or carcinogenesis in experimental animals. For example, 10 milligrams or more of fibers are often introduced into the pleural cavity to induce mesothelioma. Depending on fiber size and specific gravity of the material, this is approximately 25×10^6, or 25 million fibers localized at the pleura. These numbers are mentioned not as an estimate of the dosage as much as to introduce another question: Is there a threshold for tumor genesis? Unfortunately such information is unavailable. The amount of fibers necessary to initiate cancer in vivo by inhalation in rats, much less in humans, remains a question. Further, accurate classification of the pleural tumor is as difficult in animals as in humans (Kannerstein and Churg, 1980), and both intratracheal or intrapleural instillation, as well as inhalation of foreign particles, often cause infection, which complicates interpretation and may be cocarcinogenic, thus confounding the course of the disease.

The size of the fibrous particles that appear to induce disease in the animal models is compatible with the measured respiratory range in humans (Lippman, 1977). Most particulate deposition takes place not in the upper or conducting portion of the airways but in the alveolar region of the pulmonary tree (the respiratory unit). Some surface deposition may occur at bifurcations in the bronchial tree, but the actual amount at each location is influenced by anatomy, specific to the species—probably to an individual—as well as the variety of fiber. A large proportion of airborne particulates are rejected as part of the normal clearance mechanisms in animals, but in humans clearance mechanisms may be compromised by smoking, for example. We are unaware of any experiments on fiber toxicity using smoking rats!

Animal model results are indicative of the potential toxicity, but the mode of administration, size of the dose, and duration of exposure may set up different responses from those we can expect in human situations. Biological variation, side effects of treatment, and the workup may introduce artifacts or changes not directly related to the experiment, or may mask the changes sought as the result of the treatment. Some degree of disagreement and uncertainty in interpretation must be expected (even for studies submitted to statistical evaluation), which can be resolved only with further discussion and experimentation.

In Vitro Systems. Different biochemical approaches provide a variety of methods for comparing and evaluating fiber toxicity. Organ cultures, cultured cells, and cells in suspension from humans and animals can be exposed to fibrous materials or, alternatively, cells from treated animals, bacterial cells, and so on can be used. Many hundreds of experiments have been performed, but it is difficult to apply the results, and in many cases extrapolation to humans is not warranted. Nevertheless, cell systems provide excellent data on which to base our understanding of the mechanisms related to fiber-induced disease; a few selected examples follow.

It appears that asbestos and glass fibers are not mutagenic in bacterial

assays (Chamberlain and Tarmy, 1977), but several in vitro experiments suggest differences in relative activity between fiber types and fiber sizes (Allison, 1977). Chamberlain and Brown (1978) found that quartz dust, for example, had little effect on two nonphagocytic animal cell lines, but all the UICC asbestos varieties were cytotoxic.

Cultured hamster trachea exposed to crocidolite showed histologic and ultrastructural evidence of cytotoxicity, regeneration, and fiber transport into the submucosa (Mossman et al., 1977). The full range of cell reactions could be induced by fibrous materials on tissue sections.

Hemolysis, or the destruction of red blood cells (erythrocytes), has been demonstrated; it is suggested that this is directly related to the surface charge on the asbestos fibers. Different varieties of asbestos gave distinctive responses, with chrysotile being the most active (McNab and Harrington, 1967; Wright et al., 1980). Pulmonary surfactant reduces the charge on the fibers and the hemolytic activity (Light and Wei, 1977; Gabor and Anea, 1975). The red cell cytotoxicity implies that fibers can have direct cellular effects and might induce other adverse reactions, such as inflammation.

The effects of toxins are, generally, proportional to dosage. Well-controlled dosage, as in these cell systems, provides the best opportunity for relating carcinogenicity to levels of exposure. In live animal experiments, the amount administered is usually defined as the exposure. However, not all fibrous particles will ultimately reach a specific "target" tissue. Measurement of the fiber load at the tissue site and the pathologic response are tedious but necessary procedures to evaluate this aspect of the problem.

Using in vivo techniques, natural and synthetic fibrous materials have been shown to induce fibrosis and carcinogenic responses that were directly related to dose, if the materials were placed on the target tissues. Chrysotile appeared to be more biologically active than the other UICC asbestos samples or fibrous glass, with particle size and shape having some influence on the response. In vitro experiments indicate that fibers can be cytotoxic and possibly mutagenic, increase the secretory activity of fibroblasts, and possibly initiate an immune cascade.

EPIDEMIOLOGY OF EXPOSURE TO FIBROUS MATERIALS

Information on the incidence of disease related to fibrous materials is overwhelmingly focused on asbestos, with a few studies being done on glass fiber exposure. This is not surprising in view of the long history of use and the initial identification of the medical problems associated with asbestos.

Because of the international sources of asbestos minerals, the variety of manufacture and use of asbestos and asbestos products, notably as insulation and in cement pipe, coupled with the publicity given to their potential health effects, there is probably not a single country in the world that has not become attuned, in the last ten years, to the hazards of asbestos exposure. The epidemiological data collected on disease related to asbestos exposure, es-

pecially asbestosis, lung cancer, and mesothelioma, know no geographic or political boundaries.

Two types of epidemiological data are commonly encountered. One is the individual or collected medical cases that describe pathological particulars in detail and may suggest the etiology (mode or mechanism of induction, source or agent of trauma) of the disease. The other type of data are studies that examine health statistics for groups of individuals (cross-sectional or cohort studies). Group studies might examine the health of workers from a particular industry, usually geographically defined, such as the chrysotile miners in Quebec (McDonald et al., 1980) or females employed in the manufacture of gas masks in Britain during World War II, who were exposed to crocidolite (Wignall and Fox, 1982). The mortality of a well-defined group (cohort) is followed over time to ascertain the incidence of disease in response to duration and degree of exposure. Deaths in the group are compared to those in a reference group (e.g., the general population of the United States), and Standardized Mortality Ratios (SMR) are calculated.

$$\text{SMR} = \frac{\text{deaths from a particular disease}}{\text{expected deaths from the disease}} \times 100$$

Expected deaths are obtained from mortality tables, which are compiled from documented causes of death (usually death certificate) for the population of a nation or an area of a country. The usual sources of mortality data are mortality rates, commonly in five-year age groupings, published annually by vital records offices of a country or political subdivision (state, county, etc.). Some of the data sets are available through the World Health Organization tabulations of disease worldwide, which are based on the International Classification of Diseases.

To determine whether there is a direct cause and effect relationship (i.e., of mortality and asbestos exposure) an estimation of the exposure level or cumulative dose is required. The group may be subdivided into "heavily exposed," "lightly exposed," "unlikely to have been exposed," or some other scaling method may be employed. Biases due to age, sex, or race in a single study or in a group of studies are worrisome and have been the cause of lengthy discussions (Armitage, 1971). The specific methodology used in epidemiological studies are usually discussed as part of the reports and become especially important when the projections, based on the results of statistical data, are examined (Doll and Peto, 1985).

It is not possible to present the range of studies that have documented the occurrence of disease associated with exposures to fibrous materials succinctly; they number in the thousands. Nor could we begin to do justice to the large body of data in the cohort studies that have been analyzed by epidemiologists. We will try to present current overviews. In 1981 Doll and Peto, two well-known epidemiological investigators, examined the quantitative aspects of the causes of cancer, and induction of lung cancer and mesothelioma by asbestos was one of the topics covered (Doll and Peto,

1981). Their more recent review (Doll and Peto, 1985) specifically on asbestos should be consulted for details, because here we present only a summary of our understanding of the present status of the expected risks based on epidemiologic data.

Some caveats should be taken into account in interpreting epidemiological data. Foremost, from our viewpoint, is the fact that in some reports the actual fibrous species—minerals or synthetics—considered to be the traumatizing agents are inferred rather than known. The agent for a workforce in a chrysotile mine is obvious, but in many industrial or manufacturing situations, where more than one fibrous material may be used, it is not so. Second, although the mineral/synthetic varieties may be known, it will probably require a great deal of work, if it is possible at all, to document the history of exposure for a particular worker. The levels of exposure and cumulative dosage received by an individual must be estimated, in spite of the availability of data on the general level of dustiness, air pollution, or fiber content in the workplace. Measurements of the amount of fibers (not dust) in the environment through assay (usually optical examination of membrane filter samples of the air at work stations) have only relatively recently been developed and consistently used to monitor the potential airborne hazards in the workplace (Timbrell et al., 1968). The exposure level of an individual vary with the particular job and tenure in the position. Actual workday exposure history, scaled to arrive at cumulative exposure, is more guesswork than factual, and error factors of orders of magnitude must be considered. The statistical analysis of a group of workers must also take into account the fact that the workforce is mobile. The method of obtaining the most reliable data on exposure—examination of the lung burden postmortem (Mow'e et al, 1985)—is also open to question because it is known that fibrous particulates in the (human) biologic environment have different dissolution rates. One might expect very small fibers (with large surface areas) to more easily dissolve, thus clouding the results from this quantitative approach.

Determining exposures through measurement has changed since the initial identification of fibers as potential health hazards. Originally the weight of particulates per unit of time was equated with exposure, whether caught on a filter or in the lung tissues. Now the number of fibers (fibers per milliliter of tissue, or fiber counts) and the dimensions, including the ranges, of the several types of particles in a sample are considered critical information in estimating the hazards and possible etiologies of disease (Pooley and Clark, 1979; Wagner et al., 1982). With more sophisticated approaches, the designation of a "legal" fiber (a particle with a 3:1 aspect ratio and diameter of less than 5 μm) has been criticized (Doll and Peto, 1985). Accurate counts and identification of smaller fibers usually requires ultramicroscopy (Churg, 1982; Rogers, 1984), which is hardly practical for workplace air pollution monitoring.

Researchers are also concerned that the certificates designating cause of death may be misinterpreted. In many cases the demise does not obviously

bear a direct relationship to trauma from fibrous materials per se (i.e., cardiac arrest, pneumonia), and extrapolation to include or exclude such information is necessarily subjective. In addition, the cause of death may be assigned without the examination of tissues that is essential for specification (of mesothelioma, for example).

In spite of these confounding aspects, higher SMR and elevated risk are usually associated with occupational exposure to asbestos materials, especially for those workers employed before 1970 when dust levels were higher (Nicholson, 1985). A direct relationship has also been established between cumulative exposure (dose) and asbestosis, which may or may not include pleural involvement (Acheson and Gardner, 1983). Lung cancer and mesothelioma (of either the pleura or the peritoneum) have also been related to exposure to asbestos and erionite, but a direct relationship between dose and these diseases, although generally accepted, is less clear (Wright et al., 1984).

Asbestosis or fibrosing alveolitis are more obviously and easily defined and documented as the direct result of occupational asbestos exposure. However, the Simpson Report states that there is a "paucity of data on the frequency of asbestosis to fiber type for jobs of comparable dustiness" (Simpson, 1979, p. 8). Although no definitive conclusion can be drawn from epidemiological studies, there appear to be differences in responses between the several asbestos mineral species (Acheson and Gardner, 1983). Crocidolite, the mineral first associated with mesothelioma (Wagner et al., 1960), appears to be the most virulent. The data linking crocidolite with mesothelioma incidence come mostly from small groups compared with the size of chrysotile cohorts (Doll and Peto, 1985); in discussions on Rochdale, where workers were exposed to both crocidolite and chyrsotile, Peto (1980) implied that high concentrations but short duration of exposure to crocidolite were responsible for producing the observed mesotheliomas. No published data link exposure to crocidolite *only* directly to lung cancer, but amphiboles in general seem to be related to more malignant disease than chrysotile, the serpentine asbestos. Exposure to chrysotile alone does not seem to initiate mesotheliomas (McDonald and Fry, 1982), although it has been strongly associated with lung cancer (McDonald et al., 1983).

The risk of gastrointestinal cancer from exposure to amosite asbestos has been suggested, but the reported studies are inconsistent (Peto et al., 1977; Selikoff et al., 1979; Morgan et al., 1985). Other cancers ascribed to asbestos exposure (ovarian, alimentary tract, for example) have low incidence (low SMRs), inconclusive evidence in establishing cause and effect. The amphibole materials, with their characteristic cleavage into sharp, finely divided particles and their low solubility (relative to chrysotile), are cited by many investigators as the "bad actors" in disease induction.

Mindful that mesotheliomas are rare tumors, publications describing non-asbestos-related malignant mesothelioma have now appeared as more critical pathological diagnostic techniques have focused on this particular cancer (Peterson et al, 1984). There are cases of juvenile mesothelioma (Wasser-

man et al., 1980), which complicate theories on both the induction by asbestos materials and the lengthy lag time typical of the occupational incidences. Cofactors, particularly smoking, do not appear to be important in the gestation of the disease (McDonald and McDonald, 1977). It is difficult, however, to assess all possible contributing factors without some obvious lead. Indeed, based on the reported deaths in isolated townships, the zeolite erionite seems to be the most hazardous mineral material. Furthermore, because the exposure is nonoccupational, morbid fear has been generated in other sections of the world. Questions on the idiosyncracies of the populations and the local concentration of erionite relative to other possibile fibrous materials (tremolite, for example) have been raised.

Interestingly, facilities producing MMVF, some of which have been operating for more than seventy years, show minimal respiratory or digestive tract disease, either malignant or nonmalignant, in the workers (Hill, 1977). After more than twenty years of exposure to fibrous glass, relatively few abnormal pulmonary function tests or radiographic evidence of excess fibrosis have been determined (Saracci, et al., 1984). Ongoing health problems recorded in glass fiber workers relate to mechanical irritation of the skin—dermatitis—which disappears when the trauma is removed (Lockey and Moatamed, 1984). The Occupational Safety and Health Administration (OSHA) recommended maximum exposure of 3 fibers/cm^3 of 3.5-micrometer diameter and less than 10-micrometer length is higher than that permitted for mineral fibers, reflecting the lack of documented hazardous health effects. The absence of disease may be a result of the initial and continued low levels of dust in these production facilities; another possibility suggested by Hill (1977) is that glass fibers, usually of relatively larger diameter than asbestiform minerals, do not fracture to smaller-diameter particles. Glass fibers with diameters of less than 1 micrometer are a more recent product (late 1950s), and the latency period for the diseases ascribed to exposure to these fibrous materials may not yet have peaked.

Evaluating environmental exposure to fibers, including asbestos, is probably the most difficult problem, and extrapolating results from hazardous occupational levels to nonoccupational environments, although it has been attempted (Breslow, 1985), may not be justified. Identifying the fiber type and amount, and accurately determining the fiber count for city areas have rarely been accomplished, much less estimating the exposure for the general population. However, no significant increase in disease attributable to exposure to fibers was demonstrated from either inhalation or ingestion in a limited comparative study done in Austria (Neuberger et al., 1984).

Differences of opinion are common among epidemiologists based on what appears to be similar, if not comparable, data. In spite of the numerous large-scale and long-term investigations, the debate continues over whether there is a safe (threshold) level for asbestos or other fibrous materials, or if there is a linear dose–response relationship in the induction of cancer. Conclusions and interpretations of this body of data usually reflect personal philosophy and tolerance of risk.

The confusion and frustration of nonepidemiologists, especially those who must act on behalf of the public, contribute further to the disarray. For ethical reasons, they propose regulations that seek the lowest possible level of asbestos exposure. But economics, not to mention common sense, continues to bring the results of these decisions to our attention. Inorganic fibers are ubiquitous. Are asbestos and other fibrous materials major health hazards for the world's population?

SUMMARY

Health hazards associated with exposure to fibrous materials have been studied since the turn of the century. Fibers less than 5 microns in diameter are likely to become airborne and, as part of the environment, may be inhaled or ingested. The relationship of fiber size to cell size and function, especially clearance once the fiber is inside the human body, sets off a cascade of events that can, and often does, lead to disease. The dimensions, dose, and durability of inorganic fibers are the salient determinants of disease (Leineweber, 1981).

The human lung, with its associated lymphatics and vascular systems, is composed of airways, ducts, and sacs, along with the channels and nodes, arteries, veins and capilaries, and a host of specialized cells that conduct, transfer, protect, and aid the inspiration of air and the respiration of oxygen and carbon dioxide. These structures, together with the pleura—the connective tissues lining the thoracic cavity—are susceptible to change and disruption when confronted with foreign bodies such as inorganic fibers.

The lung is a most efficient filtration system that sequesters the fibers (or other particles) if it cannot reject them through the normal physiological pathways. Changes in the extracellular architecture of the epithelial and mesothelial lung tissues through fibrosis characterizes one class of disease related to inhalation of dusts. These diseases, called pneumoconioses, as well as the formation of nodes or plaques and ferruginous or asbestos "bodies" signify the inflammation caused by the impact or deposition of particulates in the lung or its associated structures (i.e., bronchi, pleura). Asbestosis, technically fibrosing alveolitis, is a disease characterized by fibrotic lesions that continue to increase over many years, even after exposure to asbestos fiber ceases.

The scarring of the lung tissue—in effect deposition of inelastic fibrous collagen—is the result of local trauma. It is initiated and carried out by several cells normally in the tissues or air spaces of the lung—macrophages, polymorphonuclear leukocytes, other monocytes, fibroblasts, and other specialized cells. Fibrosed areas of the lung become stiff, may calcify, and in the process not only occlude the airways and alveolar sacs but permanently alter the architecture of the lung and preclude adequate transfer of gasses. As trauma and fibrosis continue, shortness of breath and hypoxia develop, eventually leading to heart failure. Chest x-rays and physiological lung func-

tion tests, together with occupational exposure to asbestos, are necessary to diagnose asbestosis. However, understanding the trauma and the cellular mechanisms that may lead to the lesions and the following destructive cascade remain under study with animal models (in vivo experiments) and specific in vitro techniques.

It is postulated from epidemiologic studies that fibrous materials are also carcinogenic or cocarcinogenic. Lung cancer and mesothelioma (cancer of the pleura) have both been linked to occupational exposure of fibrous materials. The mechanisms of induction of these, as most cancers, are thought to start as changes in the affected cells.

Both natural and synthetic fibrous materials were shown to induce fibrosis and carcinogenic responses in animals. Some fibers, such as chrysotile, appeared to be generally more biologically active, although amphiboles and fibrous glass of a variety of sizes, some coated with different compounds, showed responses even in short-term experiments. From in vivo experiments the particle shape and dimensions were shown to be important in the clearance or retention and deposition of the particles. Small particles (<10 μm in length; 3 μm in width), inhaled or ingested, can be transported through the pulmonary tree to the bottom of the lung and intrathoracic cavity and moved to the pleura or lymph nodes. Partially or totally engulfed by macrophages, the particles can have cytotoxic and other effects on a variety of cells in the vascular and pulmonary tissues.

Although direct extrapolation of the results of animal experiments to the human condition is not warranted, the ability of fibers to induce disease appears to relate more to fiber size and physical properties than to fiber chemistry (Wright and Kushner, 1977). In vitro experimentation, intrapleural instillation, and intratracheal implantation demonstrated that the smaller, and especially the thinner particles, could act as carcinogens although these techniques bypass normal biological defense mechanisms. However, long, thin fibers of a range of compositions, structures, and surface characteristics have all been shown to be biologically active (Leineweber, 1981; Table 1, p. 433).

Epidemiological studies conducted over the past 25 years in many countries on workers exposed to asbestos minerals or glass fibers have documented occupational hazards from asbestosis, lung cancer, and mesothelioma to dermatitis. In spite of the problems of estimating the dose, the precise identity of the fibrous species, the long latency for expression of cancers, and the confounding effects of smoking among these workers, there appears to be a cause-and-effect dynamic—higher exposure to fibers produce elevated risk and mortality. In addition, the recent discovery of mesothelioma in Turkey, associated with environmental exposure to a fibrous zeolite mineral, erionite, has broadened the base for concern. The general public is alerted and seems convinced that any and all fibers are carcinogens. The scientific base for such a sweeping conclusion is lacking.

Mesothelioma is a rare cancer. Five hundred deaths were recorded for the United States in 1982, compared to the more than 110,000 deaths attributed

to lung cancer (see Table 3.2). If low levels of fibers in the environment contribute to nonoccupational cancers, then mesothelioma could increase, although some of any increase may be a result of more accurate diagnosis and awareness on the part of physicians. Workers employed in the shipyards and mines 40 years ago are now prime candidates for the asbestos-related cancers. Mesothelioma should be at a peak in those populations. Mandated reduction of the level of asbestos exposure in the workplace since the mid-1960s should reduce respiratory disease. Asbestosis certainly will decrease if not disappear in most countries of the Western world over the next two decades. We also expect a reduction in occupationally related lung cancer and mesothelioma.

Future research is needed to clarify the possible role(s) of inorganic fibers in carcinogenesis. The current hypotheses of foreign-body trauma initiating a cascade of reactions implies both extra and intracellular changes, stimulating certain enzyme systems or factors leading to malignancy. It has been suggested that fibers are merely the vehicle that "pierces" a cell to allow adhering or circulating chemical carcinogens to enter and react with the DNA. It is possible that the exceedingly long, thin fibers, thought by some researchers to be the most carcinogenic, could directly interfere with nucleic acid replication. There are many experiments to be conducted before disease induction by fibrous foreign bodies is elucidated at the molecular biological level.

Asbestos is today one of the most heavily regulated materials. In the United States, maximum workplace exposure of 0.01 fiber per cubic centimeter (f/cc) of air has been suggested by individuals concerned that there may be no safe level of exposure. The EPA has banned spray-applied asbestos-containing materials, regulated the removal of friable fibrous materials during demolition, and required all schools to inspect, sample, and analyze any friable materials in the buildings. If asbestos is present, it must be reported to employees and parent–teacher groups and either be confined or removed. In Great Britain the exposure to dust containing crocidolite asbestos must not exceed 0.2 f/ml for a 4-hour sampling period, and importing of this type of asbestos is banned.

After a thousand years of use, asbestos is being replaced by other, often fibrous, materials. It remains to be seen whether the substitutes will be as successful, commercially and financially, or more or less hazardous. We are certainly not going to do without fibrous inorganic materials nor expunge them from our environment.

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APPENDIX 1

Fibrous Minerals

The following list is a presentation of all minerals, mineral series, and mineral groups described in standard mineralogy texts and references as occurring in fibrous, acicular, or needlelike forms. The presentation follows the outline given in *The System of Mineralogy of J. D. Dana and E. S. Dana* (7th ed.; Palache, Berman, and Frondel, eds.). The silicates and aluminosilicates follow the classifications of *Rock Forming Minerals* (Deer, Howie, and Zussman, eds.).

Minerals are listed individually. Mineral series that contain several fibrous species are presented as hyphenated pairs. Mineral group names are italicized. The mineral name and chemical formula are followed by a condensed citation in which the journal or text is abbreviated as follows: AM = American Mineralogist; BB = Brindley and Brown; BMines = Bureau of Mines (US); CM = Canadian Mineralogist; D.F. = Dana (Ford edition); DHZ = Deer, Howie, and Zussman; MW = Medenbach and Wilk; NM = Nriagu and Moore; PBF = Palache, Berman, and Frondel; Reviews = Reviews in Mineralogy. For example, the citation following Arsenic is "As AM 45:479 (1960)." The chemical symbol is given (As), and the article discussing the occurrence can be found on page 479 of the American Mineralogist, volume 45, published in 1960. The mineral names, chemical formulas, and format of the citation is identical to that used in the *Glossary of Mineral Species* (5th ed., M. Fleischer ed., 1987), a compendium of up-to-date information on minerals. Complete citations for the journals and books that have been abbreviated, and the few references cited by author and date can be found at the end of Appendix 2.

MINERALS

Names and chemical formulas conform with *Glossary of Mineral Species*, Fleischer, 1987.

ELEMENTS (metals, semimetals)

Arsenic As AM 45:479 (1960); PBF I:128 dimorph arsenolamprite
Schreibersite $(Fe,Ni)_3P$ PBF I:124 (rhabdite = synonym)
Selenium Se PBF I:136
Silver Ag MW:13
Sulfur S PBF I:145 dimorph rosickyite
Tellurium Te PBF I:138

SULFIDES

Argentite Ag_2S DF:418 dimorph acanthite
Bismuthinite Bi_2S_3 PBF:I:276
Bravoite $(Ni,Fe)S_2$ PBF I:290
Galena PbS PBF I:200
Guanajuatite Bi_2S_3 PBF I:278
Lautite CuAsS PBF I:327
Marcasite FeS_2 DF:438 dimorph pyrite
Millerite NiS PBF I:240
Orpiment As_2S_3 PBF I:267
Pyrite FeS_2 PBF I:283 dimorph marcasite
Rammelsbergite $NiAs_2$ PBF I:309
Realgar AsS MW:13
Safflorite $CoAs_2$ PBF I:307
Sphalerite ZnS PBF I:210
Stibnite Sb_2S_3 PBF I:271
Tungstenite WS_2 PBF I:233
Wurtzite ZnS PBF I:227

SULFO-SALTS

Aikinite $PbCuBiS_2$ AM 61:15 (1976)
Berthierite $FeSb_2S_4$ PBF I:481
Boulangerite $Pb_5Sb_4S_{11}$ PBF I:420
Cosalite–veenite $Pb_2(Bi,Sb,As)_2S_5$ AM 53:1422 (1968)
Galinobismutite $PbBi_2S_3$ PBF I:471
Hammarite $Pb_2Cu_2Bi_4S_9$ PBF I:442
Heyrovskyite $Pb_{10}AgBi_5S_{18}$ AM 57:325 (1974) (goongarite = synonym)
Hutchinsonite $(Pb,Tl)_2As_5S_9$ PBF I:469
Jamesonite $Pb_4FeSb_6S_{14}$ PBF I:451
Kobellite–tintinaite $Pb_{22}Cu_4(Bi,Sb)_{30}S_{69}$ AM 54:573 (1971)
Lillianite–gustavite $(Pb,Ag)_3Bi_2S_6$ CM 13:411 (1975)
Livingstonite $HgSb_4S_8$ PBF I:485
Meneghinite $Pb_{13}CuSb_7S_{24}$ CM 16:393 (1978)
Owyheeite $Pb_{10-2x}Ag_{3+x}Sb_{11+x}S_{28}$ AM 70:440 (1985)
(warrenite = synonym PBF I:454)
Weibullite $Pb_5Bi_8(S,Se)_{17}$ AM 62:397 (1979)
Wittichenite Cu_3BiS_3 PBF I:373
Zinkenite $Pb_9Sb_{22}S_{42}$ AM 71:194 (1986)

OXIDES

Baddeleyite ZrO_2 PBF I:608
Cassiterite SnO_2 PBF I:574 (rutile group)
Cervantite $Sb^{+3}Sb^{+5}O_4$ AM 47:1221 (1962)
Coronadite $Pb(Mn^{+4},Mn^{+2})_8O_{16}$ PBF I:742 (crytomelane group)
Cuprite Cu_2O DF:478
Curite $Pb_2U_5O_{17} \cdot 4H_2O$ PBF I:630
Downeyite SeO_2 AM 62:316 (1977)
Hematite α-Fe_2O_3 PBF I:528 dimorph maghemite;
Turgite = hematite + water PBF I:532
Hollandite $Ba(Mn^{+4},Mn^{+2})_8O_{16}$ PBF I:743 (cryptomelane group)
Kermesite Sb_2S_2O PBF I:279
Plattnerite PbO_2 PBF I:581 (rutile group)
Pyrolusite MnO_2 PBF I:562 dimorph ramsdellite (rutile group)
Rutile TiO_2 PBF I:555 trimorph anatase, brookite
Tellurite TeO_2 PBF I:594

HYDROXIDES

Boehmite AlO(OH) AM 13:72 (1928) dimorph diaspore
Brucite $Mg(OH)_2$ PBF I:636
Nemalite $(MgFe^{+2})_2(OH)_2$ PBF I:638
Chalcophanite $(Zn,Fe^{+2},Mn^{+2})Mn^{+4}{}_3O_7 \cdot 3H_2O$ PBF I:739
Gibbsite $Al(OH)_3$ AM 49:819 (1964) polymorphs bayerite, doyleite, nordstrandite
Goethite–akaganeite $Fe^{+3}O(OH,Cl)$ polymorphs feroxyhyte, lepidocrocite AM 62:1057 (1979)
Hydrohetaerolite $Zn_2Mn^{+3}{}_4O_8 \cdot H_2O$ PBF I:717
Limonite = hydrous iron oxides, mostly goethite PBF I:685
Manganite MnO(OH) MW:95

HALIDES

Bischofite $MgCl_2 \cdot 6H_2O$ PBF II:46
Bromyrite AgBr PBF II:11
Eriochalcite $CaCl_2 \cdot 2H_2O$ PBF II:45
Fluorite CaF_2 PBF II:30
Halite NaCl PBF II:4
Sal ammoniac NH_4Cl PBF II:16
Sellaite MgF_2 PBF II:38

Oxyhalides and Hydroxyhalides

Atacamite $Ca_2Cl(OH)_3$ PBF II:71 polymorphs paratacamite, botailackite PBF II:74
Daubreeite BiO(OH,Cl) PBF II:61
Eglestonite Hg_4Cl_2O AM 62:396 (1977)
Gearksutite $CaAl(OH)F_4 \cdot H_2O$ PBF II:119
Lorettoite $Pb_7O_6Cl_2$ AM 64:1303 (1979)

CARBONATES

Anhydrous Carbonates

Aragonite $CaCO_3$ PBF II:184 trimorphs calcite, vaterite
Bismutite $Bi_2(CO_3)O_2$ PBF II:259
Calcite $CaCO_3$ PBF II:153 trimorph aragonite, vaterite AM 45:1316 (1960) (satin spar = synonym)
Cerussite $PbCO_3$ PBF II:201 (aragonite group)
Magnesite–siderite $(Mg,Fe)CO_3$ PBF II:162 (calcite group)
Rutherfordine $UO_2(CO_3)$ AM 41:127 (1956)
Smithsonite $ZnCO_3$ MW:97 (calcite group)
Strontionite $SrCO_3$ PBF II:197 (aragonite group)
Witherite $BaCO_3$ PBF II:195 (aragonite group)

Hydrous Carbonates

Alumohydrocalcite $CaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$ PBF II:280
Artinite $Mg_2(CO_3)(OH)_2 \cdot 3H_2O$ PBF II:263
Aurichalcite $(Zn,Cu)_5(CO_3)_2(OH)_6$ PBF II:249
Azurite $Cu_3(CO_3)_2(OH)_2$ MW: photo, inside cover
Barbertonite $Mg_6Cr_2(CO_3)(OH)_{16} \cdot 4H_2O$ PBF II:659 (manasseite group)
Bayleyite $Mg_2(UO_2)(CO_3)_3 \cdot 18H_2O$ PBF II:237
Dawsonite $NaAl(CO_3)(OH)_2$ PBF II:276
Hydromagnesite $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ PBF II:272
Hydrotalcite $Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$ PBF II:654 dimorph manasseite
Hydrozincite $Zn_5(CO_3)_2(OH)_6$ PBF II:247
Malachite $Ca_2(CO_3)(OH)_2$ PBF II:253
Nesquehonite $Mg(HCO_3)(OH) \cdot 2H_2O$ PBF II:225
Pyroaurite $Mg_6Fe^{+3}{}_2(CO_3)(OH)_{16} \cdot 4H_2O$ DF:532 dimorph sjogrenite (hydrotalcite group)
Rosasite $(Cu,Zn)_2(CO_3)(OH)_2$ AM 70:217 (1985)
Sharpite $Ca(UO_2)_6(CO_3)_5 \cdot 6H_2O$ AM 70:220 (1985)
Sjogrenite $Mg_6Fe^{+3}{}_2(CO_3)(OH)_{16} \cdot 4H_2O$ DF:532 dimorph pyroaugite (manasseite group)
Stichtite $Mg_6Cr_2(CO_3)(OH)_{16} \cdot 4H_2O$ PBF II:655 dimorph arbertonite DF:532 (hydrotalcite group)
Tengerite $CaY_3(CO_3)_4(OH)_3 \cdot 3H_2O$ PBF II:275
Trihydrocalcite $CaCO_3 \cdot H_2O$ PBF II:227
Trona $Na_3(CO_3)(HCO_3) \cdot 2H_2O$ PBF II:138
Zaratite $Ni_3(CO_3)(OH)_4 \cdot 4H_2O$ PBF II:245

NITRATES/IODATES

Buttgenbachite $Cu_{19}Cl_4(NO_3)_2(OH)_{32} \cdot 2H_2O$ PBF II:572
Nitrocalcite $Ca(NO_3)_2 \cdot 4H_2O$ PBF II:306
Dietzeite $Ca_2(IO_3)_2(CrO_4)$ PBF II:318

BORATES

Boracite–ericaite $(Mg, Fe^{+2},Mn)_3B_7O_{13}Cl$ PBF II:379 dimorph congolite
Fluoborite $Mg_3(BO_3)(F,OH)_3$ PBF II:369
Hydroboracite $CaMgB_6O_8(OH)_6 \cdot 3H_2O$ PBF II:353
Inderite $MgB_3O_3(OH)_5 \cdot 5H_2O$ PBF II:360 dimoroph kurnakovite
Kernite $Na_2B_4O_6(OH)_2 \cdot 3H_2O$ PBF II:336
Ludwigite–vonsenite $(Mg, Fe^{+2})_2Fe^{+3}BO_5$ PBF II:322
Lueneburgite $Mg_3B_2(PO_4)_2(OH)_6 \cdot 5H_2O$ PBF II:385
Meyerhofferite $Ca_2B_6O_6(OH)_{10} \cdot 2H_2O$ PBF II:357
Pinnoite $MgB_2O_4 \cdot 3H_2O$ PBF II:334
Probertite $NaCaB_5O_7(OH)_4 \cdot 3H_2O$ PBF II:343
Seamanite $Mn_3(PO_4)B(OH)_6$ AM 56:1529 (1971)
Sussexite–szaibelyite $(Mn,Mg)BO_2(OH)$ PBF II:375
Ulexite $NaCaB_5O_6(OH)_6 \cdot 5H_2O$ AM 44:712 (1959)
Veatchite $Sr_2B_{11}O_{16}(OH)_5 \cdot H_2O$ PBF II:348 polymorphs AM 56:1934 (1971)

SULFATES

Aluminite $Al_2(SO_4)(OH)_4 \cdot 7H_2O$ PBF II:600
Alunite $KAl_3(SO_4)_2(OH)_6$ PBF II:556
Alunogen $Al_2(SO_4)_3 \cdot 17H_2O$ PBF II:537
Amarantite $Fe^{+3}(SO_4)(OH) \cdot 3H_2O$ PBF II:612
Anhydrite $CaSO_4$ PBF II:425
Antlerite $Cu_3(SO_4)(OH)_4$ PBF II:544
Apjohnite $MnAl_2(SO_4)_4 \cdot 22H_2O$ PBF II:527 (halotrichite group)
Arnimite $Cu_5(SO_4)_2(OH)_6 \cdot 3H_2O$ PBF II:592
Barite $BaSO_4$ PBF II:409
Bassanite $2CuSO_4 \cdot H_2O$ PBF II:476
Bilinite $Fe^{+2},Fe^{+3}{}_2(SO_4)_4 \cdot 22H_2O$ PBF II:529 (halotrichite group)
Boothite $CuSO_4 \cdot 7H_2O$ PBF II:504 (melanterite group)
Brochantite $Cu_4(SO_4)(OH)_6$ PBF II:541
Celestite $SrSO_4$ PBF II:415 (barite group)
Chalcanthite $CuSO_4 \cdot 5H_2O$ PBF II:489
Chalcoalumite $CuAl_4(SO_4)(OH)_{12} \cdot 3H_2O$ PBF II:580
Connellite $Cu_{19}Cl_4(SO_4)(OH)_{32} \cdot 3H_2O$ PBF II:572
Creedite $Ca_3Al_2(SO_4)(F,OH)_{10} \cdot 2H_2O$ PBF II:129
Cyanotrichite $Cu_4Al_2(SO_4)(OH)_{12} \cdot 2H_2O$ PBF II:578
Dietrichite $(Zn,Fe^{+2},Mn)Al_2(SO_4)_4 \cdot 22H_2O$ PBF II:528 (halotrichite group)
Epsomite $MgSO_4 \cdot 7H_2O$ PBF II:510
Ferrinatrite $Na_3Fe^{+3}(SO_4)_3 \cdot 3H_2O$ PBF II:456
Fibroferrite $Fe^{+3}(SO_4)(OH) \cdot 5H_2O$ PBF II:615
Goslarite $ZnSO_4 \cdot 7H_2O$ PBF II:514
Gypsum $CaSO_4 \cdot 2H_2O$ PBF II:482
Halotrichite $Fe^{+2}Al_2(SO_4)_4 \cdot 22H_2O$ PBF II:523
Hexahydrite $MgSO_4 \cdot 6H_2O$ PBF II:494
Jarosite $KFe^{+3}{}_3(SO_4)_2(OH)_6$ PBF II:560 (alunite group)
Johannite $Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 8H_2O$ AM 68:851 (1983)

Kalinite $KAl(SO_4)_2 \cdot 11H_2O$ PBF II:471
Klebelsbergite $Sb^{+3}_4O_4(OH)_2(SO_4)$ AM 65:499 (1980)
Koktaite $(NH_4)_2Ca(SO_4)_2 \cdot H_2O$ PBF II:444
Kornelite $Fe^{+3}_2(SO_4)_3 \cdot 7H_2O$ BPF II:531
Langite $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$ PBF II:584
Lausenite $Fe^{+3}_2(SO_4)_3 \cdot 6H_2O$ PBF II:530
Leightonite $K_2Ca_2Cu(SO_4)_4 \cdot 2H_2O$ PBF II:461
Mallardite $MnSO_4 \cdot 7H_2O$ PBF II:507 (melanterite group)
Melanterite $FeSO_4 \cdot 7H_2O$ PBF II:499
Mendozite $NaAl(SO_4)_2 \cdot 11H_2O$ PBF II:470
Meta-uranopilite $(UO_2)_6(SO_4)(OH)_{10} \cdot 5H_2O$ AM 37:950 (1952)
Mirabilite $Na_2SO_4 \cdot 10H_2O$ PBF II:439
Misenite $K_2SO_4 \cdot 6KHSO_4$? PBF II:396
Morenosite $NiSO_4 \cdot 7H_2O$ PBF II:517
Natroalunite $NaAl_3(SO_4)_2(OH)_6$ PBF II:556 (alunite group)
Natrochalcite $NaCu_2(SO_4)_2(OH) \cdot H_2O$ PBF II:602
Pickeringite $MgAl_2(SO_4)_4 \cdot 22H_2O$ PBF II:523 (halotrichite group)
Polyhalite $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$ PBF II:458
Ransomite $CuFe^{+3}_2(SO_4)_4 \cdot 6H_2O$ PBF II:519
Redingtonite $(Fe^{+2},Mg,Ni)(Cr,Al)_2(SO_4)_4 \cdot 22H_2O$ PBF II:529 (halotrichite group)
Retgersite $NiSO_4 \cdot 6H_2O$ PBF II:497
Sideronatrite $Na_2Fe^{+3}(SO_4)_2(OH) \cdot 3H_2O$ PBF II:604
Siderotil $Fe^{+2}SO_4 \cdot 5H_2O$ AM 49:820 (1964) (chalcanthite group)
Tamarugite $NaAl(SO_4)_2 \cdot 6H_2O$ PBF II:466
Uranopilite $(UO_2)_6(SO_4)(OH)_{10} \cdot 12H_2O$ AM 37:950 (1952)
Wattevillite $Na_2Ca(SO_4)_2 \cdot 4H_2O$? PBF II:452
Woodwardite $Cu_4Al_2(SO_4)(OH)_{12} \cdot 2\text{–}4H_2O$? PBF II:580

SELENATES/TELLURATES/CHROMATES

Chalcomenite $CuSeO_3 \cdot 2H_2O$ PBF II:638
Emmonsite $Fe^{+3}_2Te^{+4}_3O_9 \cdot 2H_2O$ Min. Rec. 3:82 (1972)
Vauquelinite $Pb_2Cu(CrO_4)(PO_4)(OH)$ PBF II:650

PHOSPHATES

Aldermanite $Mg_5Al_{12}(PO_4)_8(OH)_{22} \cdot 32H_2O$ AM 66:1099 (1981); NM:6
Alluaudite–ferroalluaudite $(Na,Ca)_4Fe^{+2}_4(MN^{+2}Fe^{+2}Fe^{+3}Mg)_8(PO_4)_{12}$ AM 43:227 (1979); NM:6
Andrewsite $(Cu,Fe^{+2})Fe^{+3}_3(PO_4)_3(OH)_2$ PBF II:802; NM:8
Apatite $Ca_5(PO_4)_3(OH,F)$ NM:8–11
Augelite $Al_2PO_4(OH)_3$ NM:12
Beraunite $Fe^{+2}Fe^{+3}_5(PO_4)_4(OH)_5 \cdot 4\ H_2O$ PBF II:959; NM:16
Bobierrite $Mg_3(PO_4)_2 \cdot 8H_2O$ PBF II:754; NM:20
Brazilianite $NaAl_3(PO_4)_2(OH)_4$ PBF II:841; NM:22
Brockite $(Ca,Th,Ce)(PO_4) \cdot H_2O$ AM 47:1346 (1962) NM:24
Brushite $CaHPO_4 \cdot 2H_2O$ PBF II:704; NM:24
Buchwaldite $NaCaPO_4$ AM 62:362 (1977); NM:25
Cacoxenite $(Fe^{+3},Al)_{25}(PO_4)_{17}O_6(OH)_{12} \cdot 17\ H_2O$ AM 70:220 (1985); NM:25

Cassidyite $Ca_2(Mg,Ni)(PO_4)_2 \cdot 2H_2O$ AM 52:1190 (1967); NM:27
Childrenite–eosphorite $(Fe^{+2},Mn)Al(PO_4)(OH)_2 \cdot H_2O$ PBF II:937; NM:28
Chloroapatite $Ca_5(PO_4)_3Cl$ PBF II:879; NM:29 (apatite group)
Churchite $YPO_4 \cdot 2H_2O$ PBF II:772; NM:129 (weinshenkite = synonym)
Coeruleolactite $(Ca,Cu)Al_6(PO_4)_4(OH)_8 \cdot 4–5H_2O$ PBF II:961; NM:30 (turquoise group)
Collinsite $Ca_2(Mg,Fe^{+2})(PO_4)_2 \cdot 2H_2O$ PBF II:722; NM:30 (fairfieldite group)
Crandallite $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$ PBF II:835; NM:32
Davisonite $Ca_3Al(PO_4)_2(OH)_3 \cdot H_2O$ AM 37:362 (1952); NM:33
Dufrenite $Fe^{+2}Fe^{+3}{}_4(PO_4)_3(OH)_5 \cdot 2H_2O$ PBF II:873; NM:36
Erythrite $Co_3(AsO_4)_2 \cdot 8H_2O$ MW:157
Faheyite $(Mn,Mg)Fe^{+3}{}_2Be_2(PO)_4 \cdot 6H_2O$ AM 49:395 (1964); NM:40
Fairfieldite $Ca_2(Mn,Fe^{+2})(PO_4)_2 \cdot 2H_2O$ PBF II:721; NM:40
Fluorapatite $Ca_5(PO_4)_3F$ PBF II:879; NM:44 (apatite group)
Frondelite–rockbridgeite $(Mn^{+2},Fe^{+2})Fe^{+3}{}_4(PO_4)_3(OH)_5$ AM 34:541 (1949); NM:45
Gatumbaite $CaAl_2(PO_4)_2(OH)_2 \cdot H_2O$ AM 63:793 (1978); NM:46
Herderite–hydroxylherderite $CaBe(PO_4)(F,OH)$ PBF II:820; NM:50
Hureaulite $Mn_5(PO_4)_2[PO_3(OH)]_2 \cdot 4H_2O$ PBF II:700; NM:53
Hydroxyapatite $Ca_5(PO_4)_3(OH)$ PBF II:879; NM:54 (apatite group)
Isokite $CaMg(PO_4)F$ AM 41:167 (1955); NM:55
Kidwellite $NaFe^{+3}{}_9(PO_4)_6(OH)_{10} \cdot 5H_2O$ AM 64:242 (1979); NM:58
Kingsmountite $(Ca,Mn^{+2})_4(Fe^{+2} \cdot Mn^{+2})Al_4(PO_4)_6(OH)_4 \cdot 12H_2O$ AM 66:1275 (1981); NM:59
Koninckite $Fe^{+3}PO_4 \cdot 3H_2O$ PBF II:763; NM:60
Laplandite $Na_4CeTiPSi_7O_{22} \cdot 5H_2O$ AM 60:487 (1975); NM:62
Laubmannite $Fe^{+2}{}_3Fe^{+3}{}_6(PO_4)_4(OH)_{12}$ AM 34:513 (1949); NM:62
Lehiite $(Na,K)_2Ca_5Al_8(PO_4)_8(OH)_{12} \cdot 6H_2O$ AM 15:307 (1930); NM:64
Lermontovite $U^{+4}(PO_4)_4 \cdot 6H_2O$? AM 69:214 (1984); NM:64
Luneburgite $Mg_3B_2(PO_4)_2(OH)_6 \cdot 5H_2O$ NM:69
Melonjosephite $CaFe^{+2}Fe^{+3}(PO_4)_2(OH)$ AM 60:946 (1975); NM:71
Messelite $Ca_2(Fe^{+2},Mn)(PO_4)_2 \cdot 2H_2O$ AM 44:469 (1959); NM:71 (fairfieldite group)
Metavauxite $Fe^{+2}Al_2(PO_4)_2(OH)_2 \cdot 8H_2O$ PBF II:971; NM:75 dimorph paravauxite
Millisite $(Na,K)CaAl_6(PO_4)_4(OH)_9 \cdot 3H_2O$ AM 15:307 (1930); NM:75
Minyulite $KAl_2(PO_4)_2(OH,F) \cdot 4H_2O$ AM 62:256 (1977); NM:75
Moraesite $Be_2(PO_4)(OH) \cdot 4H_2O$ AM 38:1126 (1953); NM:78
Morinite $NaCa_2Al_2(PO_4)_2(F,OH)_5 \cdot 2H_2O$ AM 43:585 (1958); NM:79
Ningyoite $(U,Ca,Ce)_2(PO_4)_2 \cdot 1–2H_2O$ AM 44:633 (1959); NM:83 (rhabdophane group)
Parsonite $Pb_2(UO_2)(PO_4)_2 \cdot 2H_2O$ AM 35:245 (1950); NM:88
Phosphoferrite–reddingite $(Fe^{+2}Mn)_3(PO_4)_2 \cdot 3H_2O$ PBF II:727; NM:90
Phosphosiderite $Fe^{+3}PO_4 \cdot 2H_2O$ PBF II:770; NM:91 dimorph strengite
Plumbogummite $PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$ PBF II:831; NM:93 (crandellite group)
Pseudomalachite $Cu_5(PO_4)_2(OH)_4 \cdot H_2O$ AM 35:365 (1950); NM:94
Pyromorphite $Pb_5(PO_4)_3Cl$ NM:95 (apatite group)
Reddingite–phosphoferrite $(Mn^{+2},Fe^{+2})_3(PO_4)_2 \cdot 3H_2O$ PBF II:727; NM:96
Renardite $Pb(UO_2)_4(PO_4)_2(OH)_4 \cdot 7H_2O$ AM 39:448 (1954); NM:96
Rhabdophane $(CeLa)PO_4 \cdot H_2O$ PBF II:774; NM:97
Richellite $Ca^3Fe^{+3}{}_{10}(PO_4)_8(OH,F)_{12} \cdot nH_2O$ PBF II:956; NM:98
Robertsite $Ca_3Mn^{+3}{}_4(PO_4)_4(OH)_6 \cdot 3H_2O$ AM 59:48 (1974); NM:98
Roscherite $Ca(Mn,Fe^{+2})_2Be_3(PO_4)_3(OH)_3$ AM 63:427 (1978); NM:99

Sarcopside $(Fe^{+2},Mn,Mg)_3(PO_4)_2$ AM 57:24 (1972); NM:102
Satterlyite $(Fe^{+2},Mg,Fe^{+3})_2(PO_4)(OH)$ AM 64:657 (1979); NM:103 dimorph wolfeite
Seamanite $Mn_3(PO_4)B(OH)_6$ AM 56:1527 (1971); NM:106
Souzalite–gormanite $(Mn,Fe^{+2},Al)_3(Al,Fe^{+3})_4(PO_4)_4(OH)_6 \cdot 2H_2O$ AM 67:622 (1982); NM:109
Stewartite $Mn^{+2}Fe^{+3}{}_2(PO_4)_2(OH)_2 \cdot 8H_2O$ AM 59:1272 (1974); NM:111 trimorph laueite, strunzite
Strengite–variscite $(Fe^{+3},Al)PO_4 \cdot 2H_2O$ PBF II:757; NM:111 dimorph phosphosiderite (variscite group)
Strunzite–ferrostrunzite $(Mn^{+2},Fe^{+2})Fe^{+3}{}_2(PO_4)_2(OH)_2 \cdot 8H_2O$ AM 43:793 (1958); NM:112 trimorph stewartite, laueite
Triploidite–Wolfeite $(Mn,Fe^{+2})_2(PO_4)(OH)$ AM 34:692 (1949); NM:119
Variscite $AlPO_4$ AM 57:36 (1972) dimorph metavariscite
Vashegyite $Al_{11}(PO_4)_9(OH)_6 \cdot 38H_2O$ CM 21:489 (1983); NM:123
Vauquelinite $Pb_2Cu(CrO_4)(PO_4)(OH)$ NM:123
Vivianite $Fe^{+2}{}_3(PO_4)_2 \cdot 8H_2O$ PBF II:742; NM:126
Wardite $NaAl_3(PO_4)_2(OH)_4 \cdot 2H_2O$ NM:128
Wavellite $Al_3(PO_4)_2(OH,F)_3 \cdot 5H_2O$ NM:128
Weinschwenkite = churchite NM:129
Whitmoreite $Fe^{+2}Fe^{+3}{}_2(PO_4)_2(OH)_2 \cdot 4H_2O$ NM:131
Wolfeite–triploidite $(Fe^{+2},Mn^{+2})_2(PO_4)(OH)$ AM 34:692 (1949); NM:132 dimorph satterlyite
Xanthoxenite $Ca_4Fe^{+3}{}_2(PO_4)_4(OH)_2 \cdot 3H_2O$ AM 64:466 (1979); NM:133

ARSENATES

Adamite–olivenite $(Zn,Cu)_2AsO_4(OH)$ PBF II:860
Annabergite–erythrite–hoernesite $(Co,Ni,Mg)_3(AsO_4)_2 \cdot 8H_2O$ PBF II:747 (vivianite group)
Arsenocrandellite $(Ca,Sr)Al_3[(As,P)O_4]_2(OH)_5 \cdot H_2O$ AM 67:854 (1982) (crandellite group)
Austinite–cinichalcite $Ca(Zn,Cu)(AsO_4)(OH)$ PBF II:809 (adelite group)
Beraunite $Fe^{+2},Fe^{+3}{}_5(PO_4)_4(OH)_5 \cdot 4H_2O$ PBF II:959
Brandtite $Ca_2(Mn,Mg)(AsO_4)_2 \cdot 2H_2O$ PBF II:726
Carminite $PbFe^{+3}{}_2(AsO_4)_2(OH)_2$ PBF II:912
Chenevixite $Cu_2Fe^{+3}{}_2(AsO_4)_2(OH)_4 \cdot H_2O$ PBF II:840
Clinoclase $Cu_3(AsO_4)(OH)_3$ PBF II:788
Cornwallite $Cu_5(AsO_4)_2(OH)_4 \cdot H_2O$ PBF II:925
Haidingerite $CaHAsO_4 \cdot H_2O$ PBF II:708
Hemafibrite $Mn_3(AsO_4)(OH)_3 \cdot H_2O$ PBF II:919
(synadelphite = synonym) AM 53:1779 (1968)
Koettigite–parasymlesite $(Zn,Fe^{+2})_3(AsO_4)_2 \cdot 8H_2O$ PBF II:751 (vivianite group)
Liskeardite $(Al,Fe^{+3})_3(AsO_4)(OH)_6 \cdot 5H_2O$ PBF II:924
Magnesiumchlorophoenicite $(Mg,Mn)_3Zn_2(AsO_4)(OH,O)_6$ CM 19:333 (1981)
Mansfieldite–scorodite $(Al,Fe^{+3})AsO_4 \cdot 2H_2O$ PBF II:764 (variscite group)
Mimetite $Pb_5(AsO_4)_3Cl$ AM 54:993 (1969) (apatite group)
Mixite $BiCu_6(AsO_4)_3(OH)_6 \cdot 3H_2O$ PBF II:943
Pharmacolite $CaHAsO_4 \cdot 2H_2O$ PBF II:706

Picropharmacolite $H_2Ca_4Mg(AsO_4)_4 \cdot 11H_2O$ PBF II:740
Rosslerite $MgHAsO_4 \cdot 7H_2O$ PBF II:712
Symplesite $Fe^{+2}{}_3(AsO_4)_2 \cdot 8H_2O$ PBF II:752 dimorph parasymplesite
Tyrolite $CaCu_5(AsO_4)_2(CO_3)(OH)_4 \cdot 6H_2O$ PBF II:925

VANADATES and VANADIUM OXYSALTS

Brackebuschite $Pb_2(Mn,Fe^{+2})(VO_4)_2 \cdot H_2O$ PBF II:1052
Calciovolborthite–cinichalcite $CaCu[(V,As)O_4](OH)$ PBF II:817 (adelite group)
Descloizite–mottramite $Pb(Zn,Cu)(VO_4)(OH)$ PBF II:812 (descloisite group)
Fernandinite $CaV^{+4}{}_2V^{+5}{}_{10}O_{30} \cdot 14H_2O$ PBF II:1062
Fervanite $Fe^{+3}{}_4(VO_4)_4 \cdot 5H_2O$ PBF II:1049
Hewittite $CaV_6O_{16} \cdot 9H_2O$ PBF II:1060 dimorph metahewittite PBF II:1061
Mottramite $PbCu(VO_4)(OH)$ PBF II:812 (descloisite group)
Pucherite $BiVO_4$ Min Mag 39:847 (1974) trimorph clinobisvanite, dreyerite
Pyrobelonite $PbMn(VO_4)(OH)$ PBF II:815 (descloisite group)
Steigerite $AlVO_4 \cdot 3H_2O$ PBF II:1049
Turanite $Cu_5(VO_4)_2(OH)_4$? PBF II:818
Vanadinite $Pb_5(VO_4)_3Cl$ PBF II:896 (apatite group)
Volborthite $Cu_3(VO_4)_2 \cdot 3H_2O$ PBF II:818

TUNGSTATES/MOLYBDATES

Ferrimolybdite $Fe^{+3}{}_2(MoO_4)_3 \cdot 8H_2O$ AM 48:14 (1963)
Lindgrenite $Cu_3(MoO_4)_2(OH)_2$ PBF II:1094
Wolframite [intermediate in huebnerite–ferberite] $(Fe^{+2},Mn)WO_4$ PBF II:1065

ORGANIC

Calclacite $CaCl(C_2H_3O_2) \cdot 5H_2O$ PBF II:1107
Humboldtine $Fe(C_2O_4) \cdot 2H_2O$ PBF II:1102
Julienite $Na_2Co(SCN)_4 \cdot 8H_2O$ PBF II:1106

SILICATES AND ALUMINOSILICATES

(See Liebau, F. [1980] for discussion of classification scheme)

Isolated Tetrahedra Structures

Cebolite $Ca_4Al_2Si_3O_{12}(OH)_2$ DHZ I:248
Epidote $(Ca,Ce,Pb,Sr,Y)_2(Al,Fe^{+3},Mn^{+3},V^{+3})_3(SiO_4)_3(OH)$ DH21B:2–179
Epidote–clinozoisite $Ca_2(Al,Fe^{+3})_3(SiO_4)_3(OH)$
Piedmontite $Ca_2(Al,Mn^{+3}Fe^{+3})_3(SiO_4)_3(OH)$
Zoisite $Ca_2Al_3(SiO_4)_3(OH)$ dimorph clinozoisite
Humite (morphotrophic series with olivine)
$1–4(Mg,Fe^{+2},Mn^{+2})_2SiO_4(Fe^{+2},Mg,Mn^{+2})(OH,F)_2$ DHZ IA:379
Olivine $(Mg,Fe^{+2},Ca,Mn,Co,Ni)_2SiO_4$ DHZ IA:3
Fosterite–fayalite $(Mg,Fe^{+2})_2SiO_4$
Pumpellyite–shuiskite

$Ca_2(Mg,Mn,Fe^{+2},Al)(Al,Fe^{+3},Cr,Mn^{+3})_2(SiO_4)(Si_2O_7)(OH)_2H_2O$ AM 67:860 (1982); AM 68:1250 (1983)

Tourmaline

$(Ca, K, Na)(Al, Fe^{+2}, Fe^{+3}, Li, Mg, Mn^{+2})(Al, Cr^{+3}, Fe^{+3})_6(BO)_3Si_6O_{18}(O, OH, F)_4$ Dietrich (1986)

Elbaite $Na(Li,Al)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$

Schorl $NaFe^{+2}{}_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$

Single-Chain Structures

Bustamite $(Mn,Ca)_3SiO_3O_9$ DHZ IIA:575; AM 59:632 (1974)

Pectolite–serandite $Na(Ca,Mn^{+2})_2Si_3O_8(OH)$ DHZ II:182

Pyroxenes

$(Ca, Fe^{+2}, Li, Mg, Mn^{+2}, Na)(Al, Cr^{+3}, Fe^{+2}, Fe^{+3}, Mg, Mn^{+2}, Sc, Ti, V^{+3})(Si, Al_2O_6)$ DHZ IIA:3–546; Reviews 5

Acmite $NaFe^{+3}Si_2O_6$ DHZ IIA:482 (aegirine = synonym)

Augite $(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$ DHZ IIA:294

Enstatite–hypersthene–orthoferrosilite $MgSiO_3$–$(Mg,Fe^{+2})_2Si_2O_6$–$Fe^{+2}{}_2Si_2O_6$ DHZ IIA:69 dimorph clinoenstatite

Fassaite $Ca(Mg,Fe^{+3}Al)(Si,Al)_2O_6$ DHZ IIA:399

Jadeite $Na(Al,Fe^{+3})Si_2O_6$ DHZ IIA:461

Johannsenite $CaMnSi_2O_6$ DHZ IIA:415

Spodumene $LiAlSi_2O_6$ DHZ IIA:527

Rhodonite $(Mn^{+2},Fe^{+2},Mg,Ca)SiO_3$ DHZ IIA:586

Wollastonite Ca_2SiO_3 DHZ IIA:547; polymorphs AM 64:658 (1979)

Double-Chain Structures

Amphiboles

$(Ca, Na, K)(Ca, Fe^{+2}, Li, Mg, Mn^{+2}, Na)(Al, Cr, Fe^{+2}, Fe^{+3}, Mg, Mn^{+2}, Ti)_5(Al, Si, Ti)_8O_{22}(OH,F,Cl_2)$ DHZ II:203–374; Reviews 9A & B [Classification and nomenclature: Leake, B. E. AM 63:1023–1052 (1978)]

Alkalai Amphiboles

Arfvedsonite (when $Mg/Mg + Fe^{+2} = 0.0$–0.49; $Fe^{+3}/Fe^{+3} + Al = 0.5$–$1.0$)–magnesioarfvedsonite $Na_3(Mg,Fe^{+2})_4(Fe^{+3},Al)Si_8O_{22}(OH)_2$ (when $Mg/Mg + Fe^{+2} = 0.5$–1.0; $Fe^{+3}/Fe^{+3} + Al = 0.5$–$1.0$)

Eckermanite (when $Mg/Mg + Fe^{+2} = 0.5$–1.0; $Fe^{+3}/Fe^{+3} + Al = 0.0$–$0.5$)–ferroeckermanite $Na_3(Mg,Fe^{+3})(Al,Fe^{+3})Si_8O_{22}(OH)_2$ (when $Mg/Mg + Fe^{+2} = 0.0$–0.49; $Fe^{+3}/Fe^{+3} + Al = 0.0$–$0.5$)

Glaucophane (when $Mg/Mg + Fe^{+2} = 0.5$–1.0)–ferroglaucophane $Na_2(Mg,Fe^{+2})_3Al_2Si_8O_{22}(OH)_2$ (when $Mg/Mg + Fe^{+2} = 0.0$–0.49)

Riebeckite (when $Mg/Mg + Fe^{+2} = 0.0$–0.49; $Fe^{+3}/Fe^{+3} + Al = 0.7$–$1.0$)–magnesioriebeckite $Na_2(Mg,Fe^{+2})_3Fe^{+3}{}_2Si_8O_{22}(OH)_2$ (when $Mg/Mg + Fe^{+2} = 0.5$–1.0; $Fe^{+3}/Fe^{+3} + Al = 0.7$–$1.0$) Crocidolite BMines RI 8452

Sodic-Calcic Amphiboles

Barroisite (when $Mg/Mg + Fe^{+2} = 0.5$–1.0)–ferrobarroistite $NaCa(Mg,Fe^{+2})_3Al_2Si_8O_{22}(OH)_2$ (when $Mg/Mg + Fe^{+2} = 0.0$–0.49)

Richterite (when $Mg/Mg + Fe^{+2} = 0.5$–1.0)–

ferrorichterite $Na_2Ca\ (Mg,Fe^{+2})_5Si_8O_{22}(OH)_2$ (when $Mg/Mg + Fe^{+2} = 0.0–0.49$)

Calcic Amphiboles

Edenite (when $Mg/Mg + Fe^{+2} = 0.5–1.0$)–ferroedenite $NaCa_2\ (Mg,Fe^{+2})_5Si_7AlO_{22}(OH)_2$ (when $Mg/Mg + Fe^{+2} = 0.0–0.49$)

Tremolite (when $Mg/Mg + Fe^{+2} = 1.0–0.9$)–actinolite (when $Mg/Mg + Fe^{+2} = 0.89–0.50$)–ferroactinolite $Ca_2(Mg,Fe^{+2})_5Si_8O_{22}(OH)_2$ (when $Mg/Mg + Fe^{+2} = 0.49–0.00$) BMines RI 8367

Iron Magnesian Amphiboles

Ferroanthophyllite (when $Mg/Mg + Fe^{+2} = 0.0–0.1$)–Anthophyllite (when $Mg/Mg + Fe^{+2} = 0.1–0.89$)–magnesioanthophyllite $(Fe^{+2},Mg)_7Si_8O_{22}(OH)_2$ (when $Mg/Mg + Fe^{+2} = 0.9–1.0$)

Ferrogedrite (when $Mg/Mg + Fe^{+2} = 0.0–0.1$)–gedrite (when $Mg/Mg + Fe^{+2} = 0.1–0.89$)–ferrogedrite $(Fe^{+2},Mg)_5Al_2(Si_6Al_2)O_{22}(OH)_2$ (when $Mg/Mg + Fe^{+2} = 0.9–1.0$)

Grunerite (when $Mg/Mg + Fe^{+2} = 0.0–0.3$)–cummingtonite (when $Mg/Mg + Fe^{+2} = 0.30–0.69$)–magnesiocummingtonite $(Mg,Fe^{+2})_7Si_8O_{22}(OH)_2$ (when $Mg/Mg + Fe^{+2} = 0.7–1.0$) DHZ II:243 amosite BMines RI 8452

Sillimanite Al_2SiO_5 DHZ IA:719 trimorph kyanite, andalusite

Sheet Structures

Chlorites $(Al,Fe^{+2},Fe^{+3},Li,Mg,Mn^{+2},Ni)_{4-6}\ (Al,B,Fe^{+3},Si)_4O_{10}(OH,O)_8$ Min.Mag. 30:277 (1954); CM 13:178 (1975); BB:88

Chamosite $(Fe^{+2}{}_5,Al)(Si_3Al)O_{10}(OH)_8$ dimorph orthochamosite

Clays DHZ III:191–257

Illites $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,H_2O]$ BB:58, 182

Brammallite $(Ni,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,H_2O]$ BB:133

Kandites

Amesite $Mg_2Al(Si,Al)_2O_5(OH)_2$ AM 66:185 (1981)

Berthierine $(Fe^{+2},Fe^{+3},Mg)(Si,Al)_2O_5(OH)_4$ BB:24

Halloysite $Al_2Si_2O_5(OH)_4$ AM 40:1110 (1955); BB:152 polymorphs dickite, kaolinite, nacrite BB:153

Hydrohalloysite $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ BB:153 (endellite = synonym)

Kaolinite $Al_2Si_2O_5(OH)_4$ BB:31

Nacrite $Al_2Si_2O_5(OH)_4$ BB:34

Smectites

Hectorite $Na_{0.33}(Mg,Li)_3Si_4O_{10}(F,OH)_2$ BB:178

Montmorillonite $(Na,Cl)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$ DHZ IV:273; BB:170

Saponite $(Ca/2,Na)_{0.33}(Mg,Fe^{+2})_3(Si,Al)_4O_{10}(OH)_2 \cdot 4H_2O$ BB:98

Palygorskite $(Mg,Al)_2Si_4O_{10}(OH) \cdot 4H_2O$ BB:104 (attapulgite = synonym)

Yofortierite $(Mn,Mg)_5Si_8O_{20}(OH)_2 \cdot 8–9H_2O$ AM 61:341 (1976)

Sepiolite $Mg_4(OH)_2Si_6O_{15}$ BB:106

Falcondoite $(Ni,Mg)_4Si_6O_{15}(OH)_2 \cdot 6H_2O$ CM 14:407 (1976)

Loughlinite $Na_2Mg_3Si_6O_{16} \cdot 8H_2O$ AM 45:270 (1960)

Vermiculites $(Mg,Fe^{+2},Al)_2Si_4O_{10}$ BB:98

Micas

$[Ba,Ca,(H_3O),K,Na,(NH_4)](Al,Cr^{+3},Fe^{+2},Fe^{+3},Li,Mg,Mn^{+2},V^{+3},Zn)(Al,Be,Fe^{+3},Si)_4O_{10}(OH,F)_2$ DHZ III:1–102; Reviews 13

Biotite–phlogopite $K(Mg,Fe^{+2})_3(Al,Fe^{+3})Si_3O_{10}(OH,F)_2$ Reviews 13
Muscovite $KAl_2(Si_3Al)_{10}(OH,F)_2$ BB:56,64 hydromuscovite = illite
Minnesotaite $(Fe^{+2}Mg)_3Si_4O_{10}(OH)_2$ AM 54:1740 (1969)
Pyrophyllite–ferripyrophyllite $(Al,Fe^{+3})SiO_4O_{10}(OH)_2$ DHZ III:115; BB:42
Prehnite $Ca_2Al_2Si_3O_{10}(OH)_2$ DHZ III:263
Serpentines $(Mg,Fe^{+2})Si_2O_5(OH)_4$ DHZ III:170
Antigorite $(Mg,Fe^{+2})_3Si_2O_5(OH)_4$ dimorph orthoantigorite
Chrysotile $Mg_3Si_2O_5(OH)_4$ polymorphs orthochrysotile, parachrysotile, clinochrysotile (picrolite, povlen crysotile = varieties)
Lizardite–pecoraite $(Mg,Ni)_3Si_2O_5(OH)_4$ AM 60:863 (1975) dimorph nepouite
Deweylite = a mixture of clinochrysotile and lizardite AM 64:244 (1979)
Stilpnomelane $K(Fe^{+2},Fe^{+3},Al)_{10}(Si_{12}O_{30}(OH)_{12}$ DHZ III:103
Talc $Mg_3Si_4O_{10}(OH)_2$ DHZ III:121
Willemseite $(Ni,Mg)_3(OH)_2Si_4O_{10}$ AM 55:31 (1970)

Framework Structures

Feldspars [Ba,Ca,K,Na,(NH_4),Sr](Al,B,Si)$_4O_8$ DH21:1
Orthoclase $KAlSi_3O_8$ DF:538
Opal $SiO_2 \cdot nH_2O$ DF:476; PBF 111:287
Quartz SiO_2 DHZ IV:181; PBF III dimorph cristobalite
Agate AM 70:975 (1985)
Chalcedony AM 67:1248 (1982) also carnelian, sard, amethyst, flint, chert
Zeolites DHZ IV:351; Breck (1978); Reviews 4 [Classification after Breck (1974), as found in Reviews 4, pp. 19–52]

Group 1
Harmatome $(Ba,K)_{1-2}(SiAl)_8O_{16} \cdot 6H_2O$
Laumontite $CaAl_2Si_4O_{12} \cdot 4H_2O$
Phillipsite $(K,Na,Ca)_{1-2}(Si,Al)_8O_{16} \cdot 6H_2O$
Wellsite $(Ba,K_2,Ca)Al_2Si_6O_{16} \cdot 6H_2O$

Group 2
Erionite $(K_2,Ca,Na_2)_2Al_4Si_{14}Si_{14}O_{36} \cdot 15H_2O$ Mumpton and Ormsby (1976)

Group 4
Chabasite $CaAl_2Si_4O_{12} \cdot 6H_2O$
Faujasite $(Na_2Ca)Al_2Si_4O_{12} \cdot 8H_2O$
Gmelinite $(Na_2Ca)Al_2Si_4O_{12} \cdot 6H_2O$

Group 5
Edingtonite $BaAl_2Si_3O_{10} \cdot 4H_2O$
Gonnardite $Na_2CaAl_4Si_6O_{20} \cdot 7H_2O$
Mesolite $Na_2Ca_2Al_6Si_9O_{30} \cdot 8H_2O$
Natrolite $Na_2Al_2Si_3O_{10} \cdot 2H_2O$
Scolecite $CaAl_2Si_3O_{10} \cdot 3H_2O$
Thomsonite $NaCa_2Al_5Si_5O_{20} \cdot 6H_2O$

Group 6
Bikitaite $LiAlSi_2O_6 \cdot H_2O$
Clinoptilolite $(Na,K,Ca)_{2-3}Al_3(AlSi)_2Si_{13}O_{36} \cdot 12H_2O$

Ferrierite $(Na,K)_2MgAl_3Si_{15}O_{36}(OH) \cdot 9H_2O$
Mordenite $(Ca,Na_2,K_2)Al_2Si_{10}O_{24} \cdot 7H_2O$
Mountainite $(Ca,Na_2,K_2)Si_4O_{10} \cdot 3H_2O$ AM 43:624 (1958)
Rhodesite $(Ca,Na_2K_2)_8Si_8O_{40} \cdot 11H_2O$ AM 43:624 (1958)

Other Silicates

Allophane hydrous aluminum silicate AM 48:434 (1963)
Cancrinite $Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$ DHZ IV:318
Chrysocolla $(Ca,Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O$ AM 54:993 (1969); BB:165
Dumortierite $Al_7(BO_3)(SiO_4)_3O_3$ DF:637
Holtite $Al_4(Ta,Sb,Li)[(Si,As)O_4]_3(BO_3)(O,OH)_3$ AM 57:1556 (1972)
Imogalite $Si(OH)_4$ AM 54:50 (1969)
Tobermorite $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$ AM 39:1038 (1954)

APPENDIX 2

Synthetic Fibers

The listing of synthetic inorganic fibers follows the format and compositional outline presented for minerals (Appendix 1). The list does not include proprietary names. Each entry includes the chemical composition (if known) of the synthetic compound followed by a reference. When only the general composition has been described as fibrous (or occurring as a whisker) the compound name is given. References are found in a variety of journals, many in foreign languages. For some entries an abbreviated form is used (e.g., Bracke: 36, which refers to a page in Bracke [1984]). In most cases a complete citation (author, journal, volume, page, and year) is given. Occasionally only patent data are available. The owner may be either an individual or a company (e.g., B_4C Clifton, T. A. US 3525589, is boron carbide with a U.S. patent held by T. A. Clifton).

ELEMENTS

Ag	Surmava, G. M., and Svanidze, K. G., *Metalloved I Korroziya. Met. Tbilisi:* 161–162 (1980)
Al	Barber, D. J., and Tighe, N. J., *Philos. Mag.* (8) 11:445–512 (1965)
Au	Jostan, J. L., *Galvanotechnik.* 71:946–955 (1980)
B	Sitarik, J. P., and Ellis, W. C., *J. App. Phys.* 37:2399–2401 (1966)
Be	Amonenko, V. M. et al., *Fizika Metallov. Metalloved* 13:928–930 (1962)
Bi	Burchakova, N. M., and Nikolaeva, A. A., *Materialy Dlya Poluprovol. Elektron. Kishinev:* 163–169 (1984)
C	Carbon. Bracke: 89, 90, 113 (1984) Graphite: Minikoff, I., *Prep. Prop. Solid State Matter* 4:1–48 (1979) Diamond: Derjaquin et al., *J. Cryst. Growth* 2:380–384 (1968)
Cd	Yumoto, H. et al., *J. Cryst. Growth* 67:383–384 (1984)
Co	Morita, T. et al., *Fukuoka Daigaka Rigaku Shuho* 9:81–88 (1979)
Cr	Okuyama, F., *Jpn. J. Appl. Phys* (Part 1) 22:245–251 (1983)
Cu	Nittono, O. et al., *J. Cryst. Growth* 42:175–182 (1977)
αFe	Gardner, R. N., *J. Cryst. Growth* 43:425–432 (1978)
Fe	Heinrich, B. et al., *J. Appl. Phys.* 49:1395–1397 (1978); Lashmore, D. S. et al., *J. Appl. Phys.* 48:478–480 (1977)
Ga	Oya, G., and Onodera, Y., *J. Cryst. Growth* 49:643–650 (1980)

Ge	Kamadjiev, P. R. et al., *Dokl. Bolgar. Akad. Nauk.* 19:779–782 (1966); Neumann, K., and Dittmar, W., *Naturwiss.* 42:510 (1955); Tatsumi, Y. et al., *Jpn. J. Appl. Phys.* 16:1861–1862 (1977)
Hg	Sears, G. W., *Acta Metallurg.* 1:457–459 (1953); 3:361–366 (1955)
In	Slama, G., and Tidecks, R., *Solid State Commun.* 44:425–429 (1982): Bogomolov, V. N., et al., *Pisima Zhesp. Teor. Fiz.* 26:79–81 (1977)
βMn	Webb, W. W., and Riebling, E. F., *J. Chem. Phys.* 28:1242–1245 (1958)
Mo	Bracke: 63
Nb	Bracke: 87, 99, 129
Ni	Taradze, F. N. et al., *Tezisy Dokl. Vses. Soveshch. Rostu Krist.* 5th 1:163–164 (1977)
Pb	Thompson, W. A., *J. Chem. Phys.* 68:1854–1856 (1978); Takeuchi, Y., and Fujiwara, K. J., *J. Appl. Phys.* 54:6053–6054 (1983)
Pd	Riebling, E. E., and Webb, W. W., *Science* 126:309 (1957)
Pt	Melmed, A. J., and Hayward, D. O., *J. Chem. Phys.* 31:545 (1959)
Re	Bracke: 131
S	Bourne, D. J., ed., *New Uses of Sulfur II*, Am. Chem. Soc. Washington, D.C. (1978)
Sb	Bracke: 131
Si	Osada, Y. et al., *J. Electrochem. Soc.* 126:31–36 (1979); Voronin, Yu.A. and Garshina, T. B., *Icv. Voronezh. Gos. Pedagog. Inst.* 156:71–75 (1976)
Sn	Zahraysek, L., *Plat. Surf. Finish.* 64:38–43 (1977)
Ta	Bracke: 99
Te	Syrbe, G., *Ann. Physik* 4:132–139 (1959)
Ti	Oota, T. et al., *J. Cryst. Growth* 66:262–268 (1984)
V	Bracke: 99, 129
W	Okuyama, F., *J. Cryst. Growth* 38:103–108 (1977); Savitskii, E. M. et al., *Metallich. Monokristally* 30–33 (1976)
Zn	Sugiarto, H. et al., *Trans. Inst. Met. Finish.* 62:92–97 (1984)

ALLOYS

Al_4Ce	Bracke: 85
Al_9Co_2	Bracke: 85
Al_6Fe	Bracke: 127
AlMg	Forsyth, P. G. E. et al., *Phil. Mag.* 4:447–450 (1959)
Al_3Ni	Hussey, C. L. et al., *J. Electrochem. Soc.* 124:1451–1454 (1977)
Al, Ni, Cr	Zies, G., *Strukt. Krist. Phasengrenzen/Elektronenmikrosk. Bildkontrase:*116–141 (1977)
$Bi_{1-x}Sb_x$	Dolma, V. A., Ponomarev, Ya.G., *Polumet. l Uskozon. Poluprovod. Pod. Vliyaniem Vnesk. Vozdeistrll. Kishinev.*:88–103 (1983)
$Bi_{100-x}Sb_x$	Grabko, D. Z. et al., *Poluchinie l issled. Nov. Materialov Poluprovod. Tekhn. Kishinev:* 105–110 (1980)
$CeAl_4$	Bracke: 85, 131
Co(Au, Fe, Ni)	Morelock, C. R., *Acta Metallurg.* 10:161–167 (1962)
Co_3Nb	Bracke: 131

$CrAl_3Ni$	Bracke: 82
$(Cr_1Fe)_7Cr_3$	Bracke: 129
$CuCd_3$	Bracke: 127
CuNi	Hamamura, K., Takenouchi, K., *J. Cryst. Growth* 46:804–806 (1979)
CuSi	Suto, H. et al., *Trans. Jpn. Inst. Met.* 17:596–603 (1976)
CuSn	Nohara, A. et al., *Jpn. J. Appl. Phys.* 21:194–195 (1982)
Cu_6Sn_5	Bracke: 82
CuZn	Nittono, O. et al., *J. Cryst. Growth* 36:41–46 (1966)
FeCo	Bondarenko, A. V. et al., *Kristalliz. I Svoistva Kristallov*:98–102 (1978)
Mg,Al	Leningrad Technological Institute, USSR 280477 (1975)
MnBi	Bracke: 131
Nb_3Sn	Watari, T. et al., *Less-Common. Met.* 91:L9–L12 (1983)
$NiAl_3$	Bracke: 82
Ni_3Al	Bracke: 85, 127, 129
(Ni, Al, Ta)	Bracke: 127
NiBe	Bracke: 127
$Ni_{42}Cr_6Fe$	Umeda, M., *Sumitomo Tokushu Kinzoku Giho.* 5:55–63 (1980)
$Ni_{42}FePt$	Umeda, M. ibid.
Ni_2In (rods)	Bracke: 127
Ni_3Sn	Bracke: 127
Ni_3Ta	Bracke: 87
NiZn	Gvichiya, M. M., and Tatishvilli, N. G., *Metalloved. I Korroziya Met. Tbilisi:* 38–40 (1984)
SeTe	Bhatt, V. P., and Trivedi, S. B., *Krist. Tech.* 13:1435–1438 (1978)
Ta_2Cr	Bracke: 131
UPt_3	Menovsky, A. et al., *J. Cryst. Growth* 67:31–36 (1984)
ZnAl	Ishida, Y. et al., *Sor. Metall.* 12:999–1002 (1978)
ZnCdSn	Lindborg, U., *Acta Metall.* 24:181–186 (1976)
ZrCuSi	Bracke: 127
Steel	Wilsdorf, H. G. F., *Strength Met. Alloys, Proc. Int. Conf.* 5th 1:669–674 (1979)
Eutectic Alloy	Brooks, C. S. et al., *Conf. in Situ Compos. Proc.* 3:221–231 (1979)

PHOSPHIDES, ARSENIDES, ANTIMONIDES

BP	Motojima, S. et al., *J. Cryst. Growth* 49:1–6 (1980)
$Bi_{1-x}Sb_x$	Motojima, S. et al., ibid.
$Cd_4(P, As)$ (Cl, Br, $I)_3$	Motojima, S. et al., ibid.
$CdGeP_2$	Miotkowski, I. et al., *J. Cryst. Growth* 48:479–482 (1980)
Cd-selenide	Khukhryanskii, Yu.P., and Nikolaeva, E. P., *Izv. Akad. Nauk SSSR, Neorg. Mater.* 14:1406–1407 (1978)
GaAs	Stone, J. et al., *J. Appl. Phys.* 51:3038–3041 (1980)
Ga(As, P)	Gorog, T., and Es-Lendvay, O., *Magy. Fiz. Foly.* 27:97–101 (1979)

GaP	Noras, J. M., and Ryall, M. D., *J. Phys. D.* 12:277–278 (1979)
(GaP_xAs_{1-x})	Kuziv, A. G., *Fiz. Elektronika*: 24–27 (1978)
GaSb	Sandulova, A. V. et al., *Rost. i Legirovanie Poluprovodn. Kristallov. i Plenok.* 115–120 (1977)
InAs	Takahashi, K., and Mortizumi, T., *Jpn. J. Appl. Phys.* 5:657–662 (1966)
InGaAsP	Mizuishi, K. et al., *IEEE J. Quantum Electron.* QE-19:1294–1301 (1983)
InP	Klinkova, L. A. et al., *Izv. Akad. Nauk SSSR Neorg. Mater.* 1:2100–2101 (1965)
InSb	Klinkova, L. A. et al., *Izv. Akad. Nauk SSSR Neorg. Mater.* 1:2100–2101 (1965)
MnAs	Baerner, K., and Berg, H., *J. Cryst. Growth* 46:763–770 (1979)
SiAs	Ing, S. W. Jr. et al., *J. Electrochem. Soc.* 114:761–762 (1967)
Tin selenide	Numata, T. et al., *Kagoshima Daigaku Kogakubu Kenkyu Hokoku* 19:85–90 (1977)
Titanium phosphide	Sugiyama, K. et al., *J. Cryst. Growth* 44:499–501 (1978)
W_2As_3	Taylor, J. B. et al., *Canad. J. Chem.* 43:3045–3051 (1965)
α-, β-Zn_3P_2	Martsenyik, L. S., *Fiz. Kondensir. Sostoyaniya, Kiev*: 54–57 (1978)
$ZnSiP_2$	Siebel, W. et al., *Kristall und Technik* 15:947–954 (1980)
ZrP	Motojima, S., *J. Cryst. Growth* 30:1–8 (1975); Motojima, S., *J. Electrochem. Soc.* 123:290–295 (1976)

SULFIDES, SELENIDES, TELLURIDES

α-Ag_2S	Okabe, T., and Nakagawa, M., *J. Cryst. Growth* 46:504–510 (1979)
β-Ag_2S	Kasukabe, S., *J. Cryst. Growth* 65:384–390 (1983)
Arsenic selenide	Kothiyal, G. P. et al., *J. Cryst. Growth* 53:519–522 (1981)
Bi-telluride	Grabko, D. Z. et al., *Izv. Akad. Nauk. Mold. SSR, Ser. Fiz. Teka. Mat. Nauk.*:37–41 (1981)
CdS	Takahashi, R., *Jpn. J. Appl. Phys.* 17:1275–1276 (1978); Chikawa, J., and Nakayama, T., *J. Appl. Phys.* 35:2493–2501 (1964)
CdSe	Yoshile, T. et al., *J. Cryst. Growth* 51:624–626 (1981)
CdTe	Lynch, R. et al., *J. Appl. Phys.* 33:1009–1011 (1962)
$CdTlS_2$	Gusejnov, G. D. et al., *Izv. Akad. Nauk SSSR Neorg. Mater.* 5:33–34 (1969)
Ca-Cr-S	Lutz, H. D., Becker, R. A., *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* 32B:787–789 (1977)
Sr-Cr-S	Lutz, H. D., ibid.
Ba-Cr-S	Lutz, H. D., ibid.
$CuAlS_2$	Honey, W. N., *J. Phys. Chem. Solid* 30:1935–1940 (1969)
$CuBrSe_3$	Honey, W. N., ibid.
CuBrTe	Honey, W. N., ibid.

$CuBrTe_2$	Honey, W. N., ibid.
$CuClSe_2$	Honey, W. N., ibid.
CuClTe	Honey, W. N., ibid.
$CuClTe_2$	Honey, W. N., ibid.
$CuGaS_2$	Yamamoto, N. et al., *Jpn. J. Appl. Phys.* 11:1383–1384 (1972)
$CuGa_{(1-x)}In_xS_2$	Yamamoto, N. et al., ibid.
CuITe	Yamamoto, N. et al., ibid.
$CuITe_2$	Yamamoto, N. et al., ibid.
$Ge_xSe_{(1-x)}$	Chen, C. H., and Tai, K. L., *Appl. Phys. Lett.* 37:1075–1077 (1980)
HgS	Chen, C. H., and Tai, K. L., ibid.
Hg_3S_2Cl	Chen, C. H., and Tai, K. L., ibid.
$HgGa_2S_4$	Chen, C. H., and Tai, K. L., ibid.
HgSe	Chen, C. H., and Tai, K. L., ibid.
$HgGa_2Se_4$	Chen, C. H., and Tai, K. L., ibid.
InSe	Inoue, S. et al., *Jpn. J. Appl. Phys.* 21:242–248 (1982)
In_5S_4	Wadsten, T., *J. Cryst. Growth* 52:673–678 (1981)
PbS	Abdulkhadar, M. et al., *J. Cryst. Growth* 55:398–401 (1981)
PbSe	Gancheva, V. et al., *J. Mater. Sci.* 10:1943–1946 (1975)
PbTe	Herrmann, R. et al., *Phys. Status Solidi A.* 59:51–56 (1980); Banar, V. F. et al., *Izv. Akad. Nauk Mold. SSR, Ser. Fiz.-Tekh. Mat. Nauk:* 66–67 (1982)
SbSI	Dziuba, Z., *J. Cryst. Growth* 35:340–342 (1976)
SnS	Dziuba, Z., ibid.
SnS_2	Bracke: 130
SnSe	Bracke: 130
SrS	Cheroff, G. et al., *J. Chem. Phys.* 27:300–331 (1957)
TlTe	Furata, N. et al., *Jpn. J. Appl. Phys.* 11:1753–1754 (1972)
β-US_2	Furata, N. et al., ibid.
WTe	Kabashima, S., *J. Phys. Soc. Jpn.* 21:945–948 (1966)
ZnS	Abdulkhadar, M. et al., *J. Cryst. Growth* 55:398–401 (1981)
ZnTe	Akhromenko, Yu. G. et al., *Izv. Akad. Nauk SSSR, Neorg. Mater.* 19:570–572 (1983)

AZIDES

Azide	Ivanov, F. I. et al., *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk.* 62–67 (1983)
Silver azide	Ivanov, F. I. et al., *Kristallografiya* 28:194–195 (1983)

BORIDES

CrB	Motojima et al., *J. Cryst. Growth* 51:568–572 (1981)
HfB_2	Bracke: 83
LaB_6	Givargizov, E. I., and Obolenskaya, L. N., *J. Cryst. Growth* 51:190–194 (1981)

(Eu, Y, Ce, Ba, Cs, La) B_6	Olsen, G. H. et al., *J. Cryst. Growth* 44:287–290 (1978)
Mo_2NiB_2	Bracke: 127
NiB	Bracke: 82
TiB	Bracke: 92

CARBIDES

B_4C	Clifton, T. A., US 3525589
Co_7C_3	Bracke: 129–130
Cr_3C_2	Bracke: 129
$(Cr, Co)_{23}C_6$	Bracke: 129
$(Cr, Co, Ni)_7C_3$	Bracke: 130
Fe_7C_3	Bracke: 129–130
HfC	Bracke: 129
NbC	Bracke: 83
Nb_2C	Bracke: 129
NiC	Bracke: 82
SiC	Lee, S. A. et al., US 3709981; Lonza, R., FR 2097792; Donomoto, T. et al., *Eur. Pat. Appl.* 83/110183, 101283, 131082 JP 82/179648
α-SiC	Ryan, C. E. et al., *J. Cryst. Growth* 1:255–262 (1967)
TaC	Bracke: 129
Ta_2C	Bracke: 129
TiC	Kato, A. V., and Tamari, N., *J. Cryst. Growth* 49:199–203 (1980)
TiC_x	Wokulski, Z., and Wokulska, K., *J. Cryst. Growth* 62:439–446 (1983)
VC	Bracke: 129
WC	Bracke: 130
ZrC	Tamari, N., and Kato, A., *J. Less-Common Met.* 58:147–160 (1978); Kato, A., and Tamari, N., *J. Cryst. Growth* 49:199–203 (1980)

HALIDES, OXYHALIDES

AgCl, AgBr, AgI	Konishi, Y., and Saijo, H., *Nippon Shashin. Gakkaishi* 45:348–352 (1982); Konishi, Y., and Matsubara, T., *Nippon Shashin. Gakkaishi* 45:436–44 (1982)
BaP_2	Mimura, Y. et al., *Jpn. J. Appl. Phys.* 19:269–272 (1980)
CaF_2	Desai, C. C., and John, V., *J. Cryst. Growth* 44:625–628 (1978)
$CaIO_3$	Joshi, M. S. et al., *Krystall. und Technik.* 15:1131–1135 (1974)
CdI_2	Kleber, W., and Fricke, P., *Z. Physik. Chem* 224:353–363 (1963)
CsCl	Webb, W. W., and Bertolone, N. P., *J. Appl. Phys.* 31:207–209 (1960)
CsI	Okumara, Y. et al., *Jpn. J. Appl. Phys.* 19:649–651 (1980)

KCl, KBr, KI	Mimamura, Y. et al., *Jpn. J. Appl. Phys.* 19:269–272 (1980)
$KClO_3$	Borchardt-Ott, W., and Kleber, W., *Z. Physik. Chem.* 211:79–92 (1959)
LiF	Mimamura, Y. et al., *Jpn. J. Appl. Phys.* 19:269–272 (1980)
NaCl	Marks, J. A., *Sch. Sci. Rev.* 58:480 (1977)
$NaClO_3$	Sears, G. W., *J. Chem. Phys.* 26:1549–1552 (1957)
NH_4Cl	Borchardt-Ott, W., and Kleber, W., *Z. Physik. Chem.* 211:79–92 (1959)
NH_4ClO_4	Raevskii, A. V. et al., *Dokl. Akad. Nauk. SSSR* 209:157–159 (Phys. Chem.) (1973)
$PbBr_2$	Abdulkhadar, M. et al., *Cryst. Res. Tech.* 17:33–38 (1982)
$PbCl_2$	Adkulkhadar, M. et al., *J. Cryst. Growth* 48:149–154 (1980)
$SnBr_2$	Pomeshchikov, V. D. et al., *Zh. Neorg. Khim.* 26:1958–1959 (1981)
SnI_2	Desai, C. C., and Rai, J. L., *J. Cryst. Growth* 53:432–436 (1981)
SnI_4	Desai, C. C., and Rai, J. L., *J. Cryst. Growth* 51:457–460 (1981)
$SrCl_2$	Gerasimov, Yu. M. et al., *Dokl. Akad. Nauk. SSSR* 272:1119–1122 (Crystallography) (1983)
TlCl	Vasile'v, A. V. et al., *Sov. J. Quantum Electr.* 11:834–835 (1981)
TlI	Shiojiri, M. et al., *J. Cryst. Growth* 43:61–70 (1978)

HYDRIDES

Scandium hydride	Kobayashi, T., and Takei, H., *J. Cryst. Growth* 45:29–36 (1978)

NITRIDES

AlN	Huml, J. O. et al., US. 3598526
Boron nitride	Ishii, T. et al., *J. Cryst. Growth* 52:285–289 (1981)
GaN	Inomata et al., *J. Cryst. Growth* 21:317–318 (1974)
HfN	Futamoto, M. et al., *J. Cryst. Growth* 61:69–74 (1983)
Polysulfur nitride	Stejny, J. et al., *J. Mater. Sci.* 16:3161–3170 (1981)
α-Si_3N_4	Milewski, J. V. et al., LA-9650-MS. Order No. DE83008282 NTIS; Glemser, O., and Horn, H. G., *Naturwiss.* 49:538–539 (1962)
β-Si_3N_4	Inomata et al., *J. Cryst. Growth* 21:317–318 (1974): Toshiba Ceramics-Co. Ltd., Kokai Tokyo Koho 83/16257.020483
SiON	Azuma, N. et al., Agency of Indust. Sciences & Technology, Japan, Kokai 111176
TiN	Bojarski, Z. et al., *J. Cryst. Growth* 52:290–295 (1981)
ZrN	Mivoshi, M. et al., *Nippon Kogaku Kaishi*: 822–826 (1978)

SILICIDES

Co_2Si	Bracke: 127
$CrSi_2$	Bracke: 127
Cr_5Si_3	Motojima, S., and Sugiyama, K., *J. Cryst. Growth* 55:611–613 (1981)
α-FeSi	Bracke: 127
Ge silicon	Khristosenko, L. Yu et al., *Visn. L'viv. Politekh. Inst.* 110:80–82 (1977)
Mg_2Si	Bracke: 127
Hn_5Si_3	Riebling, E. F., and Webb, W. W., *Science* 126:309 (1957)
$MoSi_2$	Zakharova, G. I. et al., *Izv. Akad. Nauk. SSSR Neorg. Mater.* 20:1143–1147 (1984)
Ti_5Si_3	Bracke: 127
ZrCuSi	Bracke: 127

OXIDES

α-Al_2O_3	Schreiner, M. et al., *Radex Rundsch*: 919–930 (1982); Pulc, V., *Chem. Vlakna* 28:135–41 (1978)
BaO	Pogorel, Skii M. M., *Pis'ma Zh. Tekh. Fiz.* 4:1068–1071 (1978)
BeO	Edwards, P. L., and Happel, R. J., Jr., *J. Appl. Phys.* 33:943–948 (1962): Houston, T., GB 1190038
CdO	Simov, S. et al., *J. Mater. Sci.* 18:623–633 (1983)
CeO_2	Strigushchenko, I. V., *Fiz. Tverd. Tela* (Leningrad) 19:1904–1906 (1977)
Cr_2O_3	Yamaguchi, A., *Am. Ceram. Soc. Bull.* 62:254 (1983)
CrO_2	Agrawal, D. K. et al., *Mater. Res. Bull.* 13:1135–1142 (1978)
CuO	Dachselt, W. D., and Pfefferkorn, Z., *Naturforch.* 149:309 (1959); 150:412–417 (1960)
FeO	Jakei, L. J., *Am. Ceram. Soc.* 41:279–281 (1965)
α-Fe_2O_3	Talman, R. L., and Gulbrandson, S., J. *Electrochem.* 114:1227–1230 (1967)
HfO_2	Bracke: 83
In_2O_3, Ir_2O_3	Shimada, S., and MacKenzie, K. J. D., *J. Cryst. Growth* 55:453–456 (1981)
MgO	Krasnikova, L. A., et al., Spstl 211 KHP-D82; Budnikov, P. P., et al., *Dokl. Akad. Nauk SSSR* 175:1045–1046 (1967)
MnO	Bracke: 131
α-MnO_2	Yamamoto, N. et al., *Jpn. J. Appl. Phys.* 13:723–724 (1974)
MoO_3	Saalfeld, H., and Jarchow, O., *Zeit. Krist.* 126:241–243 (1968)
MoO_2	Bertrand, O. et al., *J. Cryst. Growth* 35:325–328 (1976)
NbO_2	Cohen, U., *J. Cryst. Growth* 46:147–150 (1979)

Nb_2O_5	Emmenegger, F. P. et al., *J. Phys. Chem. Solid* 29:1673–1681 (1968)
NiO	Saito, S. et al., *J. Cryst. Growth* 30:113–116 (1975)
PbO	Isvoscikov V., and A. Bordovskij, *Dokl. Akad. Nauk SSSR* 145:1253–1254 (1962)
β-PbO_2	Torikai, E., US 3959453
SiO_2	Jaccondine, R. T., and Kline, R. K., *Nature* 189:298 (1969)
SnO_2	Cho-In-Gwan, *Suhak Kwa Mulli*:51–56 (1981)
ThO_2	Arthur D. Little, Inc., US 3944640
TiO_2	Berisford, R. et al., US 3728443: Izum, F. et al., *J. Cryst. Growth* 47:139–144 (1974)
Ti_2O_3	Hauptman, Z., *Collect. Czechoslov. Chem. Comm.* 32:2421–2430 (1967)
VO_2	Bonger, P. F., *Solid State Commun.* 3:275–277 (1965); Kitahiro, I., et al., *J. Phys. Soc. Jpn* 21:196 (1966)
WO_2	Bonnet, J. P. et al., *J. Cryst. Growth* 56:633–638 (1982)
WO_3	Ahmad, I., and Capsimalis, G. P., *J. Phys. Chem Solids* (Suppl. 1):325–331 (1967)
$W_{18}O_{49}$	Hashimoto, H., *J. Electr. Micros.* 9:130–138 (1960)
$W_{20}O_{58}$	Ahmad, I., and Capsimalis, G. P., J. Phys. Chem. Solids (Suppl. 1):325–331 (1961)
Yt_2O_3	Bracke: 83
ZnO	Weaver, E. A., *J. Cryst. Growth* 1:320–323 (1967); Voshile, T. et al., *J. Cryst. Growth* 51:624–626 (1981)
ZrO_2	Karpinos, D. M. et al., *Ogneupory*:47–50 (1978)

ARSENATES, PHOSPHATES, SULFATES

Ag_3PO_4	Mennicke, S. et al., *J. Cryst. Growth* 26:197–199 (1974)
Calcium aluminate monosulfate hydrate	Seto, K, and Kubo, M., Matsushita Electric Works Ltd., Japan, Kokai, 180378
$CaNH_4PO_4 \cdot 8H_2O$	Banks, E. et al., *J. Cryst. Growth* 18:185–190 (1973)
Calcium sulfate hemihydrate	Eberle, J. J. et al., FR 2179760
$CaSO_4$	DE 2752367, FR 2377970, Bayer AG
$CaSO_4 \cdot 2H_2O$	Nancollas, G. H. et al., *J. Cryst. Growth* 20:125–34 (1973); Tanaka, M. et al., *Hyoso Pre. Ger. Offen. Jpn.* 010977
$Ca_3(PO_4)_2$	Nancollas, G. H. et al., *J. Cryst. Growth* 20:125–34 (1973); Tanaka, M. et al., *Hyoso Pre. Ger. Offen. Jpn.* 010977
$Ca_{10}(PO_4)_6(OH)_2$	Eysel, W. et al., *J. Cryst. Growth* 20:245–250 (1973)
$CaHPO_4$	Chenot, C. F., US 3927180
$K_2H_2PO_4$	Ueda, R. et al., *J. Phys. Chem. Solids* (Suppl. 1):381–384 (1967)
$MgNH_4PO_4 \cdot 6H_2O$	Banks, E. et al., *J. Cryst. Growth* 18:185–190 (1973)
NdP_5O_{14}	Litvin, B. N. et al., *J. Cryst. Growth* 57:519–523 (1982)
Rare earth penta-phosphate	Bridenbaugh, P. et al., US 4002725

OTHER OXY-SALTS

Ag_2SeO_4	Boncheva, M. (see Bracke)
Al_2BeO_4	Boncheva, M., ibid.
$BaWO_4$	Oishi, S. et al., *Nippon Kagaku Kaishi*:1228–1231 (1978)
$CaWO_4$	Oishi, S. et al., *Nippon Kagaku Kaishi*:340–344 (1977)
Potassium titanate	Yanagida, H., and Shimizu, T., Kyushu Refractories Co., Ltd., Jpn. Kokai Tokkyo Koho. 130578
$K_2Ti_6O_{13}$	Oota, T. et al., *J. Cryst. Growth* 46:331–338 (1979)
$MgAl_2O_4$	Suvorov et al., GB 1511393
$MgWO_4$	Tate, I. et al., *Nippon Kagaku Kaishi*:181–185 (1978)
$Na_2B_4O_7$	Johnson, R. C., and Alley, J. K., U.S. Dept. Interior, Bureau of Mines RI 6575:1–23 (1965)
$PbCo_3$	Pillai, M., and Ittyachen, M. A., *Pramana* 10:613–619 (1978)
$PbWO_4$	Arora, S. K. et al., *J. Cryst. Growth* 57:452–455 (1982)
$(Sr_xB_{1-x})CO_3$	Garcia-Ruiz, J. M., *J. Cryst. Growth* 55:398–401 (1981)
$Y_3Al_5O_{12}$	Burrus, C. A., US 4040890
$ZnGeO_4$	Ito, S. et al., *J. Cryst. Growth* 47:310–312 (1979)
Zn_2SnO_4	Yoshida, R. et al., *J. Cryst. Growth* 36:181–184 (1976)

ODD-NAMED WHISKERS

Schladitz whiskers	Wilsdorf, H. G. F., UVA/525321/MS82/104; Order No. Ad-A115098 NTIS
Shish crystals	Feit, K., et al., *J. Polym. Sci. Polym. Phys. Ed.* 22:993–999 (1984)

APPENDIX 3

Brucite, $Mg(OH)_2$

The following is an excerpt to illustrate data available on a mineral species (From: Palache, Berman, and Frondel [1944]).

BRUCITE GROUP

HEXAGONAL — P; SCALENOHEDRAL — $\bar{3}\,2/m$

		c	a_0	c_0	G
Brucite	$Mg(OH)_2$	1.5208	3.125Å	4.75Å	2.39
Pyrochroite	$Mn(OH)_2$	1.401	3.34	4.68	3.25
Portlandite	$Ca(OH)_2$	1.365	3.585	4.895	2.23

The members of this group possess a layered-lattice structure, and this is reflected in the platy habit of their crystals and in the perfect cleavage {0001} parallel to the layers. The minerals are flexible and soft (2–2½). Limited isomorphism is found between Mg and Mn. The small number of available analyses, however, influences the record of compositional variation in the species.

The minerals of the group are formed at comparatively low temperatures (less than 200°) in hydrothermal veins.

6111 **BRUCITE** [$Mg(OH)_2$]. Native Magnesia (from New Jersey) *Bruce* (*Am. Min. J.*, **1**, 26, 1814). Hydrate of Magnesia *Aikin* (236, 1815), *Cleaveland* (429, 1822), *Hall* (28, 1824), *Robinson* (166, 1825). Brucite, ou Hydrate de magnésie *Beudant* (838, 1824). Talk-Hydrat, Magnesia-Hydrat *Germ.* Monoklinoëdrisches Magnesiahydrat oder Texalith (from Texas, Penn.) *Hermann* (*J. pr. Chem.*, **82**, 368, 1861). Amianthus (from Hoboken, New Jersey) *Pierce* (*Am. J. Sc.*, **1**, 54, 1818) = Amianthoid Magnesite, Nemalite *Nuttall* (*Am. J. Sc.*, **4**, 18, 1821) = Brucite (Talk-Hydrat, "hierher zu gehoren scheint") *Leonhard* (245, 1826), *Whitney* (*J. Soc. Nat. Hist. Boston*, 36, 1849). Manganbrucit *Igelström* (*Ak. Stockholm Öfv.*, **39**, 83, 1882). Manganobrucite. Ferrobrucite.

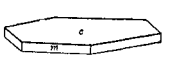
Cryst. Hexagonal — P; scalenohedral — $\bar{3}\,2/m$.

$$a : c = 1 : 1.5208;[1] \qquad p_0 : r_0 = 1.7561 : 1$$

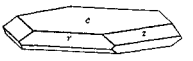
Forms:[2]

		ϕ	ρ	M	A_2
c	0001	.....	0°00′	90°00′	90°00′
m	$11\bar{2}0$	0°00′	90 00	90 00	60 00
z	$01\bar{1}3$	−30 00	30 20½	104 38	64 03
e	$01\bar{1}2$	−30 00	41 17	109 16	55 09
r	$10\bar{1}1$	30 00	60 20½	64 30	90 00
h	$07\bar{7}5$	−30 00	67 52	117 35½	36 39½
t	$04\bar{4}1$	−30 00	81 54	119 40	30 58½

Structure cell.[3] Space group $C\bar{3}m$; a_0 3.125 ± 0.005, c_0 4.75 ± 0.005; $a_0 : c_0 = 1 : 1.520$; contains $Mg(OH)_2$ in hexagonal unit.



Tilly Foster, N. Y.



Texas, Pa.

Habit. Crystals usually broad tabular {0001} often subparallel aggregates of plates; a manganoan variety is sometimes acicular [0001]. Also commonly foliated massive; fibrous, with fibers separable and elastic; rarely fine granular.

Oriented growths. Observed enclosing pyroaurite, with brucite {0001} [10$\bar{1}$0] ‖ pyroaurite {0001}[10$\bar{1}$0].[4]

Phys. Cleavage {0001} perfect. Foliae separable and flexible. Sectile. H. 2½. G. 2.39 ± 0.01; 2.40 (calc.). Luster on cleavages pearly, elsewhere waxy to vitreous. Color white, inclining to pale green, gray, or blue; in manganoan varieties honey-yellow to brownish red and deep brown (by alteration?). Streak white. Transparent. Exhibits percussion and pressure figures on {0001}.[5] Pyroelectric, on cooling — the extremities of [0001] negative, and the lateral edges positive.[6] The thermal expansion[7] is 4.47 ± 0.20 × 10^5 ⊥ {0001}, 1.10 ± 0.15 × 10^5 ⊥ {10$\bar{1}$0}.

Opt. Colorless in transmitted light. Often exhibits optical anomalies[8] due to mechanical deformation or aggregation of crystals; at times biaxial with small $2V$ due to the anomalies. Abnormal interference colors, due to marked change of birefringence with wavelength, are often observed.

O	*E*	
1.559	1.580[8]	Uniaxial pos. (+).
1.59	1.60	Anal. 5, manganoan.

Chem. Magnesium hydroxide, $Mg(OH)_2$. Mn substitutes for Mg up to at least Mg : Mn = 5 : 1 (anal. 5). Fe^2 is often present in substitution for Mg, usually in amounts of only a few per cent but sometimes as high as Mg : Fe = 25 : 2 (anal. 3). Zn also occurs in small amounts in substitution for Mg (anal. 5). The CO_2 sometimes reported is probably due to admixed hydromagnesite or other impurity. Nearly all the H_2O is lost at 410°.[9]

Anal.[10]

	1	2	3	4	5
MgO	69.12	67.34	60.33	57.81	51.46
FeO	.....	.....	9.57	.....	.....
ZnO	.....	.....	.....	.....	3.67
MnO	.....	0.89	.....	14.16	18.11
H_2O	30.88	31.52	28.60	28.00	26.76
Rem.	.....	0.39	1.95	.....	.....
Total	100.00	100.14	100.45	99.97	100.00
G.	2.40	2.385			

1. $Mg(OH)_2$. 2. Wood's mine, Texas, Pa. Rem. is SiO_2.[11] 3. Ferroan brucite, fibrous. Asbestos, Quebec. Rem. is Fe_2O_3.[12] 4. Manganoan brucite. Small amounts of SiO_2 and $CaCO_3$ have been deducted. Jacobsberg, Sweden.[13] 5. Manganoan and zincian brucite. Franklin, N. J. Recalc. after deduction of about 3 per cent $CaCO_3$.[14]

Var. *Ordinary.* In crystals, plates or foliated masses. White to pale greenish in color.

Fibrous. Nemalite *Nuttall* (*Am. J. Sc.*, **4**, 18, 1821). In fibers or laths, usually elongated [10$\bar{1}$0] but sometimes [11$\bar{2}$0].[15] Some fibrous brucite is reported to be highly ferroan, but this may be owing to admixed magnetite.

Ferroan. Ferrobrucite. Contains a considerable amount of Fe^2 in substitution for Mg (anal. 3). Turns brown on exposure.

Manganoan. Manganbrucite *Igelström* (*Ak. Stockholm, Öfv.*, **39**, 83, 1882). Manganobrucite. Contains a considerable amount of Mn^2 in substitution for Mg (anal. 4, 5).

Tests. B.B. infusible, glows brightly, and the ignited material reacts alkaline. In C.T. becomes opaque and friable, sometimes turning gray to brown; the manganoan variety becomes dark brown. Easily soluble in acids.

Occur. Brucite occurs typically as a low-temperature hydrothermal vein mineral in serpentine and chloritic or dolomitic schists; also in crystalline limestones as an alteration product of periclase. Associated with calcite, aragonite, hydromagnesite, artinite, brugnatellite, talc, magnesite, deweylite. At Kraubat, Styria, with serpentine, magnesite, and hydromagnesite. In the Tirol in the Pfitschthal, and in the Fleimsthal at Canzocoli near Predazzo as an alteration of a periclase marble. At Teulada, Sardinia, Italy. In periclase-bearing limestone blocks thrown out by Vesuvius. At Swinna Ness, Unst, Shetland Islands, Scotland, with hydromagnesite in serpentine. In Sweden at Philipstad as an alteration of periclase in limestone, and similarly at Nordmark and Jakobsberg (*manganbrucite*); also at Långban. In the Urals in the region of Slatoust, in part well crystallized.

In the United States originally found at Hoboken, New Jersey, with hydromagnesite, artinite, dolomite, in serpentine, in part fibrous (the original *nemalite*). In Pennsylvania at Texas, Lancaster County, at Wood's mine and Low's mine, in fine crystals and broad plates up to 19 cm. across; near Reading and Sinking Spring, Berks County, with aragonite and serpentine in dolomite. Finely crystallized at the Tilly Foster mine, Brewster, Putnam County, New York. In a large deposit in the Lodi district, Nevada, with hydromagnesite. At Crestmore, Riverside County, California, as an alteration of periclase in marble. Fibrous brucite with fibers over 20 in. in length occurs with chrysotile and serpentine at Asbestos, Quebec.[16]

Alter. Often observed as an alteration product of periclase, and sometimes composes brucite-calcite rocks (pencatite, predazzite) often with hydromagnesite and serpentine, by the hydration of periclase marbles. Also observed as pseudomorphs after dolomite. Alters readily to hydromagnesite; less often to brugnatellite, serpentine, and deweylite. Ignited brucite (" metabrucite ")[17] consists of an aggregate of periclase crystallites oriented with periclase $\{111\}[110] \parallel \{0001\}[10\bar{1}0]$ of the original brucite.[18]

Artif.[19] By heating to 200° mixed solutions of $MgCl_2$ and excess KOH; the crystals of brucite separate on cooling. Observed in crystals as a deposit in a steam boiler using waters containing $MgCl_2$. Also by reaction of NaOH solutions upon MgO at elevated temperatures.

Name. After Archibald Bruce (1777–1818), an early American mineralogist, who first described the species. *Nemalite* (more correctly *nematolite*) is from *νῆμα, thread*, in allusion to the fibrous structure.

Ref.

1. On crystals from Texas, Pa., by Hessenberg, in Dana (252, 1892).
2. In Dana (252, 1892).
3. Space group and structure by Aminoff, *Geol. För. Förh.*, **41**, 405 (1919); *Zs. Kr.*, **56**, 506 (1921). Cell dimensions by Garrido, *Zs. Kr.*, **95**, 189 (1936), on unanalyzed brucite from Texas, Pa. A manganoan brucite (10.46 per cent MnO) from Långban, Sweden, gave Aminoff (1919) $a_0 = 3.13$, $c_0 = 4.75$.
4. Meixner, *Cbl. Min.*, 5, 1938, from Kraubat, Styria.
5. Mügge, *Jb. Min.*, I, 57, 1884; I, 110, 1898.
6. Hankel, *Ann. Phys.*, **6**, 53 (1879).
7. Megaw, *Roy. Soc. London, Proc.*, **142A**, 198 (1933).
8. Bauer, *Jb. Min., Beil.-Bd.*, **2**, 70 (1883).
9. Kurnakov and Černych (1926), Clarke and Schneider, *Zs. Kr.*, **18**, 417 (1890).
10. For many additional analyses see Hintze (**1** [2A], 2086, 1910); also Kurnakov and Černych, *Mem. soc. russe min.*, **55**, 74 (1926) — *Jb. Min.*, I, 313, 1927; Fenoglio, *Soc. geol. ital. Boll.*, **46**, 13 (1927).
11. Kurnakov and Černych (1926).

12. Gonyer anal. in Berman, *Am. Min.*, **17**, 313 (1932).
13. Igelström, *Ak. Stockholm, Handl.*, 187, 1858 — *Am. J. Sc.*, **31**, 358 (1861).
14. Bauer anal. in Bauer and Berman, *Am. Min.*, **15**, 346 (1930).
15. Michel-Lévy and Lacroix (162, 1888); Berman, *Am. Min.*, (1932); Garrido, *Zs. Kr.*, **95**, 189 (1936); de Jong, *Bull. Inst. Geol. Yugoslav.*, **6**, 241 (1938) — *Min. Abs.*, **7**, 360 (1939).
16. Berman (1932).
17. Rinne, *Fortsch. Min.*, **3**, 160 (1913). Büssem and Koberich, *Zs. phys. Chem.*, **17**, 310 (1932).
18. Garrido, *C. R.*, **203**, 94 (1936); *Zs. Kr.*, **95**, 189 (1936). West, *Am. Min.*, **17**, 316 (1932), found periclase [110] || brucite [10$\bar{1}$0] in fibrous material from Quebec. See also Rinne, *Zs. deutsche geol. Ges.*, **43**, 234 (1891).
19. Literature in Mellor (**4**, 290, 1923).

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Glossary

The definitions in the Glossary are based on the Oxford English Dictionary (OED), Webster's International Dictionary (WEB), and unabridged dictionaries in English and foreign languages as well as the standard dictionaries and reference works in mineralogy, materials science, and medicine.

A

Acicular Needle-shaped or needlelike. The term is ordinarily applied in mineralogy to straight, greatly elongate, free-standing (individual) crystals bounded laterally, and terminated, by crystal faces. Aggregates of acicular crystals often occur in open, bristly groups. The aspect ratio of acicular crystals is in the same range as those of "fiber" and "fibrous," but the thickness may extend to several millimeters.

Actinolite-asbestos A type of amphibole-asbestos composed of the mineral actinolite. See chapter 2.

Alumen plumosum A Latin name given to the fibrous and feathery types of natural alum (hydrous alkali aluminum sulfates) and other efflorescent natural sulfates. Because of visible similarity, these materials were confused with asbestos by some early writers, and the term remained in use as a synonym of asbestos for many years.

Alveoli The small sacs or openings at the terminus of the bronchial pathway or breathing apparatus in the lung. See Fig. 3.1, p. 110.

Amianthine, amianthoid Of, pertaining to, or like amianthus. Obsolete.

Amianthus A term from ancient times applied to the exceptionally long, silky, relatively fine, and highly flexible mineral fibers capable of being woven. The actual usage establishes that the term referred to amphibole-asbestos. No longer in common use in English, *amianthus* was occasionally used to refer to all types of asbestos.

Amosite A commercial term for a type of amphibole-asbestos from South Africa consisting chiefly of fibrous members of the cummingtonite-grunerite series. Variable amounts of several fibrous members of the amphibole group and other minerals may be included in a particular sample. The name is an acronym derived from *a*sbestos *m*ines *o*f *S*outh *A*frica.

Amphibole A designation for any member of the amphibole group.

Amphibole group Amphiboles are hydrated silicates with Mg, Fe, Ca, and Na as the dominant cation species. These, together with other cations, substitute at specific

sites in the aluminosilicate crystal structure, producing a group of minerals closely related crystallographically and chemically (see chapter 2). The nomenclature and boundaries for the minerals and mineral series within the group have varied over time, reflecting research efforts.

Amphibole-asbestos A collective term for fibrous varieties of minerals in the amphibole group. Types of amphibole asbestos are more closely identified (viz: anthopyllite-asbestos). Note that not all members of the amphibole group occur in fibrous form, and those that occasionally do may also be found in other habits (prismatic, columnar, blocky).

Anthophyllite-asbestos The type of amphibole-asbestos composed of the mineral anthophyllite. See chapter 2.

Asbestiform An adjective used to describe inorganic materials that possess the form and appearance of asbestos (OED,WEB). Asbestine, asbestoid, and asbestous are obsolete synonyms. Asbestiform materials are a subset of fibrous materials. The term should be employed only when the material is one of the minerals mined as asbestos and possesses fibrosity typical of asbestos—that is, with relatively small fiber thickness, flexibility, separability, and general parallel arrangement of fibers en masse. The term asbestiform has also been used to imply that a sample or an individual fiber has morphological (gross external) characteristics similar to those of asbestos, but not necessarily the chemical or other physical properties of asbestos. In the 1700s asbestiform was used for the fibrous members of the amphibole group only. At that time virtually all asbestos in common use was amphibole-asbestos.

Asbestos A commercial and generally used name for fibrous varieties of naturally occurring silicate minerals of the amphibole or serpentine group (see chapter 2). Over the millenia many fibrous minerals have been called asbestos, including the six minerals presently accepted (see in the following), as well as other silicates such as palygorskite and nonsilicates such as brucite. The characteristics of mineral materials that have invoked the use of the term asbestos are: slender fibers that are easily separable and flexible, and fine fibers that have high tensile strength, chemical stability, and are incombustible. Natural unprocessed asbestos fibers have a large aspect ratio and may have lengths of microscopic dimensions up to, in rare instances, a meter or so. Chrysotile-asbestos fibers are commonly 10 centimeters in length. A definition of asbestos was proposed in 1984 by Ross, Kuntze, and Clifton (see chapter 2 References) as follows:

> asbestos—a term applied to six naturally occurring minerals exploited commercially for their desirable physical properties, which are in part derived from their asbestiform habit. The six minerals are the serpentine mineral chrysotile and the amphibole minerals grunerite asbestos (also referred to as amosite), riebeckite asbestos (also referred to as crocidolite), anthophyllite asbestos, tremolite asbestos, and actinolite asbestos. . . . Individual mineral particles however processed and regardless of their mineral name, are not considered to be asbestos if the length-to-width is less than 20:1.

Asbestos is used as an adjective in combination with numerous other words and phases, such as asbestos cement.

Asbestos (or ferruginous) bodies Nodular masses in the lung composed of collagen (a fibrous protein) and ferritin (an iron-containing globular protein). Although they

are benign, the presence of these nodules is taken to indicate exposure to asbestos. Occasionally the nodules become mineralized, causing disruption of the local tissue flexibility and interfere with the normal motions necessary for breathing.

Aspect ratio The numerical relationship of the length to the thickness of a fiber or cleavage fragment; usually the length divided by the thickness, but occasionally presented as thickness:length (see chapter 1).

B

Blue asbestos, blue cape asbestos Categorical and trade names for crocidolite-asbestos, which has a pale blue, lavender, or bluish green color en masse. Blue asbestos was a synonym for crocidolite in mineralogy before the term was adopted in the trade.

Bronchi, bronchus The larger passages that allow air to pass from the nose to the lower lung (see Fig. 3.1).

Brown asbestos Categorical name used primarily in reference to amosite.

C

Canadian asbestos A synonym for chrysotile-asbestos.

Cape asbestos Trade term for crocidolite-asbestos from South Africa.

Capillary Very slender, hairlike particles with a fine bore; a small tube.

Chrysotile A mineral in the serpentine group composed of hydrated magnesium silicate, which occurs in several crystalline modifications (see chapter 2) and usually in fibrous form. First described and named in 1834, chrysotile fibers were mined under the name serpentine-asbestos, or simply asbestos, long before that time.

Chrysotile-asbesots A type of asbestos composed of the mineral chrysotile. (For a full discussion, see chapter 2).

Cleavage The property of an individual crystal to fracture or break, producing planar surfaces along specific crystallographic directions dictated by the structure of the material. Some crystals lack cleavage; others possess one or more crystallographically distinct cleavage directions (see chapter 1).

Columnar Term applying to somewhat cylindrical or prismatic crystals with a thickness of more than 500 microns in which the aspect ratio is generally low.

Cor pulmonare Heart disease developed as a result of pulmonary insufficiency; latter part of the disease sequence of asbestosis reflecting the impaired transfer of oxygen and carbon dioxide through the blood vessels of the lung.

Crocidolite This mineral name was originally proposed in 1831 for what was thought to be a distinct mineral, but was later shown to be a fibrous variety in the amphibole mineral series riebeckite-magnesioriebeckite. "Crocidolite" continues in trade use and, to some extent, in mineralogical and biomedical scientific use.

Crocidolite-asbestos A trade designation for a specific type of amphibole-asbestos composed of the mineral riebeckite. It is also called blue asbestos and, if obtained from South Africa, may be labeled cape asbestos.

Cross-fiber asbestos Term applied to aggregates of asbestos in veins (see Fig. 1.1A) in which the fibers are arranged in parallel position, usually perpendicular to or sometimes at a low inclination angle to the rock surfaces. The term may be applied to either serpentine- or amphibole-asbestos.

Cummingtonite-asbestos The type of amphibole-asbestos composed of the mineral cummingtonite.

D

Dyspnea Difficult or labored breathing.

E

Emphysema The pathological accumulation of air in the organs or tissues, which usually gives rise to expansion and stretching and is followed by fibrosis and atropy.

Empyema The accumulation of pus.

Endothelial, endothelium The layer of epithelial cells that line the cavities of the blood and lymph vessels, the heart, and other cavities of the body.

Epithelial, epithelium The layers of cells and connecting tissues that form the covering of internal and external body surfaces, including the lining of small vessels and cavities.

Etiology The science dealing with the causes of disease.

F

Ferritin The iron-containing globular protein species common in all parts of the body, but especially associated with the asbestos or ferruginous bodies.

Fiber A long, thin thread or threadlike solid with distinctive elongate shape that may be natural or synthetic and organic or inorganic in composition. The properties of flexibility and toughness are also implied, especially to the layperson, but are not essential to the definition. The dimensions of an object called a fiber are usually unspecified and may range from the visible (diameter about a millimeter, and a length many times the thickness) to a particle that can be observed only with the aid of a light or an electron microscope (magnification greater than X50,000). The physical dimensions of vegetable fibers such as flax, hemp, or cotton; animal fibers such as wool, silk, and hair; mineral fibers, such as asbestos; and synthetic fibers such as nylon and glass usually have diameters between 1 and 500 micrometers and lengths between 10 and 1000 micrometers. Inorganic fibers may be flexible and elastic or stiff and brittle, and they commonly occur as aggregates or fibrous bundles. Most mineralogists apply the term when the aspect ratio of a mineral sample, individual or aggregate, is at least 10.

Fibril A small fiber or the subdivision of a fiber (OED); also a small thread or fiber (WEB). The term is usually employed to describe an elongate unit whose dimensions are smaller than *fiber* (fine-fibrous) and may be used to designate one member of a fibrous mineral aggregate, regardless of the size of the individual particles or the aggregate. In the latter usage, the implication is that a fibril is the smallest unit that expresses the characteristics of a fiber or fibrous mass, and usually that the fibril is separable by subdivision parallel to the length of the fiber. For example, chrysotile-asbestos could theoretically be disaggregated to tubular individual fibrils with di-

ameters in the range of 200 A. The term fibril therefore has an ultimate lower limit. Fibril is also related to the term *polymer*, which is defined as a chemical compound or mixture of compounds formed by polymerization and consisting of essentially repeating structural units, usually producing giant chainlike macromolecules. Such a molecule is characterized by highly asymmetric geometry and anisotropic properties. If a solid is formed from polymers, a fibril would be the smallest polymeric unit.

Fibrous Full of fibers, or formed of fibers (OED), with dimensions unspecified but implied, by comparison, to be similar to the natural materials thread and hair (see *Fiber*). Aggregates of any size of individual fibers may form relatively thick fibrous bundles, thus becoming visible to the naked eye.

Filiform Having the shape of a thread or filiment, roughly 10 microns or less in thickness (=fine-fibrous). The term is often applied to wirelike growths of native metals.

H

Hornblende-asbestos Obsolete synonym of amphibole asbestos. The term is derived from the early use of hornblende for the group of minerals now called amphiboles. Hornblende, defined today as a mineral series within the amphibole group, rarely occurs in fibrous form.

L

Linum vivum Ancient name for cloth woven from asbestos. From the Latin *linum*, meaning flax or linen, and *vivum*, used in the sense of "to endure" or "to live," in reference to the stability of asbestos cloth against fire.

Lymph The slightly yellow, transparent liquid found in the lymph vessels, but also in all tissues of the body. The lymphatic system collects lymph from these sites and returns it to the blood. Lymph contains specialized cells, ions, and molecules in suspension in the fluid (see chapter 3).

M

Mineral A naturally occurring element or compound defined by its chemical composition and crystal structure (see chapter 2). By custom in recent times, mineral species have been given names ending in "ite." Each year, about 100 new species are proposed, and usually about half are accepted by the International Mineralogical Association Commission on New Names as bona fide new species. The *Glossary of Mineral Species* (Fleischer, 1987) is a current source of information. Updates are published annually in the *Mineralogical Record*.

Mineral group A collection of mineral species and mineral series that have common basic chemical and structural units and related compositions and crystal structures.

Mineral series Minerals that have an identical basic chemical and structural unit in which small amounts of chemical substitution of similar elements (cations of similar size, stereochemical, and bonding character) in the same site in the crystal structure are usual and predictable. Mineral series are usually defined by the "end member" species, that is, those compounds that contain only one of the possible cations. Intermediate members may have specific names or be identified by the ratio of the cations (see chapter 2).

P

Parenchyma The functional or essential portions of an organ as distinguished from the framework or supporting structures.

Plaque Any flat area, but usually a deposit of material on a flat surface, such as the covering epithelium of the lung. Plaques occasionally mineralize, which makes them visible on chest x-rays (see chapter 3).

Pleural cavity The potential space between the linings or coverings of the lung and thorax.

Pleurisy Inflammation of the pleura, the membranes that line all internal and external structures of the lung and thoracic cavity.

Pneumoconioses Lung disease caused by the permanent deposition of particulates within the lung parenchyma.

Pneumonitis Inflammation of the tissues of the lung.

Prismatic A term commonly used in descriptions of minerals for crystals exhibiting aspect ratios usually below 3 and grading into equant (aspect ratio = 1). The term may refer to crystals embedded in a matrix, but is more commonly used to describe free-standing, euhedral crystals, whether micro- or macroscopic.

S

Serpentine, serpentine group Both a rock and a mineral name, serpentine is found in Latin, transposed from the Greek, as a term for a rock with serpentlike markings. After the 1700s, when magnesium and silica had been determined in these materials, the term was applied to rocks that contained these elements and appeared serpentine. In the late ninteenth century, the term serpentine designated a specific mineral species that was hydrated and contained magnesium and silica. Mineral varieties of serpentine were distinguished on the basis of their physical appearance—that is, massive, lamellar, columnar, or fibrous. Today, serpentine rock is composed of serpentine minerals, and serpentine is the name used for the mineral group that includes chrysotile, antigorite, and lizardite.

Serpentine-asbestos An early name for the fibrous form of serpentine rock that was mined. Today the term refers to chrysotile-asbestos.

Short-fiber asbestos A trade name for asbestos with relatively short fibers. Both chrysotile and amphibole asbestos may occur in short fibers.

Squamous Scaly or platelike.

T

Talc A mineral with the approximate chemical formula $Mg_3Si_4O_{10}(OH)_2$ (see chapter 2). The term has been used as a commercial name for fibrous or platy deposits formed by hydrothermal alteration of rocks rich in silica, magnesium, and iron.

Tremolite-asbestos An amphibole-asbestos composed of the mineral tremolite.

U

Unit cell The unique and smallest portion of a crystalline compound that expresses the chemical composition and structure of the material.

W

Whisker, whisker-crystal A modern technical term originating in the field of solid-state physics for highly elongate crystals resembling mineral fibers that are synthesized from a variety of inorganic substances, usually at elevated temperatures or pressures. Whiskers are synthetic fibrous materials (see chapter 2).

White asbestos Categorical term used primarily for processed chrysotile. Chrysotile en masse has a golden color.

Z

Zeolite, zeolite group A collective term for a family of aluminosilicate minerals characterized by framework structures that allow easy access and exchange of cations and small molecules (see chapter 2). The name derives from the Greek terms *zein*, meaning "to boil," and *lithos*, meaning "stone." The term is also applied to synthetic materials of comparable composition, crystal structure, and physical properties (see chapter 2).

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CHAPTER 1

Fig. 1.1J. From Evans, C. C. (1972). *Whiskers,* Mono. 8, Fig. 2, p. 11. Mills and Boon, Ltd., London.

CHAPTER 2

Fig. 2.2A and B. From Wicks, F. J. (1979). Mineralogy, chemistry and crystallography of chrysotile asbestos. Fig. 1.20, p. 36; Fig. 1.21, p. 38. In R. J. Ledoux, ed. *Mineralogical Techniques of Asbestos Determinations*. Min. Assoc. Canada, Toronto, Canada. With permission of Min. Assoc. Canada.

Figs. 2.3, 2.7, 2.12B. After Zoltai, T., and J. H. Stout (1984). *Mineralogy: Concepts and Principles*. Fig. 11.21, p. 326; Fig. 11.39, p. 341; Fig. 11.23, p. 326. Burgess Pub. Co., Minneapolis. With permission of T. Zoltai.

Fig. 2.4. From Yada, K. (1967). Study of chrysotile asbestos by a high resolution microscope. *Acta. Crystallog*. Fig. 7, p. 707.

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Fig. 3.3A and B. Photographs courtesy F. Walker Smith. Yale University School of Medicine, New Haven, Ct.

Fig. 3.6. From Gee, J. B. L., and J. Lwebuga-Mukasa (1984). Cellular and matrix mechanisms. Fig. 7.1, p. 164. In W. K. C. Morgan and A. Seaton, eds. *Occupational Lung Disease*. W. B. Saunders Company, Philadelphia, Pa. With permission of W. B. Saunders Company, Harcourt Brace Javanovitch, and the authors.

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APPENDIX 3

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