The Mineralogy of Asbestos

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Thomas A. Sporn

1.1 Introduction and Historical Background

Minerals are naturally occurring inorganic compounds of specific chemical composition and crystal structure. Their nomenclature typically stems as an honorific, to indicate a pertinent geographic area or to highlight a distinctive characteristic of the compound. The term asbestos collectively references a group of naturally occurring fibrous minerals which have been exploited in numerous commercial and industrial settings and applications dating to antiquity. Its myriad uses as a "miracle mineral" owe to its remarkable properties of extreme resistance to thermal and chemical breakdown, tensile strength, and fibrous habit which allows it to be spun and woven into textiles. Abundant in nature, it has been mined considerably, and in all continents save Antarctica. The nomenclature concerning asbestos and its related species is complex, owing to the interest held therein by scientific disciplines such as geology, mineralogy and medicine, as well as legal and regulatory authorities. The silicate minerals may have fibrous and nonfibrous habits. The group of asbestos and "asbestiform" minerals shares the common features of occurrence as flexible polyfilamentous bundles, long fiber length, and small fiber diameter. As fibrous silicates, asbestos minerals are broadly classified into the serpentine (chrysotile) and amphibole (crocidolite, amosite, tremolite, anthophyllite, actinolite) series, both of which may also contain allied but nonfibrous forms of similar or even identical chemical composition, nonpathogenic to humans. As such, amphibole minerals in the non-polyfilamentous habit are not classified as asbestos, nor are some other asbestiform amphiboles which are not commercially exploitable. Although generally grouped, classified, and regulated generically as asbestos, the serpentine and amphibole groups have different geologic occurrences and, more importantly, significant differences in crystalline structures and chemical compositions. These in turn impart differences in fiber structure and dimension, as well as biopersistence, leading to marked differences in relative potency for causing disease in humans for the group of minerals known as asbestos. Derived from the Greek term for "unquenchable" or "indestructible," asbestos is the collective term for a family of naturally occurring fibrous silicates that exist in metamorphic, altered basic, or ultra basic igneous rock. Asbestos and asbestiform minerals are narrowly defined and classified, as will be discussed below. The asbestos minerals have found much utility owing to their common properties of thermochemical and electrical resistance, high tensile strength, and flexibility. Insoluble in water and organic solvents, its fine fibers may be spun and woven into textiles and incorporated into many

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T.A. Sporn, MD
Department of Pathology,
Duke Clinics-Duke University Medical Center,
200 Trent Drive, Durham, NC 27710, USA
e-mail: sporn001@mc.duke

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other types of materials; asbestos has seen literally thousands of industrial applications. The usage of asbestos dates through fact and fable to thousands of years ago. Once believed to have almost magical capabilities, first descriptions document its usage in the manufacture of pottery in Finland ca. 2500 B.C. Additional historical attributions for early asbestos usage include cremation garments for royalty and for embalming the pharaohs of ancient Egypt. Emperor Charlemagne reportedly astonished his guests at a feast by throwing table cloths made from asbestos into a fire from which the garments would be removed clean and unharmed. Medieval alchemists termed the mineral "salamander stone" referring to a mythical fireproof animal, and during these times asbestos was used in suits of armor [1]. Deposits of asbestos in the Ural Mountains led to the development of factories producing asbestos textiles in 1720. In the seventeenth century, fibrous minerals discovered in Germany termed Bergflachs or Bergleder likely contained amphibole asbestos, and by the mid-nineteenth century, some 20 asbestos mines were operating in Europe [2]. In colonial America, asbestos deposits were discovered in Pennsylvania and New England, where it was woven into textiles, and chrysotile was discovered in Quebec, Canada, in 1860 [2]. Significant commercial usage of asbestos did not occur until the latter part of the nineteenth century, with the development of demand for insulation for the burgeoning steam technology. At the turn of the twentieth century, additional applications for the useful minerals had been developed, deposits of amphibole asbestos species had been discovered in South Africa, and asbestos was once more being mined in the Urals, this time in large quantities. Commercial exploitation of asbestos was now global and full blown, and by 1980 over 100 million tons of asbestos had been mined worldwide [2], accompanied by the development of serious health concerns related to its usage. The purpose of this chapter is to describe what the groups of minerals classified as asbestos are from a mineralogic perspective, where they occur, and what are the important distinctions that allow relative differences within members of the asbestos group to have differing potencies on the basis of such differences in terms of inducing injury and producing disease following inhalation. It is well known from animal models that the oncogenic potential of fibrous dust increases following reductions in fiber diameter and decreases with reduction in fiber length, and these considerations are generally more important than the chemical composition of the fibers themselves [3–6]. The longer fibers have more potency to induce cell injury, proliferation, oxidant release, and inflammation. It is also the durability of the fibrous dust that confers biopersistence and the potential to induce malignant disease following deposition of fibers in the peripheral airways and migration of fibers to the serosal membrane. Contemporary usage of asbestos has been curtailed following its wide recognition as a most dangerous substance; it is noteworthy that the health hazards of asbestos date to antiquity as well. Pliny the Elder cautioned against the purchase of quarry slaves from asbestos mines, noting that they tended to die young [1]. Contemporary usage of asbestos is highly variable, although global demand still measures in the millions of metric tons. The European Union, Australia, and Japan are examples of states which enforce national bans on asbestos products; other countries allow its usage and enforce variably stringent regulations on fiber type and permitted levels of exposure. In 2006, six countries (the Russian Federation, the People's Republic of China, Kazakhstan, Brazil, Canada, and Zimbabwe) contributed to 96 % of the world's production of asbestos [7, 8] In the USA, asbestos consumption fell to 1,730 metric tons in 2007, chiefly in the form of chrysotile-containing roofing products [8].

1.2 Geologic and Mineralogic Features

Asbestos is properly considered a commercial and legal rather than a mineralogic term for a group of fibrous silicate minerals with crystalline structure and by definition have lengths >5 μm and aspect (length/diameter) ratios of three or greater. In the USA, the asbestos nomenclature as defined by the Environmental Protection Agency encompasses six unique mineral species, conventionally divided into two distinct groups: the amphiboles and the serpentines [9]. Chrysotile is the sole member of the latter group and, as of the year 2000, accounted for virtually 100 % of the asbestos used commercially. Historically, at least 90 % of commercially used asbestos has been chrysotile. The amphibole group contains grunerite-cummingtonite (amosite, vide infra), crocidolite (a fibrous variant of riebeckite), tremolite, actinolite, and anthophyllite. The name amosite is derived from the acronym AMOSA—Asbestos Mines of South Africa—giving reference to the company in the Transvaal Province of South Africa, the sole mine producing the mineral. As such, amosite, too, is a commercial, rather than a true mineralogic term, but by convention, amosite is used synonymously for the fibrous forms of grunerite-cummingtonite, just as crocidolite is for the fibrous form of riebeckite. Among the amphiboles, only crocidolite and amosite have undergone significant commercial exploitation in industrialized countries and collectively account for less than 10 % of asbestos utilized in the last century. Fiber characteristics influence commercial exploitation. Long fibers are useful as insulation materials and textiles, medium-length fibers have been used in asbestos cement and friction products, and short fibers are used as reinforcing agents in floor tiles, joint compounds, and roofing material. Highly resistant to acid and salt water, large amounts of amosite were imported into the USA during World War II for usage in warship and merchant vessel insulation. The high tensile strength and extreme thermal stability of crocidolite allowed its usage as insulation material at very high temperatures, as well as packings and gaskets. The so-called noncommercial amphiboles, actinolite, tremolite, and anthophyllite, are common mineral species with wide distribution. They are relevant insofar as they are contaminants of other commercially useful mineral species such as talc and vermiculite, as well as chrysotile, and have been implicated in the induction of disease in humans. The asbestos minerals have nonpathogenic, non-asbestiform mineral counterparts of identical chemical composition. The noncommercial species of amphiboles all require the word "asbestos" after their mineral name for the purpose of distinguishing them from the non-asbestos forms. This is not necessary for crocidolite, amosite, and chrysotile as the non-asbestos forms have different names as discussed above (see Fig 1.1).

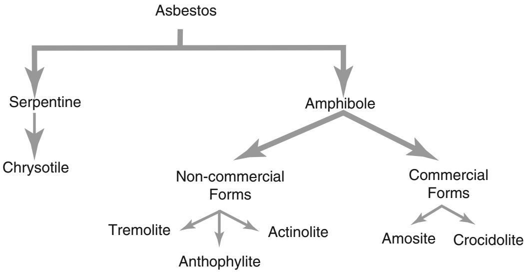

Fig. 1.1 Classification of asbestos and asbestiform silicates

Asbestos minerals owe their fibrous habit to the parallel growth of very fine and elongate crystals, producing bundles. The amphiboles may also occur as nonfibrous, chunky, acicular, and shard-like forms. Nonfibrous serpentine minerals include antigorite and lizardite. The nonfibrous forms of both serpentine and amphibole minerals are more common and widespread than the asbestiform species.

Deposits of commercial asbestos are to be found in four types of rocks: the banded ironstones, containing amosite and crocidolite; the alpine-type ultramafic rocks, containing chrysotile, anthophyllite, and tremolite; the stratiform ultramafic inclusions, containing chrysotile and tremolite; and the serpentized limestone (chrysotile) [2]. Recently in the USA, fibrous amphiboles not historically classified or regulated as asbestos (winchite, richterite) have been implicated in the causation of serious disease due to their profusion as natural contaminants (along with tremolite) of vermiculite, a commercially useful and nonfibrous silicate mineral [10, 11], vide infra. Other "asbestiform" minerals include the fibrous zeolites such as erionite. Erionite, found naturally in volcanic tuff in some areas of Turkey where it has been used as a construction material, has physicochemical characteristics resembling those of the amphiboles such as high aspect ratio and fiber diameters less than 0.25 um [12]. Fibrous erionite induces mesothelioma in animal models and has been implicated in both benign and malignant pleural disease in humans [13–15].

1.3 Distribution and Physicochemical Properties of Chrysotile

Chrysotile is a common serpentine mineral with worldwide distribution and the only one of this series mined as asbestos. The type 1 (alpine-type ultramafic rock) deposits are the most important sources of chrysotile asbestos, with principal localities occurring in the Ural Mountains of Russia and the Appalachian Mountains of the Canadian province of Quebec and the state of Vermont in the USA, as well as the state of California. Chrysotile has also been mined in the Italian Alps, Cypress, Zimbabwe, and the People's Republic of China [2] (Table 1.1). Commercially useful chrysotile is prepared from chrysotile ore in the milling process, with extracted long fiber chrysotile finding usage in textiles and shorter fibers used in construction materials such as joint compound. Among the commercially exploited seams of the mineral, geographic variations are to be expected both in terms of physical characteristics of the fibers, type, as well as proximity to fibrous species of noncommercial amphiboles. For example, the rich chrysotile ores quarried at the Coalinga, California, mines yield fibers almost exclusively less than 5 μm [16]. There is also variance in the presence of other potentially dangerous minerals even within neighboring seams. McDonald et al. attributed the difference in reported deaths due to mesothelioma among workers in several different mines within the province of Quebec to be attributable to local variances in the amount of tremolite contamination known to exist within the various mines [17]. The topic of chrysotile purity following milling and the potential contamination by noncommercial species is frequently argued in the ongoing asbestos litigation in the USA.

The basic chemical unit of all silicate materials is the silicate tetrahedron, Si04. The actual number and configuration of tetrahedral within the crystal structure provides the basis for the classification of silicate minerals. Silicates may be classified on the basis of the polymerization type of the silicate ions and the variance in crystalline structure that occurs through association of various cations. Chrysotile is a hydrated (approximately 13 % water as a crystal) phyllosilicate (sheet silicate) with chemical composition $Mg_3Si_2O_5(OH)4$, containing the typical $(Si_2O_5)n^{-2}$ building block typical of the serpentine group of minerals [18] (Fig 1.2). Whereas other serpentines and other layered silicates (clays, mica) form flat sheets, spatial imbalances between magnesium and silica ions within the tetrahedral and octahedral sheets of chrysotile cause the layers to roll to form concentric hollow cylinders. Chrysotile fibers will thus appear scroll like when viewed end on (Fig. 1.3), containing a central capillary with 2–4.5 nm in diameter. The milling of chrysotile ore yields bundles of fibers of variable length, and some fibers may exceed 100 μm. The fibers may be curvilinear ("serpentine"), often with splayed ends due to the separation of fibers into individual and smaller fibrillar units (Fig. 1.4). Some very long chrysotile fibers may be quite thin, but the diameter of chrysotile fibers tends to increase with increasing fiber length. Magnesium is an important constituent of both chrysotile and the amphiboles; the presence of soluble magnesium molecules on the outside of the curled chrysotile structure permits its leaching at the surface, facilitating the breakdown of fibers within lung tissue into successively smaller, fragile fibrils, which are then readily cleared from the body. Loss of magnesium changes the surface charge from positive to

Table 1.1 Geographic distribution of asbestos species

Asbestos mineral	Geographic distribution
Chrysotile	Canada (QC), USA (Vermont, CA), Russia, China
Crocidolite	South Africa (NW Cape Province, Transvaal), Western Australia
Amosite	South Africa
Tremolite	Turkey, Cyprus, Greece
Anthophyllite	Finland, USA
Actinolite	South Africa (Cape Province)
Winchite/Richterite[a]	USA (MT)

[a] Asbestiform amphibole species, not classified as asbestos

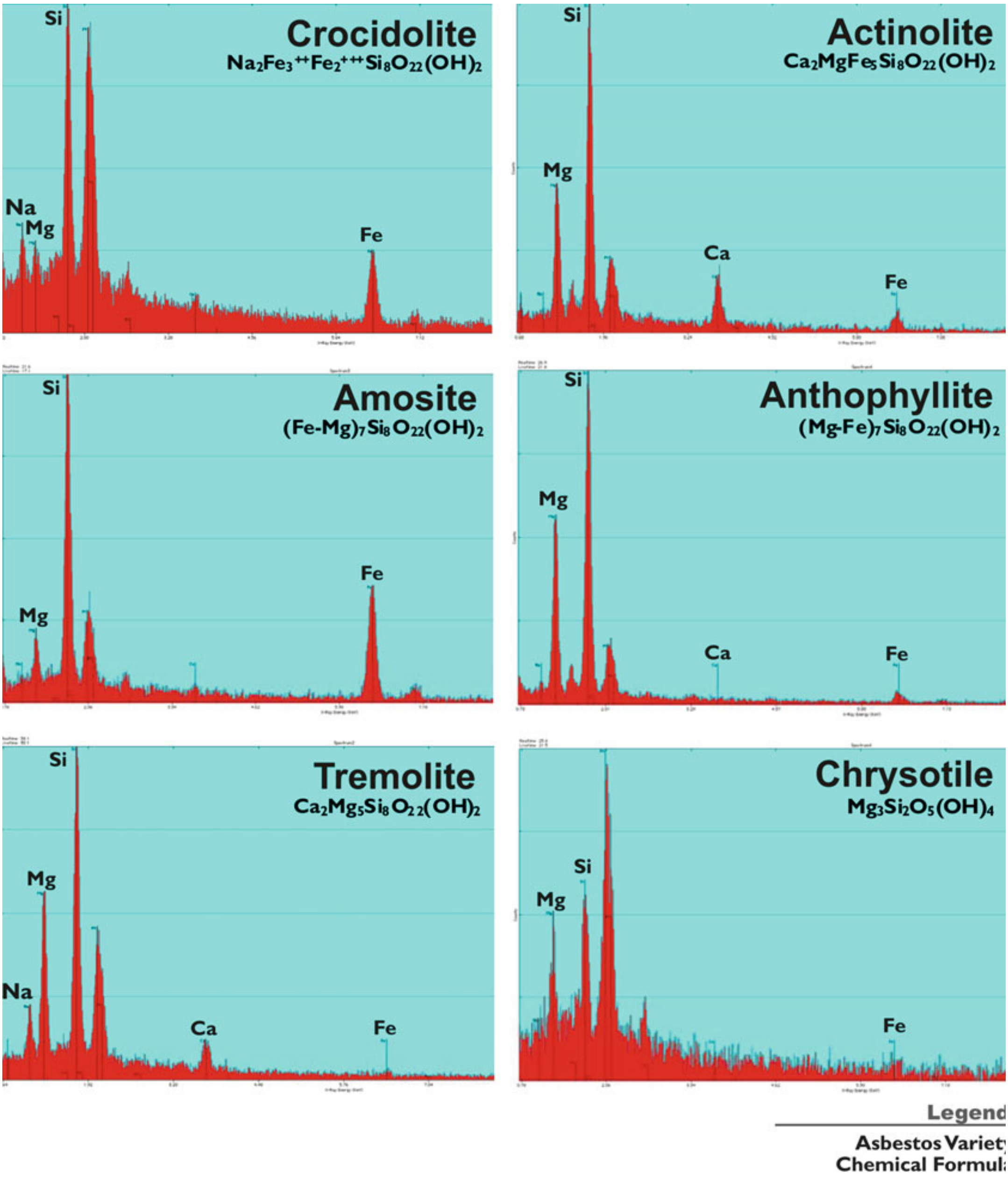

Fig. 1.2 Chemical composition and elemental spectra of asbestos

negative, which diminishes the oncogenic potential [4]. The clearance half-time of inhaled chrysotile within the lower respiratory tract is measured in only weeks and may be much less. For example, with a clearance half-time measured in hours, the chrysotile from the Coalinga mine in California is among the mineral fibers with the most rapid clearance from the lung. Other chrysotile may have biopersistence similar to the range reported for glass and stone wools [19]. Thermoresistant to a degree, 70 % of the chrysotile structure is lost at 575 °C, with complete loss of the structure occurring at 650 °C [20]. Such high temperatures may be observed in the automotive braking process, causing pyrolysis and conversion to the nonfibrous, nonpathogenic silicate mineral forsterite [20]. Due to its physicochemical characteristics, chrysotile has a greatly reduced biopersistence in contrast to the amphibole species, and those features as described above provide a likely explanation for the reported reductions in oncogenicity for this species in humans in contrast to the amphiboles [21, 22] and for the epidemiologic studies that conclude that motor vehicle mechanics performing brake repair are not at increased risk for developing mesothelioma [23].

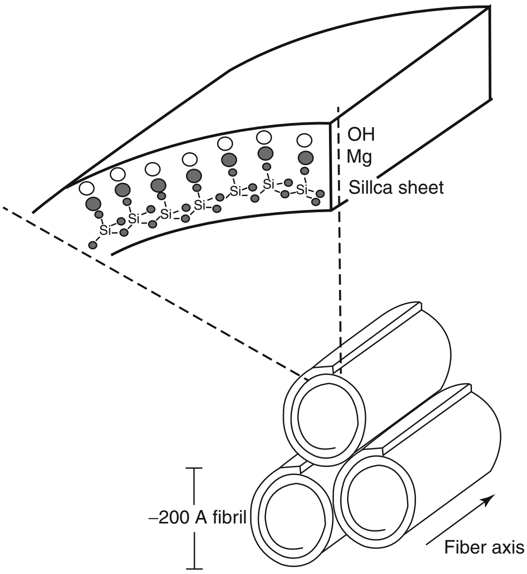

Fig. 1.3 Crystalline structure of chrysotile (Schematic diagram modified)

1.4 Distribution and Physicochemical Properties of the Amphibole Species

The amphibole asbestos minerals crocidolite, amosite, anthophyllite, tremolite, and actinolite are inosilicates, or chain silicates, indicating the arrangement and alignment of the silicate tetrahedra. Tremolite, actinolite, and anthophyllite are grouped together with chrysotile as “white asbestos” and classified under the United Nations chemical identification schema as UN2590. Amosite “brown asbestos” and crocidolite “blue asbestos” are classified as UN2212. Amphiboles typically occur when veins of the mineral are created when cracks form in rocks during movement of the earth. These conditions help provide the environment necessary for massive amphibole crystallization and transformation to the fibrous form. The amphibole minerals are common, but their occurrence as exploitable forms is limited to certain locations where they obtain the proper physicochemical characteristics and abundance to be used as commercial asbestos. The major deposits of commercial amphiboles have generally been limited to the banded ironstones of

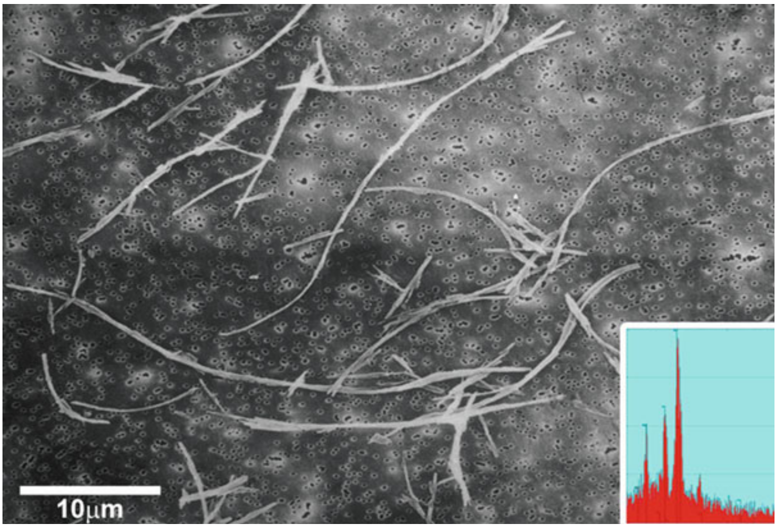

Fig. 1.4 Chrysotile asbestos fibers, scanning electron photomicrograph. Note long fibers of variable thickness and curvilinear “serpentine” morphology

Western Australia and the Transvaal and Cape Provinces of South Africa. Alpine-type and stratiform ultramafic rocks are sources of chrysotile, as well as the noncommercial amphiboles tremolite, actinolite, and anthophyllite, the major source for the latter occurring in Finland with smaller deposits in rocky outcrops of the USA [2]. Some minerals aside from the commercial amphiboles may form polyfilamentous, asbestiform crystals. An example of this type of asbestiform amphiboles is to be found in the area around Libby, Montana, USA. Libby is the site of the largest mined deposit of vermiculite in the world, and the alkaline-ultramafic rock is rich in amphiboles, chiefly richterite and winchite (sodic-calcic tremolite), all of which can exist in asbestiform or fibrous habit [24, 25]. The latter species are not listed in the US federal regulations governing asbestos, but their recognition is important in view of the abnormally high number of asbestos-related diseases and deaths in former vermiculite miners and millers and residents of this area, and the potency of the Libby amphibole in terms of inducing mesothelioma is reported to be similar to crocidolite [26, 27]. Anthophyllite, tremolite, and actinolite are common constituents of the earth's crust, but have not been exploited commercially in industrialized countries, and are frequently associated with serpentine minerals, vermiculite, and talc. The noncommercial amphiboles may assume a variety of forms, including nonfibrous forms.

The chemical and crystalline structures of the amphiboles are highly similar and generally may be distinguished only on the basis of chemical composition and in specific the cation constituents (Fig. 1.2). Crystalline amphibole minerals demonstrate perfect prismatic cleavage, with direction of the cleavage parallel to the length of the silicate chains [28]. The silicate chains are formed by linear arrays of SiO_4 tetrahedra linked by octagonal groups of cations and may be of significant length (Fig. 1.5). The crystalline amphibole fibers are substantially more brittle than chrysotile, limiting their potential for fabrication. These mineralogic attributes confer the potential for great fiber length and, accordingly, significant pathogenicity following deposition in the lung (Figs. 1.6, 1.7, 1.8, and 1.9). As their straight, broad fibers are resistant to fiber fragmentation and chemical degradation in the body, the biopersistence of the amphiboles is much greater than chrysotile, and their clearance half-time is generally measured in decades. The crystalline structure of the amphiboles also contains less water than chrysotile, and there is greater resistance to pyrolysis. Amphibole fibers are less flexible than chrysotile, permitting greater friability with potential to release respirable particles.

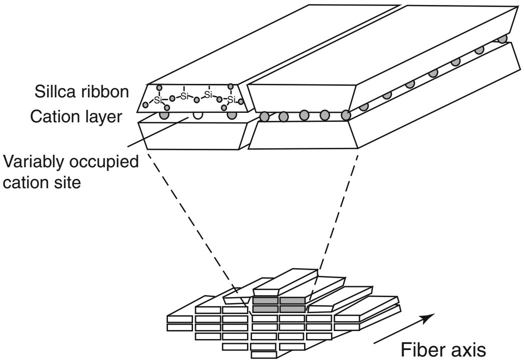

Fig. 1.5 CrystallChemical composition and elemental spectra of asbestoscture of amphibole asbestos (Schematic diagram modified from Roggli and Coin (2004))

1.5 Identification and Characterization of Asbestos

Several techniques are available for the identification of asbestos fibers, making use of the morphologic, chemical composition and crystallogic features of the mineral [29]. The techniques include phase-contrast microscopy, polarizing microscopy with dispersion staining, infrared spectroscopy, x-ray and electron diffraction, and analytical electron microscopy. Each technique has its own advantages and disadvantages; Chap. 11 offers additional description of these. In brief, phase-contrast microscopy is a relatively inexpensive means to permit basic quantitative analysis of tissue fiber burden and is used to demonstrate the morphologic features of fibers such as size, shape, and aspect ratio. It is seldom used owing to the limits of the resolution of light microscopy, its

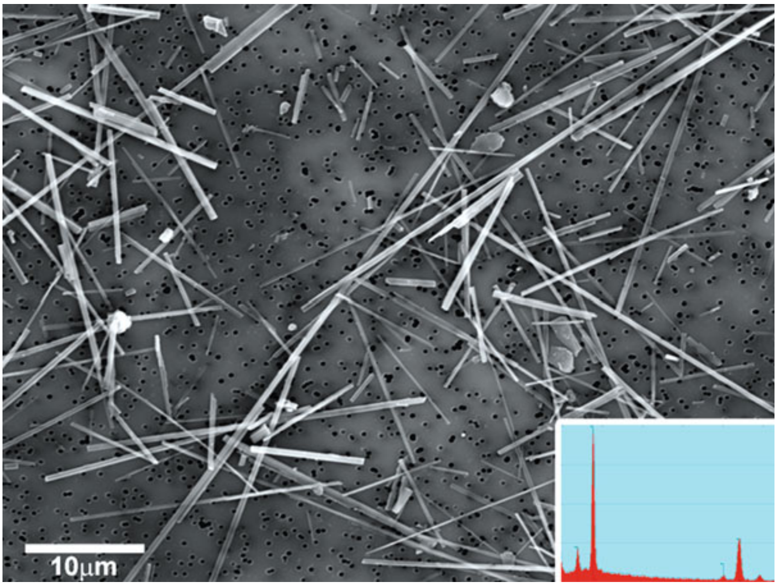

Fig. 1.6 Amphibole asbestos fibers, scanning electron photomicrograph. Note long, straight, and slender fiber morphology

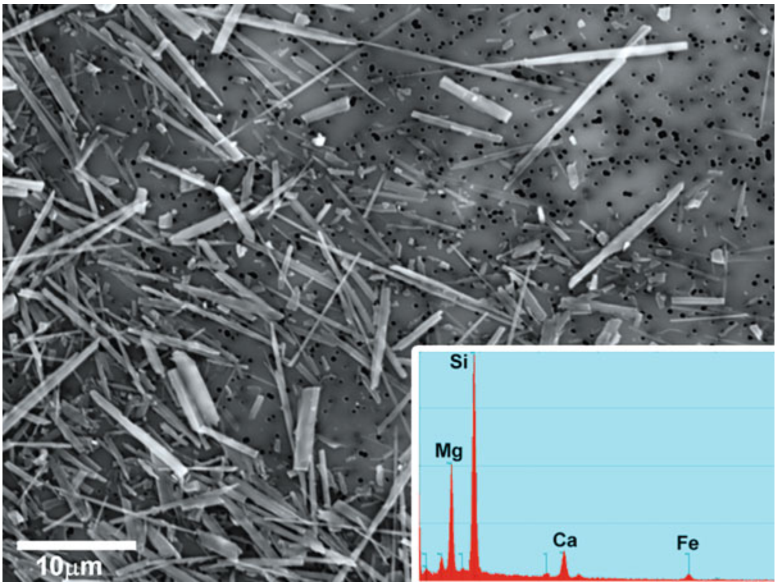

Fig. 1.7 Libby asbestiform amphibole asbestos fibers, scanning electron photomicrograph. Note varying fiber morphologies, with thick, thin, short, and long fibers all represented

inability to distinguish asbestos fibers from non-asbestos mineral fibers or provide information regarding the chemical composition of fibers. Polarizing microscopy provides information pertaining to the basic crystalline structure of fibers and may be used to distinguish among the various asbestos fiber species and to make the distinction between asbestos and non-asbestos fibers. This technique is also limited by the resolution of light microscopy. Infrared spectrophotometry is a bulk analytical technique unable to examine individual fibers and is used to identify the characteristic spectra of the asbestos minerals. It is not generally used to identify asbestos in tissue or environmental samples. X-ray diffraction is also a bulk analytical technique which identifies diffraction patterns produced as x-rays pass through various crystalline materials [30]. It is generally considered a qualitative technique to measure the quantity of asbestos within a sample.

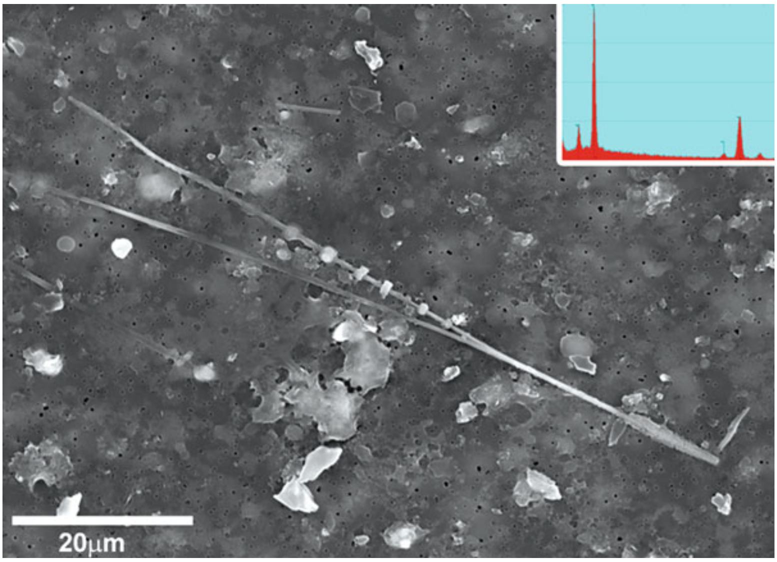

Fig. 1.8 Amosite asbestos body. Note longitudinal cleavage of long, slender fiber

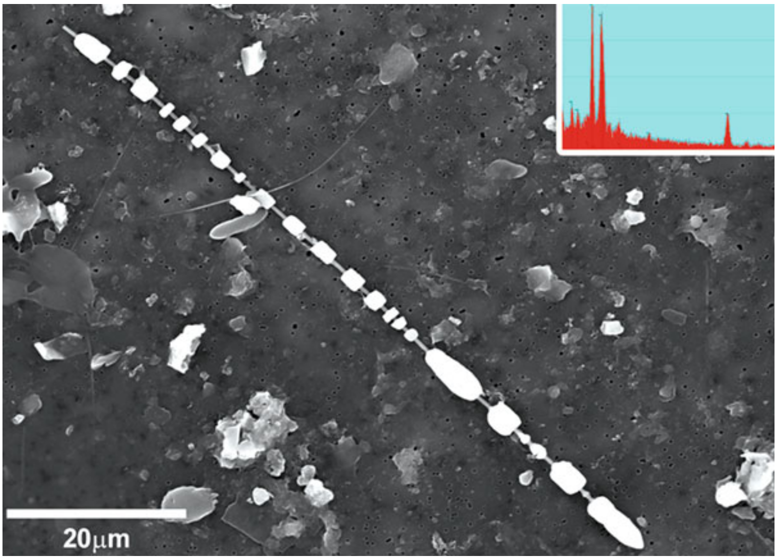

Fig. 1.9 Crocidolite asbestos body. Note characteristic long slender fiber undergoing ferruginization

Most investigators prefer some form of analytical electron microscopy for the identification of asbestos. AEM has the ability to provide high-resolution images of the details of the smallest of fibers and to provide crystallographic compositional data for individual fibers through selected area electron diffraction and elemental composition information through energy dispersive spectrometry (EDS). EDS focuses an electron beam on individual particles and observes the x-ray spectra produced by the beam and the atoms within the particle. The spectra so produced consist of peaks distributed according to the energies of the x-rays, which are in turn related to the elemental composition of the fiber or particle being studied. Such spectra may be then compared to standards for confirmation of identification (Fig. 1.2). Analytical scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are both useful, albeit expensive and time-consuming. Our lab uses SEM to measure the number and dimensions of both fibrous and nonfibrous crystalline material and provide both qualitative and quantitative analysis of fiber types and their proportionality. TEM generally offers superior resolution as well as the identification of very fine fibers and small fibrils, but the preparatory techniques are more complicated.

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