Reviews in Mineralogy & Geochemistry
Vol. 67, pp. 453-516, 2007

Amphiboles: Environmental and Health Concerns

Mickey E. Gunter

Department of Geological Sciences, University of Idaho
Moscow, Idaho, 83844-3022, U.S.A.
mgunter@uidaho.edu

Elena Belluso

Dipartimento di Scienze Mineralogiche e Petrologiche
CNR – Istituto di Geoscienze e Georisorse, sez. di Torino
Via Valperga Caluso 35, I-10100 Torino, Italy
elena.belluso@unito.it

Annibale Mottana

Università degli Studi Roma Tre, Dipartimento di Scienze Geologiche
Largo S. Leonardo Murialdo 1, I-00146 Roma RM, Italy
mottana@uniroma3.it

INTRODUCTION

In this chapter, we turn our attention to an issue that is often not based on rational science, but about fear—the issue of asbestos. As the geological community is well aware, all asbestos are minerals, and thus naturally formed; yet in the public arena, many people believe asbestos is something manufactured by humans and that one fiber is enough to kill you if inhaled. It is the intent of this chapter to provide background information for members of differing communities, be they mineralogists, geologists, medical researchers, regulatory workers, or legal professionals to better understand amphibole-related health and environmental issues. This chapter contains an introduction and overview of the health effects associated with the inhalation of amphibole minerals. Also, the chapter will discuss some of the current issues and research trends surrounding asbestos exposure, especially in the natural environment.

At the outset, anyone with knowledge of this field probably wonders why the word asbestos does not appear in the title of this article. As we will see as we progress through this article, there is a debate between the various scientific and regulatory disciplines on the definition of the word asbestos. What is well known and accepted by all is that the occupational exposure to asbestiform amphibole leads to a significant increase in asbestos-related diseases, especially mesothelioma. What is not clear is how the morphology of amphiboles affects the etiology of the disease. However, because the morphology of amphiboles is at least partially gradational from the high aspect-ratio (which is the length divided by the width of a particle) fibrous particles to the low aspect-ratio, nonfibrous particles, we might also assume that the etiology of the diseases might vary.

In this chapter, we will define terminology used by the different fields of study. It is important for those working in any field dealing with asbestos to understand that terms vary significantly among the different fields. Often, attempts by one group to simplify the nomenclature have resulted in more confusion in the scientific literature as well as for the public. For instance, recently the term "naturally occurring asbestos" has become widely used by regulatory groups in the USA to distinguish it from occupational exposure to asbestos. The issue becomes even

1529-6466/07/0067-0012$10.00 DOI: 10.2138/rmg.2007.67.12

more complicated in that the majority of the minerals of concern in the natural environment are amphiboles, and the distinction between fibers and fragments of amphiboles remains a central issue. Clearly we are exposed to amphiboles and different types of asbestos on a daily basis. Many of these exposures are natural (i.e., nonoccupational or nonanthropogenic) while others result from widespread use of asbestos-containing products over the past 70-80 years. However, because approximately 95% of asbestos used in commercial products was chrysotile (which is a sheet silicate), the majority of occupational exposure was to chrysotile, not amphibole asbestos. In the natural environment amphibole exposure is much greater than chrysotile; this is due mainly to the fact that amphiboles are much more widespread than chrysotile. So we are again left to distinguish between amphibole and amphibole asbestos. Regardless, most of us who reach the age of 60 and 70 have not thousands but millions of particles of amphibole in our lungs due to these natural exposures (Churg 1983). Thus, it seems to defy common sense that one fiber of asbestos will lead to death.

The phrase "naturally occurring asbestos" was mentioned above. Exposure relating to it is now at the forefront of health concerns of asbestos exposure, at least in the USA. Because of the general fear of the word "asbestos," the mere thought of exposure can cause panic in the general public, often driven by the popular media. Again, one of the goals in this chapter is to alleviate some of that fear. However, the media, especially in reports of Libby, Montana, USA, have continued to instill fear into the public by overstating the issues. In the USA, fear of asbestos exposure was heightened based on issues surrounding Libby that made it to the national media in 1999. These concerns were also heightened by the possible widespread asbestos exposure in the September 11, 2001, collapse of the World Trade Center. These two events combined to cause heightened concern to asbestos exposure in the natural setting of El Dorado County, California. While there was an increase in asbestos-related diseases from the miners at Libby (McDonald et al. 2004), those who worked in the processing outside of Libby (Lockey et al. 1984), and health concerns for the local citizens (ATSDR 2000, 2001), there are no confirmed deaths for nonoccupationally exposed citizens living in El Dorado County. Even so, a statistical model shows possible correlations of mesothelioma with proximity to ultramafic rocks (Pan et al. 2005) in El Dorado County. Turning our attention to Italy, there have been increased deaths from mesothelioma on a country-wide basis and even more concern on the island of Sicily in the village of Biancavilla on the side of the Mt Etna where exposure came from the first known occurrence of asbestiform amphiboles in volcanic rock (Burragato et al. 2006).

NOMENCLATURE AND BACKGROUND INFORMATION

Before we can hope to grasp the issues dealing with amphiboles and health, we need to have a working knowledge of the terms used in this field. The nomenclature used in this field is daunting, challenging, confusing, and bewildering. This is the case because several different disciplines (e.g., geology, mineralogy, industry, the medical fields, regulatory groups, and the legal system) have developed their own nomenclature somewhat independently of each other. Worse yet, they have modified nomenclatures from other disciplines so that now the same word may have different meanings and different words the same meanings.

Mineralogical

Morphology. Geology and mineralogy were two of the first disciplines to discuss asbestos, and to those groups the term generally meant that the material is fibrous. When they started working with this material, they usually did so at a large scale (i.e., hand-sample scale) where it is fairly easy to tell if any amphibole has the asbestos habit or not. Figure 1A shows three large amphibole samples all recently obtained from the Smithsonian Museum; the large dark one is a euhedral (which literally means "with good faces" or well formed) tremolite grain while the other two are asbestos—the lighter colored sample is tremolite and the darker colored

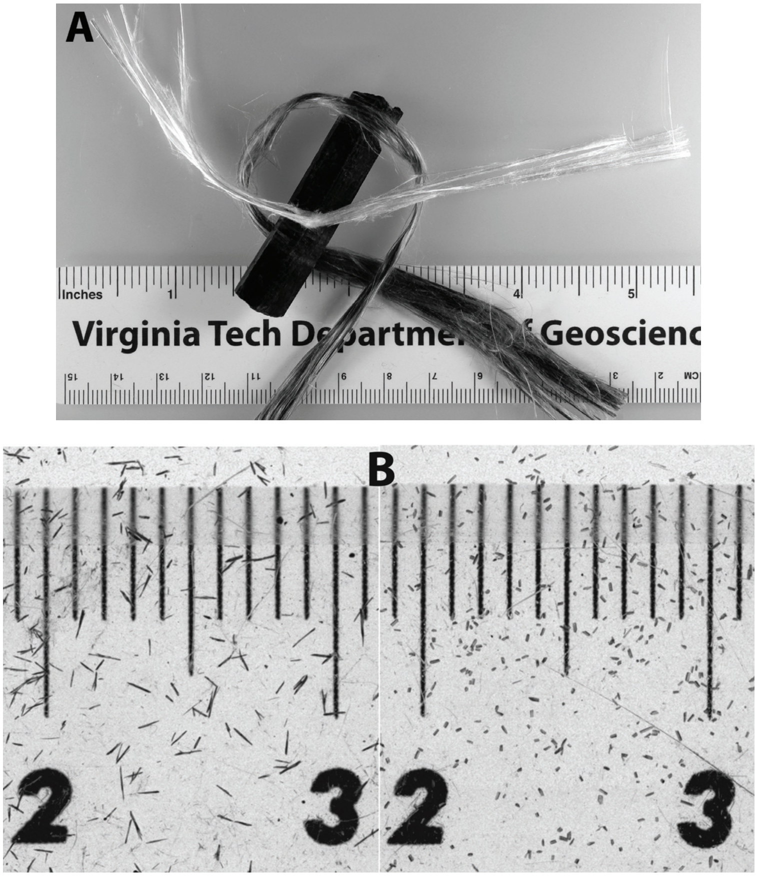


Figure 1. Photographs showing various morphologies of amphiboles at different scales. A) This photographs shows three amphiboles from the Smithsonian Institution collection: two are considered asbestos and the third is a euhedral sample with {110} faces. The light-colored fibrous mineral is tremolite asbestos and the darker one crocidolite. The darker euhedral sample is a single crystal of tremolite. (The euhedral tremolite is from Wilberforce, Ontario, Canada (#117611), tremolite asbestos from Hartford County, Maryland, USA (#118117), and crocidolite from Wittenoom, Australia (#117343)). B) Two different morphologies of an amphibole separated from the same hand sample collected near Libby, Montana, USA (obtained from the Harvard Museum (#100839)). The particles on the left exhibit asbestiform habit (i.e., separable lengthwise), while the particles on the right are near-perfect euhedral single crystals (scale bar is in mm).

one is crocidolite (which is the asbestos variety of the amphibole mineral riebeckite). As the size of the particles become smaller, it becomes harder to determine particle morphology. Figure 1B shows two differing morphologies from the same hand sample. The particles on the left show the asbestiform habit, while the sample on the right is composed of euhedral, very minute single crystals. The term “asbestiform” refers to a type of morphology where a mineral has longitudinal (i.e., lengthwise) parting, and thus can be split into individual fibers. To the mineralogical community the term “fiber” is a textural term meaning that the material looks, and more importantly, behaves as a fiber; thus, it can curve and bend under force. In the industrial world, the fibrous property of these minerals resulted in a high tensile strength in much the same way that a rope’s strength increases because it is made of many interwoven smaller “ropes.” In the regulatory community the term “fiber” has been given certain size and shape characteristics commonly referred to as the aspect ratio (the length of the particle divided by its width), and depending upon the analytical method used, a particle is considered a fiber if it has a greater than 3:1 (by light microscopy) or 5:1 (by electron microscopy) aspect ratio. These aspect-ratio criteria were never meant to define a fiber but were developed as counting criteria used to determine the amount of asbestos in a material in an industrial setting where it was known that the source of the material is a commercial asbestos product. The regulatory community has been forced to develop guidelines to determine if a particle is or is not a fiber to meet certain health-based concerns. In turn, the legal system has adopted many of the regulatory terminologies instead of the more descriptive mineralogical terminologies, even to the point of using the word "fiber" for any particle found in the human lung. For instance a blocky piece of quartz found in the lung might be called a "nonasbestos" fiber.

Often, especially in regulatory usage, if an amphibole particle does not meet the definition of a fiber (based on aspect ratio), it is termed a "cleavage fragment." Again, to a mineralogist, the term "cleavage-fragment" has a clear meaning—it is a piece of a mineral bounded by cleavage faces. As with a fiber, some action must be taken to see if a mineral has cleavage—namely it must be broken. Often, amphiboles may display growth faces which may appear as a cleavage face.

Many, especially in the popular media, use the term "asbestos" very loosely. Its use should be restricted to a commercial product, such as for the two samples shown in Figure 1A. The term "particle" should be used for any small piece of amphibole, and the terms "fiber" and "cleavage-fragment" should only be used where the particles clearly meet the mineralogical definitions as stated above. The majority of the time, what are called "cleavage-fragments" should be called "fragments." Also, many particles are called fibers (based on regulatory guidelines) where they are single crystals. The term "asbestiform" should be applied to noncommercial amphiboles (such as that shown on left side of Fig. 1B) that can split lengthwise into fibers. The term "nonasbestiform" should be used for those that cannot split lengthwise, such as those shown on the right side in Figure 1B. Generally, fibers result from the breaking apart of asbestiform amphiboles whereas fragments result from the breaking apart of nonasbestiform amphiboles.

Chemical composition. Amphiboles are a chemically diverse group of silicate minerals based on double chains of (Si,Al) tetrahedra, and all share this common building block. Also, most amphiboles are elongated parallel to these chains (Fig. 1). Cations are needed to charge balance these double chains as well as hold them together. The individual amphibole species names are based on these cations. Hawthorne and Oberti (2007 - Chapter 2, this volume) present a discussion of amphibole nomenclature and the criteria set forth by Leake et al. (1997). Although several other amphibole species can occur as asbestos (e.g., winchite (Wylie and Huggins 1980) and fluoro-edenite (Gianfagna and Oberti 2001)), currently there are only 5 (of more the 80) species of amphiboles that are regulated: anthophyllite, tremolite, actinolite, riebeckite, and grunerite. The term "crocidolite" is used for the asbestos variety of riebeckite, and amosite to that of the asbestos variety of grunerite. These two variety names originated because crocidolite and amosite are the most commonly used amphibole asbestos. And while anthophyllite was mined and used in small amounts, tremolite and actinolite are regulated because they can occur as accessory minerals in other economically important mineral deposits. As we will see later in this chapter, there are three nonregulated amphiboles species (fluoro-edenite, richterite, and winchite) that have been associated with asbestos-related diseases and should probably be added to the regulated list, as should all asbestiform amphiboles.

Accurate chemical characterization is required to correctly determine the species name of an amphibole, and these names are important for us in the geological community. Figure 2 is an example of what is required to name amphiboles and was taken from a thorough study of the mineral chemistry of amphiboles collected from the Libby vermiculite deposit (Meeker et al. 2003). In this figure, site occupancy is plotted and different regions are assigned names. However, all mineralogists realize that the lines dividing the fields in this graph are somewhat

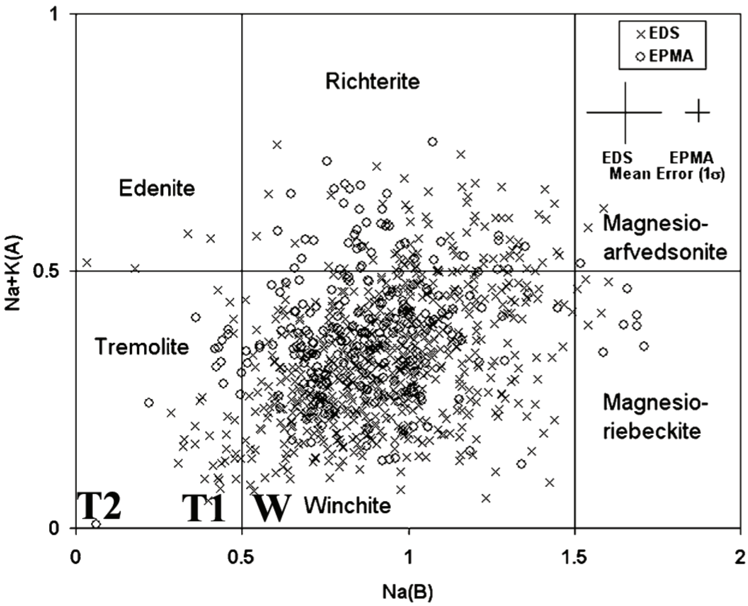


Figure 2. A plot of site occupancies required to determine the species of amphiboles obtained from the former vermiculite mine near Libby, Montana USA (Meeker et al. 2003); the circles are from EPMA-WDS data while the crosses are from EDS data. The plot shows that the amphiboles in that deposit are (at least) six different species, the majority being winchite and richterite.

arbitrary and not defined by Nature. We also know that tremolite plotting at T1 is more similar to winchite (W) than to tremolite plotting at T2. Thus minerals with different names can be more similar than minerals with the same name. This is a consequence of drawing boundaries in continuous compositional fields, and mineralogists understand these consequences of naming minerals in a solid-solution series. However, in the medical, legal, and regulatory fields, the names take on great importance, often more so than the actual compositions. Thus, chemical composition and nomenclature are areas that require different disciplines to try and understand each others needs.

Medical

To understand the issues surrounding asbestos, one needs to know the end points (i.e., the diseases) and what the etiology (i.e., causes) of these diseases might be. There are basically three asbestos-related diseases: asbestosis, mesothelioma, and lung cancer. Table 1 lists deaths and causes in the USA for these three diseases, as well as several others for comparison (modified from Gunter 1994). By far the largest number of deaths results from lung cancer (caused mainly by smoking cigarettes); numbers of deaths resulting from the other two asbestos-related are far fewer.

Table 1. Annual death statistics in the United States (population approximately 300 million). Total deaths for 2003 = 2,448,288. All data from the 2003 (most recent) U.S. Vital Statistics, *www.cdc.gov/nchs/deaths.htm.*

heart disease	685,089
cancer	556,902
strokes	157,689
lung cancer	126,382
accidents	109,277
asbestosis	583
pleura mesothelioma	181
silicosis	102
bee stings	66
lightning	47
spider bites	8
snake bites	2

We need to have some idea how the human body attempts to rid itself of the dust that we inhale. In the medical literature, the term "clearance" is used to refer to this process. Briefly, clearance first starts when particles enter the nose and are trapped there. Next, they enter the upper airways where the mucociliary escalator moves the particles back up the airway. Here they are either swallowed or spit out. It is notable that CO in cigarette smoke greatly reduces the efficiently of this clearance method. If a particle reaches the alveoli, it may be removed by a specialized white blood cell called an alveolar macrophage, and it is the last line of defense. Our respiratory system is very efficient and is believed to clear 99% of inhaled particles (see Plumlee et al. 2006 for a more complete discussion).

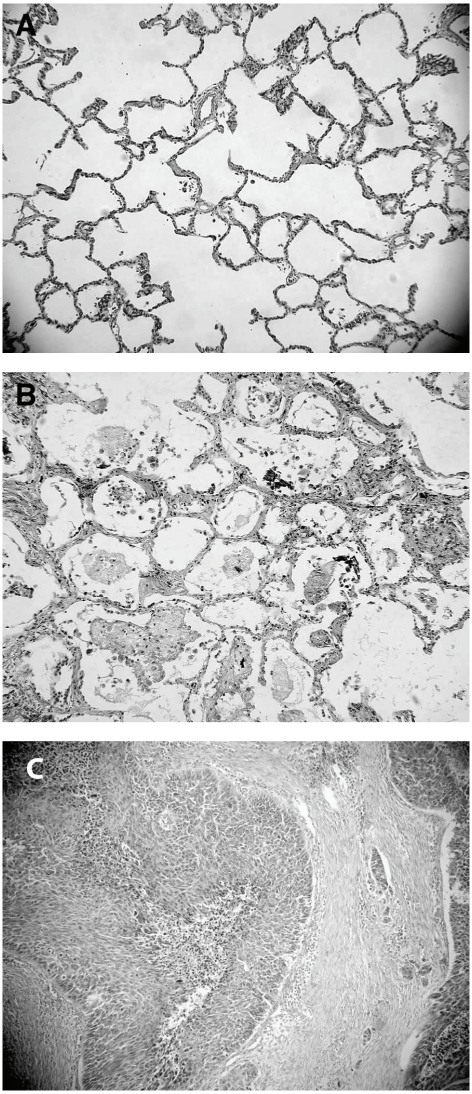


Figure 3. Three photomicrographs of human lung tissue (FOV approximately 1.5 mm). A) A normal lung section; the alveoli are the open areas surrounded by cell walls formed by capillaries. B) A lung section from an individual who suffered from asbestosis. Note that the open air spaces in the alveoli are filled and the alveoli walls thickened. Both of these would restrict O_2 – CO_2 exchange in the lung. C) A tumor (which destroys the lungs function).

Size is very important in health issues surrounding the inhalation of dust, and we often refer to a particle as being "respirable." Separate from asbestos, the United States Environmental Protection Agency (EPA) has set limits to respirable particles as function of their size in the natural environment. For instance, PM10 refers to particle matter less than 10 microns in diameter, and PM2.5 refers to particles less than 2.5 microns. Ongoing research shows that smaller particles (i.e., PM2.5) may be more harmful. We are concerned with the size range of respirable particles that cause chronic lung problems, and minerals in the natural environment often do not fall within this size range (Norton and Gunter 1999). Asbestiform minerals in the occupational setting, however, often do because they can separate into very fine fibers as a function of their morphology as they are mined and milled.

Few geologists have seen sections of normal or diseased lungs; however, the medical community uses methods similar to looking at rock thin sections to look at tissue sections. Figure 3 shows three tissue sections that have been cut and mounted on glass slides much like geologists do with minerals and rocks. Also, the samples are stained to aid in identifying cells, much like a petrologist uses different stains to differentiate carbonate or feldspar minerals. Figure 3A is a section through a normal lung showing the alveoli and the thin walls that separate them. The blood that circulates in these walls is responsible for the CO_2-O_2 exchange. In Figure 3B, the individual suffered from asbestosis. One can see that there is material within the alveoli and a thickening of the alveoli walls; both of these features inhibit the lungs' ability to perform CO_2-O_2 exchange. Figure 3C shows a tumor in the lung. When the tumor forms, it not only destroys that particular lung portion's ability to exchange air, but carcinogenic cells from the tumor spread and, unless treated early, the individual succumbs to cancer. Mesothelioma is a specific type of cancer affecting the external lining of the lung. It is not shown well on a glass slide. Most of the deaths from this disease can be correlated to asbestos exposure, especially the amphibole variety. In fact, there are some who would argue that chrysotile does not cause mesothelioma. This is the most dreaded form of all the asbestos-related diseases in that it has a latency period of 30-40 years. Mesothelioma death-rates in amphibole miner cohorts are in the range of 3-5% (McDonald et al. 2004).

Pleural plaques are masses of collagen that form in the lung. Sometimes these plaques are said to be "calcified," which means the plaques contain deposits of calcium phosphates similar in composition to hydroxylapatite. While they are found in the general population, they are found at higher rates among those exposed to asbestos. Pleural plaques can be seen on lung X-rays and can serve as a biomarker for asbestos exposure (Peipens et al. 2003). Pleural plaques do not appear to lead to other asbestos-related diseases, and there is even some debate on whether they are a disease themselves (ATSDR 2006). Regardless, they are a useful asbestos biomarker.

Probably the single most important aspect of asbestos-related disease is the dose. The large doses of asbestos fibers inhaled in the pre-regulated workplace resulted in worker mortality for asbestosis and mesothelioma. To determine dose, three criteria are needed: (1) the amount of air an individual breathes (which is about 10 m^3/day, Gunter 1994), (2) the amount of respirable particles in that air, (3) and clearance. Dose is typically measured in f/ml (= f/cc), and thus not a mass measurement because it involves the number of fibers and not their weight or volume, or probably more importantly - surface area. Table 2 gives a list of doses for regulatory purposes, as well as some other examples that will be used in this chapter. So a miner working in a very dusty environment could breathe 1,000,000,000 fibers in an 8-hour workday if there were 100 f/cc. Also, it is worth noting that in outside air (0.00039 f/cc), an individual would breath 12,000 fibers in 24 h.

Table 2. Fibers/cm^3 of asbestos (>5 μm with 3:1 aspect ratio). The first series indicates numbers in the workplace and the changing OSHA regulations from 1972 to 1992 (Gunter 1994). The second set indicates average values found in outdoor air, indoor air, schools, and public buildings with ACM (asbestos containing material) in different states of repair (Mossman et al. 1990).

> 100	preregulated workplace
5	OSHA (1972)
2	OSHA (1976)
0.5	OSHA (1983)
0.2	OSHA (1986)
0.1	OSHA (1992)
0.00039	outdoor air
0.00024	schools
0.00099	indoor air, no ACM
0.00054	indoor air, nondamaged ACM
0.00073	indoor air, damaged ACM

The RIM volume 28 (Guthrie and Mossman 1993) entitled "Health effects of mineral dusts" contains a thorough appendix of geological, mineralogical, and medical terms used in health based issues. An electronic version of that information can be found at *http://www.webpages.uidaho.edu/~mgunter/NAGT/manuscripts/glossary.pdf.*

ANALYTICAL METHODS

One of the most important aspects of dealing with minerals is their identification and characterization. This simple statement takes on certain challenges for those involved in the positive identification of asbestiform amphiboles because: (1) there can be discrepancies in defining morphology, and (2) not all species of amphiboles are regulated. Thus, under the current regulatory status, one must precisely establish the chemical composition of the amphibole to determine its species. Regardless of regulatory concerns and from a mineralogical perspective, precise chemical analyses are useful in not only identifying and naming the mineral, but also in thoroughly characterizing the mineral, which is important in understanding the minerals' health impacts. Thus, for mineral use in health-based studies, it is worthwhile to apply several analytical methods for both identification and thorough characterization. The quantity of asbestos in an asbestos-containing material is important to the regulatory community because special precautions must be taken when a material contains greater than a certain amount of asbestos. While there are debates about the specific amount, 1% is typically chosen. What will follow are three broad areas for characterizing these materials: (1) shape and morphology as determined by various microscopic methods (these methods are also used to determine the amount of asbestos in a material), (2) structure studies accomplished by various diffraction methods, and (3) chemical analysis of both single particles and bulk samples. For a more complete review of analytical methods used in characterizing minerals in health-based studies, see Guthrie (1993); for a review of regulatory methods see Millette (2006).

Microscopic methods

Because by definition asbestos deals with the morphology of the material, we will first discuss various types of microscopy methods used to determine morphology. Two of these methods involve very precise regulatory guidelines used in the identification and quantification of asbestos material in the commercial setting. In a research setting, all of these instruments can be used depending mainly on the scale of observation. The instruments are arranged below in order of increasing magnification.

Polarized-Light Microscope (PLM). The first widely used instrument in geology and the asbestos regulatory field was the PLM, and it is still in wide use today (Millette 2006). With correct use it can determine a material's morphology and often its identity. The PLM is useful for observing particles from a few mm down to about 1 μm. Not only can the PLM show sufficiently magnified images to ascertain the morphology of the material, it can also aid in identification based on the correct interpretation of the way the light interacts with the particles. For example, in cross-polarized light, it is simple to distinguish isotropic (e.g., glass) and anisotropic materials (e.g., amphiboles). Whereas there are many fibrous materials in Nature and in the commercial arena, a quick observation in the PLM can distinguish fiberglass from amphibole. The refractive indices of materials can be determined with relatively little difficulty and, in general, the different types of commercial amphibole-asbestos can be distinguished from one another, as well as from chrysotile; however, there is some overlap in refractive indices (Millette and Bandli 2005). There are also PLM techniques used to help aid in distinguishing fibers from fragments (Wylie 1979; Zoltai 1979; Langer et al. 1991; Brown and Gunter 2003).

Geologists use thin sections (30 μm thick slices of rock glued to glass slides and polished) to help identify and characterize minerals in rocks, and to describe the texture of a rock or mineral. Thus, thin sections are useful to study the morphology of amphibole grains. Figure 4 shows four separate amphiboles that exhibit blocky (4A), acicular (4B), and asbestiform (4C) habits, while (4D) contains all three morphologies. The first column in the figure shows approximately 50 mm wide samples of each cut to make thin sections; the second column shows the associated thin sections cut from the rocks viewed in cross-polarized light. In these

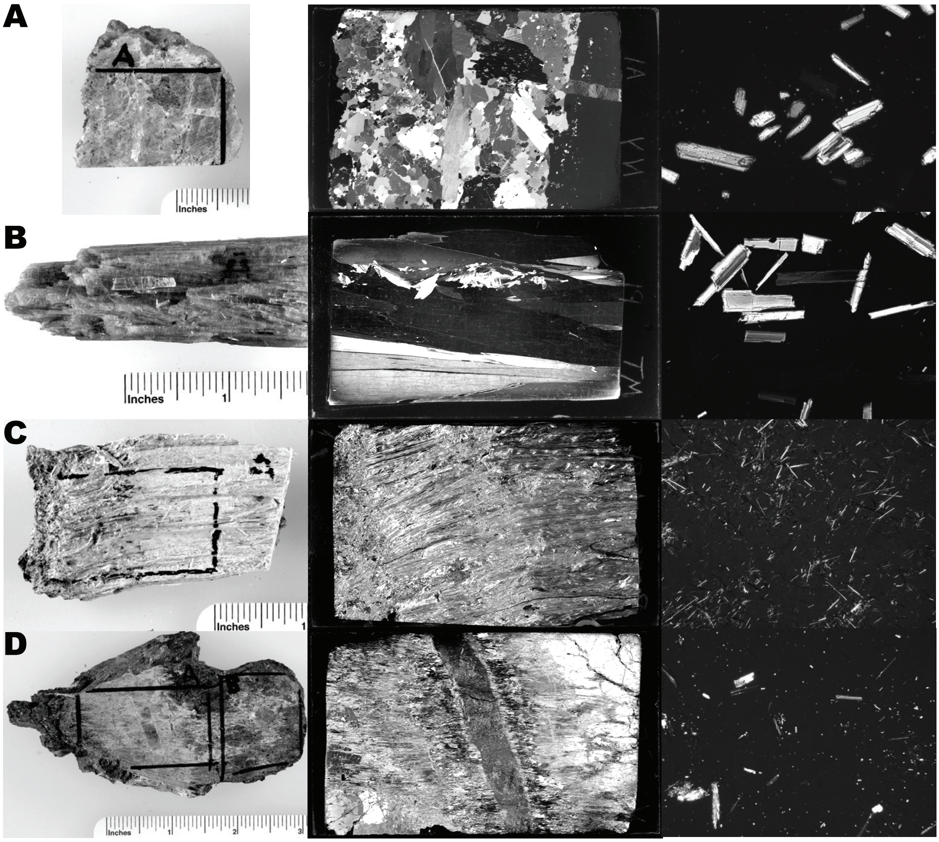


Figure 4. A series of photographs and PLM photomicrographs used to observe and characterize amphibole morphology. The left column shows a rock sample before cutting and polishing into a thin section (glass slide size = 27 x 46 mm). The center column shows sample in cross-polarized light. The right column shows individual particles obtained from the rock sample, placed in an immersion liquid and viewed in cross-polarized light (FOV = 1.2 mm). A) A blocky tremolite sample from New York, B) An acicular tremolite sample from near Bozeman, Montana, C) An asbestiform tremolite from Montgomery Country, Maryland, and D) A mixed-morphology sample from Libby, Montana, (the same sample as in Figure 1B).

images, the blocky, acicular, and asbestiform habits are seen. The last column shows immersion mounts of amphiboles from each of the rocks, which are useful in characterizing the shape of the grains liberated from the rocks. Note how the particles become longer and skinnier going from blocky to acicular to asbestiform, and how the last sample shows mixed morphologies.

To further characterize individual particles, the spindle stage can be used. Brown and Gunter (2003) discussed this method at length and used it to explore the relations between extinction angles and morphology for a suite of amphibole particles of differing morphology. The upper row of photos in Figure 5 shows three different morphologies of amphibole particles from Libby, ranging from euhedral to asbestiform. The optimal range in particle size for the spindle stage is 100-300 μm, and characterizing particles at this size range can help understand them at smaller sizes. While extinction angles are often used to aid in identification, precautions in their use should be taken (Su and Bloss 1984; Verkouteren and Wylie 2002; Brown and Gunter 2003).

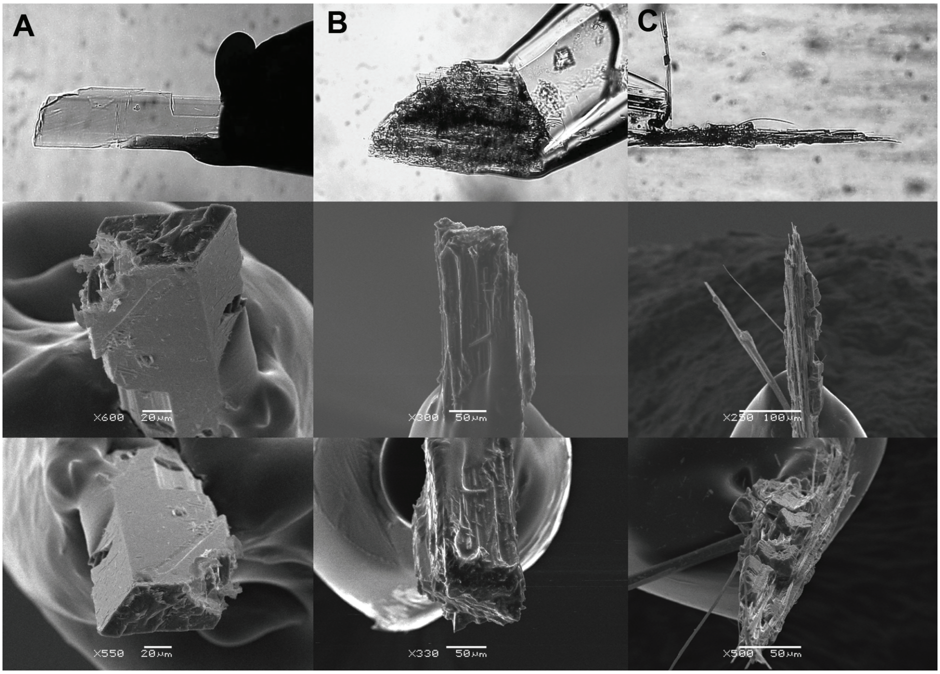


Figure 5. Three different amphibole morphologies from the Libby vermiculite deposit: A) blocky, B) intermediate morphology, and C) asbestiform. The upper row shows single crystals viewed in the PLM and mounted on a glass fiber that can be rotated to different orientations (FOV = 500, 600, and 700 µm respectively for A, B, and C). The lower two rows are the same samples except they have been placed in an SEM and rotated to different orientations to better characterize their morphology. (Sanchez et al. 2006, with SEM photos courtesy of the RJ Lee Group Inc., Monroeville, Pennsylvania, USA.)

Scanning Electron Microscope (SEM). It is surprising that the SEM has found very little use in studying asbestos, at least in the regulatory area, but it is now becoming more widely used in the study of amphiboles in their natural setting (e.g., RJ Lee 2005; Meeker et al. 2006). The regulatory discipline typically goes from the PLM to the TEM (discussed next) to work with smaller particles such as those found in air samples. However, the SEM is useful in extending particle resolution down to approximately 0.1 µm (i.e., one order of magnitude smaller than the PLM) and showing surface morphology. Also, the SEM has an increased depth in field relative to the PLM.

Another unique advantage of the SEM is that a sample can be rotated to observe it in different orientations. Bandli and Gunter (2001) showed how this method is useful in imaging particles of amphibole to better characterize morphology. The lower two rows of Figure 5 (Sanchez 2007) are the same particles as in the upper row. However, in the lower two rows, the particles were placed inside an SEM and rotated to different orientations so as to better observe their morphology. The spindle stage (placed on a PLM) is used in a similar manner, except that the spindle stage does not have as many degrees of freedom of rotation. Combined PLM and SEM studies are useful for the determination of morphology of amphibole materials.

Transmission Electron Microscope (TEM). With routine operation the TEM can resolve 10 nm particles; samples are imaged by electron transmission and thus the samples must be very thin. The TEM has become one of the most used instruments for asbestos characterization in the regulatory field (Millette 2006). The left column in Figure 6 shows three separate TEM

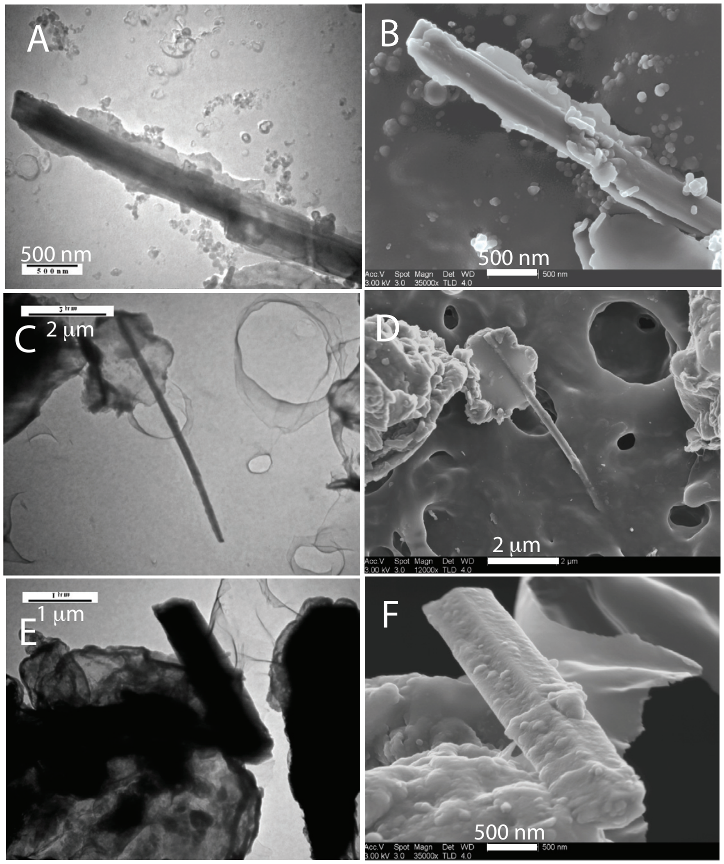


Figure 6. Three amphibole particles collected in air samples from Libby, Montana, imaged in the TEM (left column) and the FESEM (right column). The newer generation FESEMs can obtain magnifications similar to those of a TEM. A & B show an amphibole particle with what appears as wings on its sides. C & D show an amphibole particle with a sheet silicate at one end. In the TEM image, it is unclear if the particle rests on or grows into the sheet silicate; however, the FESEM image shows that the amphibole is grown into the sheet. E & F show a single crystal of amphibole. It is difficult to determine the morphology of the particle in the TEM image, but the FESEM shows a perfect euhedral amphibole with {110} growth faces. (Gunter et al. 2006, images courtesy of the RJ Lee Group Inc., Monroeville, Pennsylvania, USA.)

images obtained on amphibole particles from air samples collected in Libby, Montana. In Figure 6A and 6C, notice that portions of the particles are transparent (i.e., the electrons are going completely through the sample). The TEM is very useful for studying small particles that have been deposited on air filters, and thus determining asbestos content of the in-flowing air.

Field Emission Scanning Electron Microscope (FESEM). The FESEM is a relatively new instrument with some refined design features of the SEM that allow higher resolution than an SEM or TEM. The FESEM can also operate at lower accelerating voltages than older SEMs. Resolution of the FESEM is on the order of 1 nm, at least one order of magnitude greater than the TEM. To date, the FESEM is not routinely used by the regulatory community for analyzing asbestos-containing materials. However, it is starting to find use in the research community for high-resolution imaging of very small particles. The right column of Figure 6 shows the same three particles as the left column, except imaged in an FESEM. The backscattered images in the FESEM allow better characterization of amphibole morphology.

DIFFRACTION METHODS

Positive identification of minerals require more than observing them at higher and higher magnification. Diffraction, either by electrons or X-rays, helps determine the structure of the mineral and aids in identification.

Selected Area Electron Diffraction (SAED). One of the main advantages of using a TEM in asbestos work is that one can acquire an SAED on the very small particles often found in air samples. Figure 7 shows two particles imaged in a TEM. Below the image (in white squares with dots) are two separate SAED patterns of the two particles. These two patterns look different, suggesting that the two materials are different; interpretation of these patterns show that particle A is an amphibole and particle B is a sheet silicate.

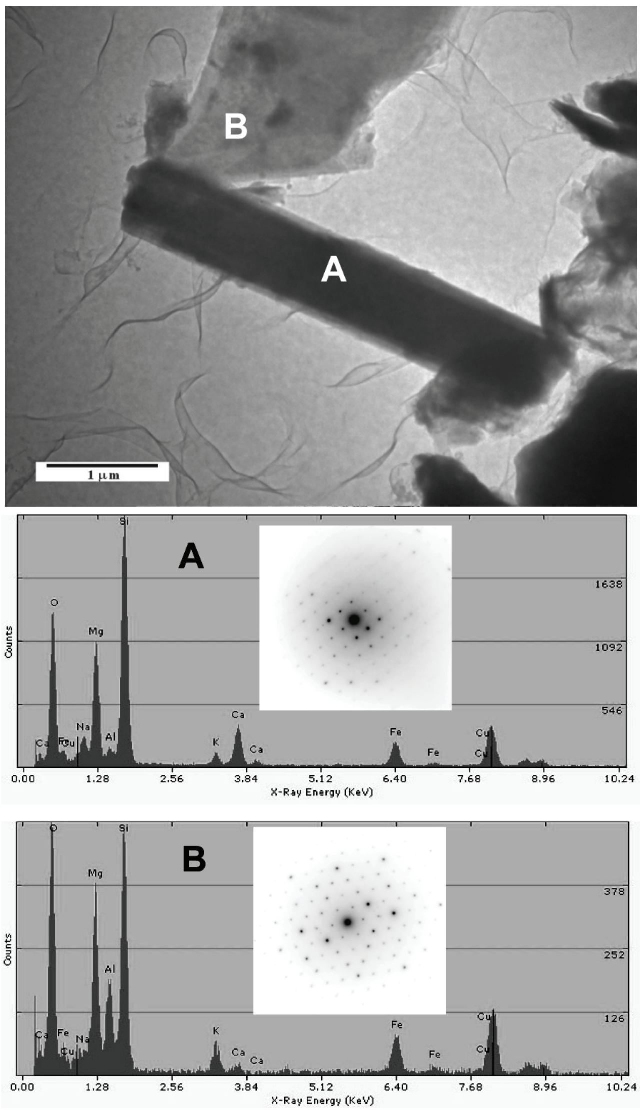


Figure 7. Along with imaging, TEMs can provide chemical and structural information needed to identify a particle. Shown here is a TEM image of two particles, with corresponding EDS plots and SAED patterns. Based on interpretation of compositional and diffraction data, particle A is an amphibole and particle B is a sheet silicate. (Gunter et al. 2006, images courtesy of the RJ Lee Group Inc., Monroeville, Pennsylvania, USA.)

Single Crystal X-ray Diffraction. This method is not used in routine analysis of asbestos particles, probably because in single crystal X-ray diffraction one strives to select perfect single crystals to obtain diffraction data. These samples are usually in the order of 20-200 μm in size, and are thus larger than respirable asbestos fibers. However, single crystal X-ray diffraction photographs can show which samples are monocrystalline or polycrystalline. For instance, Figure 8 shows single-crystal X-ray diffraction patterns of both monocrystalline and polycrystalline samples of elongated amphibole particles. Figure 8A is of a monocrystalline particle of a similar morphology as that in Figure 5B, and thus nonasbestiform, whereas Figure 8B is of a polycrystalline sample (indicating it is composed of several particles and thus would be asbestiform) such as that shown in Figure 5C. This method could find use in larger samples by distinguishing if particles are single crystals or aggregates of crystals.

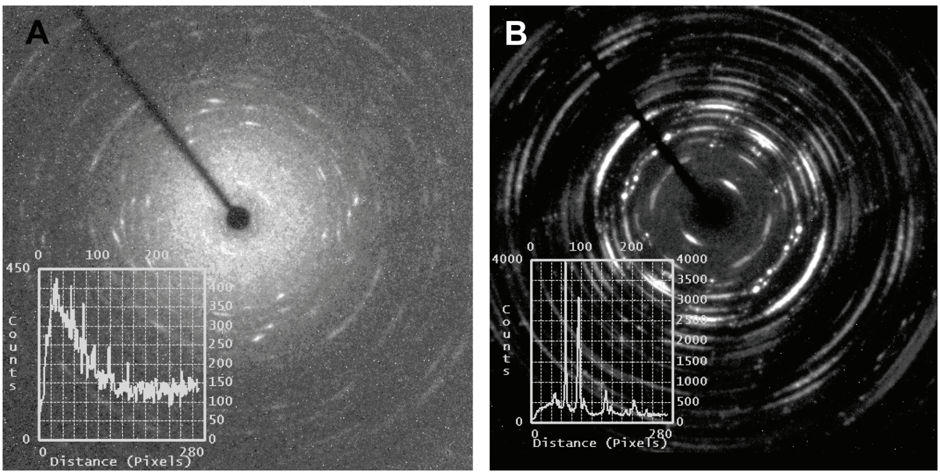


Figure 8. Two rotation X-ray diffraction photographs from Bandli et al. (2003) showing different crystallinities of amphibole particles from Libby, Montana. A) What Bandli et al. termed "monocrystalline" and B) "polycrystalline" based on the resultant diffraction pattern (i.e., the diffraction spots are more spread out in the polycrystalline material). The pattern would be rings if the particle was a powder.

Powder X-ray Diffraction (XRD). XRD methods have also found very little use in dealing with asbestos characterization, even though over 15 years ago, Addison and Davies (1990) showed how it could be used to quantify trace amounts of amphibole in chrysotile and vermiculite ores. One reason it has found little use is the typical concern of the regulatory community is in dealing with very small samples and even individual particles. However given sample sizes of 100 mg and up, XRD can be a valuable method to not only identify the minerals present, but also to quantify the amounts of individual minerals. Currently, the amounts of different minerals are often found by point counting with the PLM or TEM. With newer X-ray diffractometers and better software, it is now possible to measure trace amounts of amphiboles in bulk materials (Sanchez and Gunter 2006). Figure 9 shows three separate XRD scans; both Figures 9A and 9B are chrysotile ores. The lower diffraction scan in each has a count time of 9 s showing the major chrysotile peak. The three scans above (the longer 2θ scans) were done at much longer count times (180 s). The areas of major talc and amphibole peaks are outlined on the figures, and it appears that two of the three scans shown might contain small amounts of amphibole (Fig. 9A), whereas in Figure 9B, it appears there is more amphibole in the chrysotile ore. It should be pointed out that this method says nothing about the morphology of the materials. However, the morphology can be determined by one of the

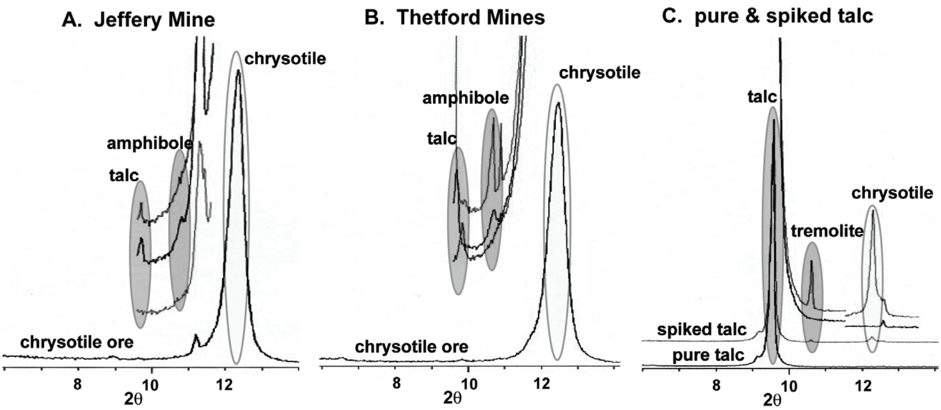


Figure 9. A set of powder X-ray diffraction scans for two chrysotile ores (A and B) and a pure- and tremolite/chrysotile-spiked talc sample. The peak regions for talc, amphibole, and chrysotile are highlighted with vertical ellipses. A) The longer 2θ lower scan shows a chrysotile ore from the Jeffery Mine (count time = 9 s) with its associated shorter 2θ scan (count time = 180 s) directly above it. The other two scans are from other ores from the same mine. One of the scans shows no amphiboles, while the other two show trace amounts. B) The longer 2θ lower scan is a chrysotile ore from the Thetford area (count time = 9 s) with its associated shorter 2θ, longer count time scans with two of three containing amphiboles. C) Long 2θ scan of a pure and 1% tremolite / 1% chrysotile spiked sample (count time = 9 s). The corresponding short 2θ scans for the pure and spiked samples show that the pure samples contain no tremolite or chrysotile, while the spiked sample shows significant peaks at the 1% level.

microscopic methods already discussed. Figure 9C shows a talc sample in both its pure and spiked states. In the spiked state, 1% chrysotile and 1 % tremolite have been added. Notice how these peaks are observable on the 9 s scans and are clearly visible on the 180 s scans. This method easily detects minerals present at the 1% or lower level.

Figure 10 shows a recent study (Gunter et al. 2007) using XRD to characterize a suite of samples from a now-closed asbestos mine in Canada. Figure 10A shows diffraction scans for these samples. As expected, these samples all contain chrysotile as the major component, and also brucite. Figure 10B shows a series of scans collected at longer count times than in Figure 10A. The Figure 10B scans were used to ascertain if any of the samples contain trace levels of amphibole. Observation of these scans shows that #10b2 contains a small amount of amphibole. To quantify that amount, a pure chrysotile ore was spiked with different amounts of tremolite; the resultant diffraction patterns are shown in Figure 10C. Notice that the detection limit is on the order of 500-1000 ppm, and sample #10b2 seems to contain approximately 1000 ppm of amphibole. Thus the maximum amount of amphibole asbestos could be 1000 ppm. However, if the amphibole was of mixed morphology (e.g., 50% nonasbestiform and 50% asbestiform), then the sample would only contain 500 ppm amphibole asbestos.

Chemical determination

Going hand in hand with diffraction data on particles, chemical data is needed for positive mineral identification as well as for mineral characterization. The methods presented below are very similar in scope to the diffraction methods presented above in that some work for individual particles while others require bulk samples.

Wavelength Dispersive Spectrometry (WDS). WDS is the most precise way to determine the chemical composition of minerals. WDS is also synonymous with the use of EPMA (electron probe micro analyzer). The sample preparation for this method is very important and requires flat, well-polished mineral samples; unfortunately asbestos particles are often too

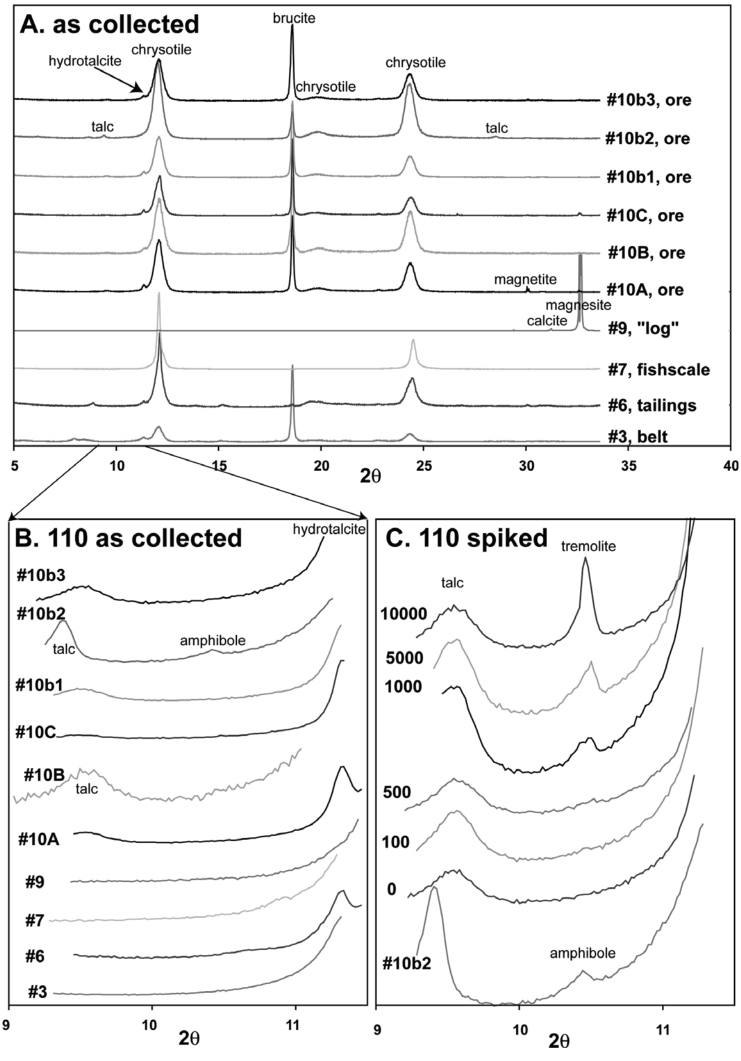


Figure 10. A series of powder X-ray diffraction scans obtained from a suite of samples collected at the former Carey Canadian chrysotile mine. A) The ten samples collected from the mine with brief names (count times = 9 s). B) The same set of samples as in A, except over the 2θ region corresponding to the 110 peak in amphibole with count times of 180 s; all the samples appear amphibole free except #10b2. C) Sample #10b2 is overlain by a series of tremolite-spiked samples made from sample #10b3. The scans over the 110 region show amphibole detection at the 500 ppm level (count times = 180 s; modified from Gunter et al. 2007).

small for this type of sample preparation. This is the best method for determining the chemical composition of an amphibole to determine its species. Figure 2 shows a series of chemical analyses determined by WDS on an EPMA for different amphiboles from Libby, Montana (Meeker et al. 2003). WDS is rarely used in the regulatory community but are widely used in the geological community for the precise and accurate chemical determination of minerals. Even though these instruments are costly and often require a dedicated technician, they are required for precise and accurate chemical analysis of minerals.

Energy Dispersive Spectrometry (EDS). EDS is by far the most routine method for chemical analysis related to asbestos work. EDS systems are commonly on both SEMs and TEMs. Thus one can obtain an EDS spectrum and a semi-quantitative chemical composition of micron-sized areas in the SEM and submicron-sized areas in the TEM. However, EDS data are not as precise or accurate as WDS data. An example showing the differences of precision is shown in Figure 2. The circles on the plot represent WDS data obtained with the EPMA, and the crosses represent EDS data on the same samples. Notice also that the error bars (in the upper right hand corner of the plot) are bigger for EDS than for WDS. However, even though EDS is less precise and accurate than WDS, WDS cannot commonly be used on the smaller particles often encountered in air samples because the samples are not large enough to prepare as polished mounts. Moreover, the accuracy of the EDS data can often be enhanced by using standards (see Gunter et al. 2007). Lastly, along with SEMs and TEMs, FESEMs can also be equipped with an EDS. On FESEMs, light-element EDS spectra can be obtained at voltages as low as 3 kV, which greatly reduces the excitation volume, allowing for chemical determination of particles down 200-300 nm (Gunter et al. 2006).

Figure 7 shows an EDS spectrum from the two particles shown in the accompanying TEM photograph. In this case, with the use of the TEM, one can observe the morphology of the particle, obtain the structural information on the particle by obtaining an SAED pattern, and determine the composition of the particle by obtaining an EDS (also shown in the figure), all on particle sizes down to a micron. This trilogy of data makes the TEM a useful instrument for studying small particles.

X-Ray fluorescence (XRF), Inductively Coupled Plasma (ICP) and Atomic Absorption (AA). XRF, ICP, and AA are all bulk methods that typically require at least a gram of material. These methods are often used in geology to determine the composition of a rock by first crushing and then homogenizing it. In Geology, these methods are often referred to as "whole-rock analysis." Williams-Jones et al. (2001) suggested this method might be used to determine the tremolite content in chrysotile ores. This suggestion was based upon measuring the Ca content of the ore and assuming the only source for Ca is tremolite. Gunter et al. (2007) adopted this method and used the Ca content as a proxy for the tremolite content in the ten samples shown in Figure 10. For each of these ten samples, they measured the Ca content by AA. Figure 11 shows an ideal content of Ca ppm and tremolite concentration in a chrysotile ore (squares). By powder X-ray diffraction, Gunter et al. (2007) determined a small fraction of magnesite occurred in the sample, and the magnesite contained a small amount of Ca as shown by SEM EDS. Thus they acid-treated the samples to remove the magnesite. As Figure 11 shows, this method seems to work for the unique case of tremolite in chrysotile. There might be other mineral relations whereby one can use whole-rock analysis to gain a semi-quantitative estimate for trace minerals.

Laser Ablation Mass Spectroscopy (LAMS). This is a fairly new method in geology and requires little sample preparation while providing precise and accurate analysis of many trace elements and their isotopes. To our knowledge, no one has yet published any of this type of data on asbestos minerals. An issue still confronting mineralogists is the formation of asbestos minerals. We know part of the answer relates to the material forming into a nonhydrostatic stress field; however, possible chemical differences may have an effect. For instance, we know that trace-element compositions can cause different habits of calcite. Currently, some preliminary work (Sanchez 2007) shows different trace-element compositions in fibers and fragments of the same amphibole sample (Fig. 4C).

Mössbauer spectroscopy. To fully characterize amphiboles, one needs to measure $Fe^{3+}/\Sigma Fe$ content; while several methods exist to do this, Mössbauer spectroscopy has been the only one used to our knowledge on asbestiform samples. In the health effects field, it has often been

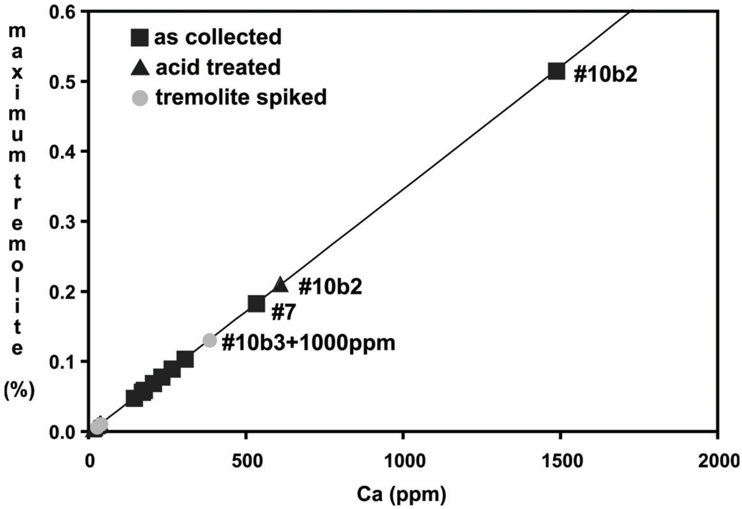


Figure 11. A plot of calculated maximum tremolite content of the ten natural samples of chrysotile ore (squares), the same ten samples after microwave acid treatment used to remove the carbonates (triangles), and three tremolite-spiked samples (circles) as a function of measured Ca content. The line represents the ideal relation between observed Ca and maximum tremolite content. This type of relation could be used to help predict tremolite content in a chrysotile ore in near real-time as in an actual mining operation (Gunter et al. 2007).

hypothesized that the Fenton reaction may play a major role in lung disease, and this reaction would be largely controlled by Fe^{2+}. Thus the oxidation state of Fe is not only important to fully characterize the amphibole, but may play a role in disease. Interestingly, Gianfagna et al. (2007) found differences in the $Fe^{3+}/\Sigma Fe$ values for asbestiform and nonasbestiform morphologies of fluoro-edenites from Biancavilla.

MORPHOLOGY MATTERS

It might seem that too much emphasis is being placed on morphology in this chapter, but morphology is at the heart of the issues involving the health effects of exposure to amphiboles. There have been many papers on this single issue over the years, along with several different methods proposed on how to distinguish between fibers and fragments (e.g., Wylie 1979; Nolan et al. 1991; Brown and Gunter 2003). And some of the recommendations for nomenclature to be used to discuss morphology now date back almost 30 years (e.g., Zoltai and Wylie 1979). First, there is the problem that methods developed for commercial asbestos issues are now being applied to all amphiboles, even those found in the natural setting. When this is done, particles that clearly are not asbestos, or even asbestiform, can often meet the definition of asbestos, such as all the particles shown in the grain mounts in Figure 4 and the single crystal shown in Figure 5A. This has led to ongoing issues (discussed later) with amphiboles located in El Dorado Hills, California, where the EPA and its subcontractors (Ecology and Environment 2005) termed many particles as asbestos while another group found almost none (RJ Lee 2005), looking at the same material. As another example, by applying standard fiber-counting methods, Brown and Gunter (2003) found that 48% of the particles in the sample shown in Figure 4B meet the definition of a fiber, whereas none of them have the morphology of a fiber. What is currently needed are clear definitions of what is and what is not a fiber, especially when applied to amphiboles found in a natural setting.

Figure 12 shows an approximately 1-mm long particle of amphibole from Libby in plane- (A) and cross-polarized (B) light. From the left side, there is no argument that the particle is asbestiform; however, from the right side, the particle appears nonasbestiform. Thus a single particle can have different morphologies at either end. Scale also becomes an issue in trying to determine morphology. Figure 13 shows a series of FESEM images at low (left column) and high (right column) magnification. The NIST (The US National Institute of Standards and Technology) crocidolite (Figs. 13A, B) is clearly a fibrous habit in Figure 13A but somewhat less so in Figure 13B. This is a sample similar to that in Figure 1A where there is no doubt that the material is fibrous. Thus as the scale decreases, as is common for single particles found in air sampling, it becomes more difficult to tell fibers from fragments. The particles shown in Figures 13C and 13D are of the NIST tremolite-asbestos standard; this material appears even less fibrous at this scale. Brown and Gunter (2003) found this material to be 100% fibers based on 3:1 aspect ratio counting rules and 92% fibers based on morphology. The last sample in Figures 13E and 13F is an amphibole from Libby, Montana. This sample appears intermediate in morphology from the other two. In a PLM study of this sample, Brown and Gunter (2003) found the samples to be 95% fibers by counting rules, while they found it to be 36% fibers and 33% fragments based on morphology. Notice that these numbers do not sum to 100; they judged they could not determine between fibers or fragments for 31% of the particles.

Going hand-in-hand with trying to determine the morphology of amphiboles are explanations for the formation of asbestos and asbestiform amphiboles (Zoltai 1981). There seems to be a general agreement that stress fields are required to form asbestos. In fact, there are two types of asbestos fibers: cross-fibers that grow to fill joints in rocks (i.e., the growth direction is across the vein) and slip fibers that form along the face of a fault plane in the rock (i.e., the growth occurs between the layers of the slipping surface). Ross and Nolan (2003) give a thorough discussion of asbestos formation in ophiolite complexes, along with associated health concerns.

Others have noticed that asbestiform amphiboles seem to have low (<0.15) apfu values for Al (Dorling and Zussman 1987; Verkouteren and Wylie 2000). In these works, the authors examined amphiboles of differing morphologies from various locations and found no asbesti-

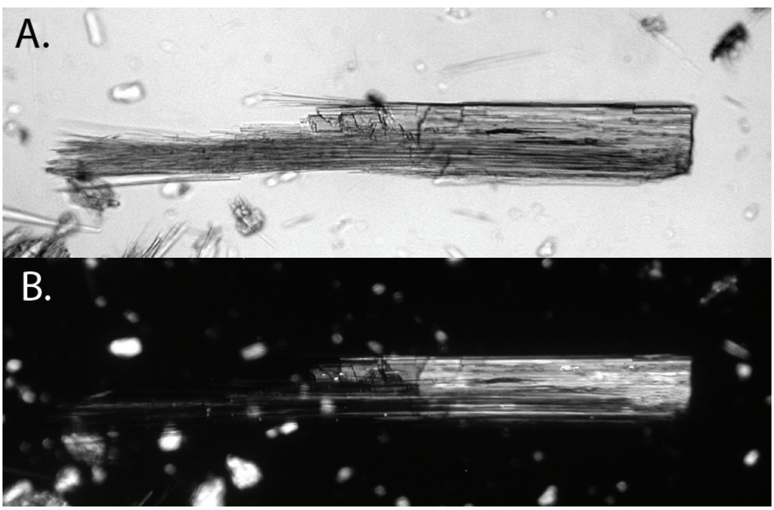


Figure 12. PLM photographs of an amphibole particle from Libby, Montana, in plane-polarized light (A) and crossed-polarized light (B). Notice how the right side of the particle is nonasbestiform, while the left side appears asbestiform (FOV = 1.2 mm).

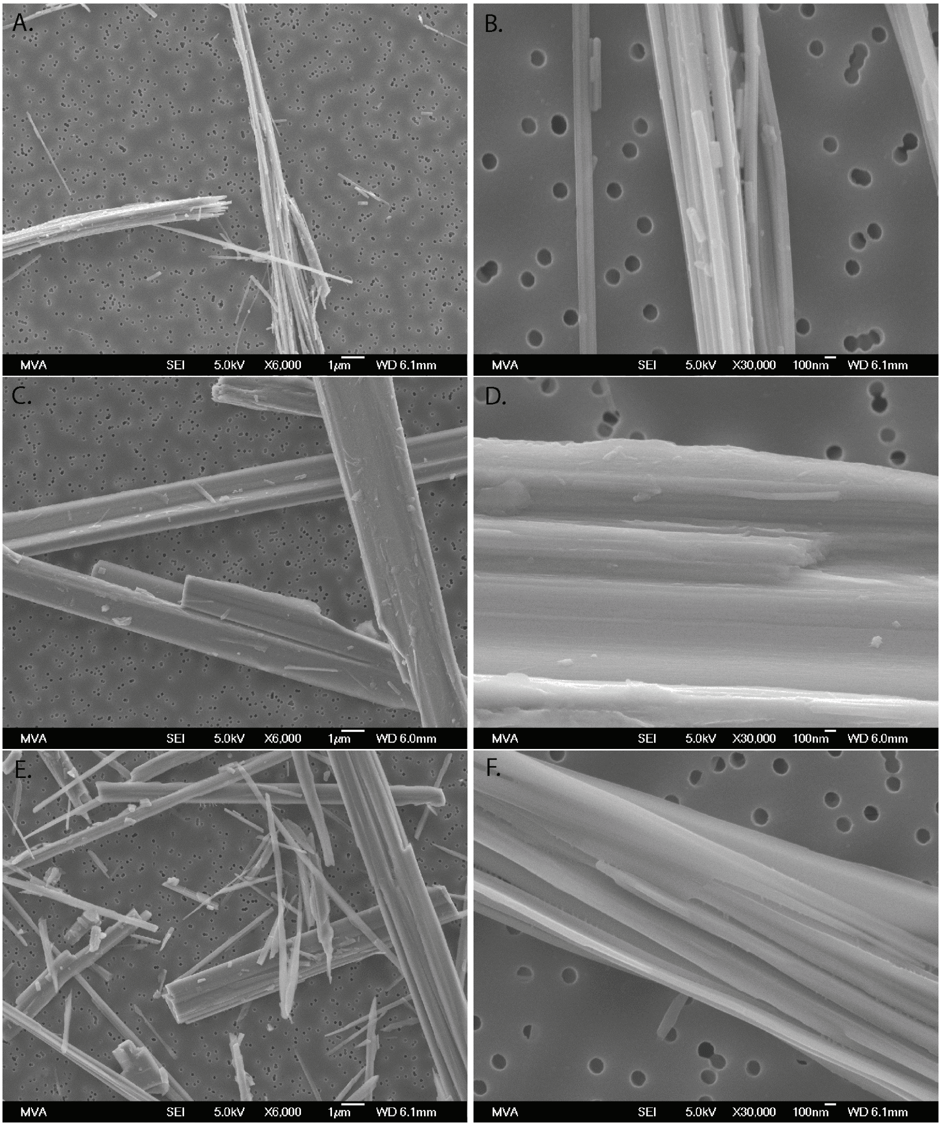


Figure 13. A series of FESEM images at low (left column) and high (right column) magnification of three separate amphiboles. A and B show NIST fibrous riebeckite (i.e., crocidolite), C and D show the NIST tremolite asbestos standard, and E and F show amphiboles from Libby. At the higher magnifications, note that both the riebeckite and Libby sample appear separable into particles on the range of 100 nm, while the NIST tremolite does not appear to have the closely spaced partings. (Photos courtesy of Bryan Bandli, MVA Scientific Consultants, Duluth, Georgia, USA.)

form varieties with Al above 0.15 apfu. The asbestiform fluoro-edenite recently found in Sicily (Gianfagna and Oberti 2001) has an Al content of 0.5 apfu, and violates this trend. There are two possible reasons why Al content could affect morphology: (1) it inhibits the formation of fibers or (2) it relates to the fact the Al is rare in the mafic rocks where most asbestiform amphiboles occur. (The asbestiform fluoro-edenite is associated with more Si- (and in turn) Al-rich rocks.)

Returning to the issue of mixed morphology shown in Figure 12; Figure 14A shows a thin-section photograph of the asbestiform tremolite in Figure 4C. The fibers are obvious, but so are single crystals of tremolite in the center of the image. Also, note how the single crystals appear to be rotated with respect to the fabric formed by the fibers; this rotation indicates a nonhydrostatic stress field, supporting the idea that these asbestiform samples form in rocks that have undergone stress. However, what is also interesting in this photo is that single crystals of amphibole are directly associated with fibers. Figure 14B, a thin section of the rock shown in Figure 4D, is even more intriguing. Here, what appears as a perfect euhedral single crystal of amphibole is in contact with fibrous amphiboles of the same composition (Sanchez 2007). In this case, there are no stress indicators apparent (and for those with a keen eye for optics, note the right side of the crystal exhibits isochromes showing how the sample is dipping into the slide). This single crystal also exhibits perfect {110} growth (*not* cleavage) faces. We know this because the crystal was not broken. This also reinforces the above comments concerning amphiboles as fibers and fragments. Lastly, it is worth pointing out here that the amphiboles at Libby formed from low-temperature alteration of pyroxenes, which differs from amphibole formation in metamorphic rocks.

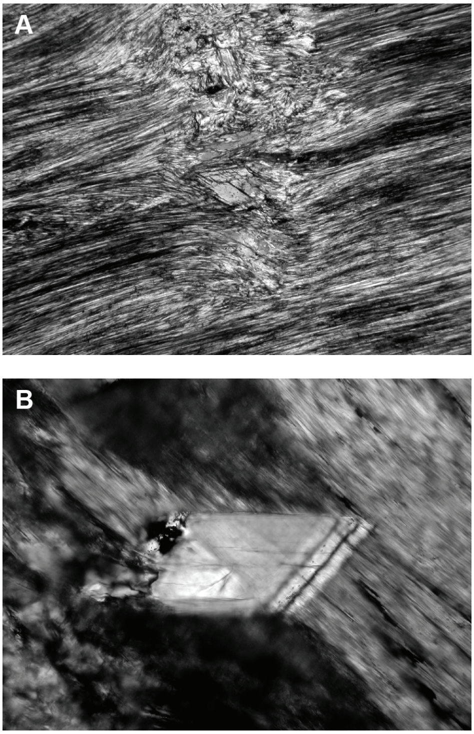


Figure 14. Photomicrographs of two thin sections of asbestiform amphiboles containing euhedral amphiboles. A) Asbestiform material encapsulating a single crystal of tremolite with what appears to be a gradational contact with the fibrous material (FOV = 4 mm, this is the same sample shown in Fig. 4C). B) This is the same sample shown in Figure 4D except at higher magnification; the euhedral crystal has a sharp contact with the fibers (FOV = 1 mm).

While regulatory definitions are important, health concerns of exposed individuals are more so. The ongoing debate in this arena is this: are particles derived from non-asbestos sources just as harmful as those derived from asbestos sources? Health studies (e.g., Davis et al. 1991) presented to the US Occupational Safety and Health Administration (OSHA 1992) suggest regulating only the asbestiform varieties of the regulated amphibole minerals because the nonasbestiform amphiboles seems to pose less of a health risk to humans. This would mean that anthophyllite, actinolite, and tremolite would only be regulated if they occurred with asbestiform habit (by definition, crocidolite and amosite always have this habit). Currently, there is debate over the health effects of respirable amphibole particles, regardless of whether they derive from an asbestiform or nonasbestiform source.

REGULATORY AND LEGAL ISSUES

The regulatory and legal communities are more foreign to most geologists than the medical community. Yet as geologists, we must: (1) interact with these communities to help establish regulations that protect worker health while not hamstringing industry, and (2) assist in establishing laws that promote this end. Over the years, there has been some success in setting exposure limits in the industrial setting. Currently, the issues at hand deal more with natural (i.e., the nonanthropogenic) exposure. Thus it is even more critical for geologists to assist in this realm because now we have moved the exposure from the factories to the geological environment.

Regulated mineral species

Currently, the OSHA classifies asbestos as: chrysotile, amosite, crocidolite, tremolite asbestos, anthophyllite asbestos, and actinolite asbestos (OSHA 29 CFR 1910.1001 subpart Z (b)). Asbestos has been added to the name of the last three amphiboles to distinguish them from their massive forms. There are no specific names for the asbestiform varieties of anthophyllite, tremolite, or actinolite, probably because these species have never occurred in commercial asbestos bodies (except for anthophyllite). As reported by the U.S. Senate Committee on the Judiciary (April 19, 2005), there is currently a bill proposing the term asbestos to include: chrysotile, amosite, crocidolite; tremolite asbestos; winchite asbestos; richterite asbestos; anthophyllite asbestos; actinolite asbestos; any of the listed minerals "that has been chemically treated or altered and any asbestiform variety, type or component thereof; asbestos-containing material, such as asbestos-containing products, automotive or industrial parts or components, equipment, improvement to real property, and any other material that contains asbestos in any physical or chemical form." This redefinition may or may not pass, but it is the result of the majority of the amphibole species being nonregulated and issues surrounding the discovery that winchite and richterite are the most abundant amphibole species in the vermiculite deposit near Libby, Montana.

In the European Union (EU), Directive 2003/18/EC of the European Parliament and of the European Council of 27 March 2003 has modified Directive 83/477/EEC, so that the six minerals classified as asbestos are: actinolite of asbestos (n. 77536-66-4 of the Chemical Abstract Service); grunerite of asbestos (or amosite) n. 12172-73-5 of the CAS); anthophyllite of asbestos (n. 77536-67-5 of the CAS); chrysotile (n. 12001-29-5 of the CAS); crocidolite (n. 12001-28-4 of the CAS); tremolite of asbestos (n. 77536-68-6 of the CAS). Member states belonging to the EU, as recipients of the above-mentioned directive, are therefore obliged to implement it in their own legislation and to conform to it by passing the necessary regulations and adopting the new nomenclature by April 15, 2006, when the Directive came into force. The asbestiform amphibole fluoro-edenite, to date found only in Sicily, Italy, and linked to the onset of mesothelioma, has not been included by the Directive as belonging to asbestos.

There are restrictions for the disposal of asbestos in Italy. Asbestos in general (mostly chrysotile, which makes up 95% of asbestos, but also actinolite, anthophyllite, amosite, crocidolite, and tremolite). These are the five amphiboles classified as asbestos (amianto in Italian) according to Italian law DPR 915/82. Fluoro-edenite is currently not one of them, although a site remediation has been carried out in the Biancavilla area based upon health concerns there for the local citizens. Asbestos-containing materials are classified as such when they release fibers in an amount greater than 100 mg/Kg (i.e., 0.01%). They should be disposed of in special sites, depending on their *index of release (I.R.) = wt% asbestos/relative density* (Table 3), and special procedures are imposed to protect workers during the entire clearing, disposal, and beneficiation work. The preferred special types of disposal sites are mostly sites just for asbestos because: (1) it creates fewer problems than the disposal of multiple types of waste; (2) they have higher levels of environmental security than multiple disposal sites; and (3) there is no requirement about closing the system to underground waters because fibers are dangerous only when airborne. Asbestos waste can, however, be mixed with drilling muds and with gypsum produced in the fume-desulfuration process because these two wastes help bind the asbestos and minimize possible re-exposure. In general, disposal is done after packing asbestos-containing materials in sealed polyethylene bags of 0.15 mm thickness, which then

Table 3. Disposal sites for different types of asbestos-containing waste.

Asbestos-containing waste	Dust viz. free fibers (mg kg^{-1}: min÷max)	Dump Type
Asbestos-cement cover board (new)	35÷105	2 A
Asbestos-cement cover board (damaged)	75÷150	2 B
Asbestos-cement cover board (strongly damaged)	90÷200	2 B
Asbestos-cement pipe (new)	35÷70	2 A
Asbestos-cement pipe (damaged)	60÷120	2 B
Asbestos-cement wallboard (new)	90÷150	2 B
Asbestos-cement wallboard (damaged)	90÷400	2 B
Asbestos board: gypsum viz. carbonate binder	0.1×10^6÷0.2×10^6	2 C
Asbestos board: quartz binder	0.1×10^6÷0.2×10^6	2 B+
Asbestos-bearing particle board	0.1×10^6÷0.2×10^6	by case
Asbestos-vinyl tiles (new)	0÷10	2 A
Asbestos-vinyl tiles (cut, pierced, damaged)	5÷40	2 B
Asbestos-reinforced polymeric components	not determined	by case
Asbestos felts and bulk insulations	0.1×10^3÷0.7×10^3	2 C
Asbestos-based powder viz. flake fillers	indeterminable	2 C
Asbestos paper and cardboard	0.1×10^6÷0.2×10^6	2 C
Asbestos sprayed (encapsulated)	0.1×10^6÷0.2×10^6	2 C
Asbestos sprayed (not encapsulated)	0.1×10^6÷0.2×10^6	2 C
Asbestos tissues, textiles, ropes	0.1×10^6÷0.2×10^6	2 C
Friction materials (new)	50÷500	2 B
Friction materials (used)	200÷3000	2 B+
Friction material dust	indeterminable	2 C
Other materials from asbestos-bearing wastes that have been modified in some manner		Case by case

Dump types:
2A – for compact asbestos waste derived from demolitions, buildings and diggings;
2B – for waste containing loose asbestos fibers and/or fine dust < 100 mg Kg-1;
2B+ – the same, but with > 100 < 10000 mg Kg-1 (0.01-1 wt% total asbestos);
2C – insulated dumps appropriate for waste with > 10000 mg Kg-1 loose fibers (>1 wt%)

are packed into large metallic cans for further safety. If the asbestos material is friable, the plastic bags must be doubled and thermo-sealed; they should not exceed 1 m^3 in size before being disposed. Most disposal cost is shouldered by the private person compelled to clear asbestos from their dwelling, with a small contribution by local authorities. A widespread illegal trade of asbestos-containing waste is known but is difficult to control.

It might seem strange to a mineralogist to read the phrase "How asbestos is defined is a legal question…," yet this quote is taken directly from the ruling of a U.S. federal judge dealing with the federal case of W.R. Grace (Molloy 2006). What prompted the judge to make this ruling were issues surrounding the species names of the amphiboles in the former vermiculite mine of Libby, Montana. The majority of the amphiboles from the deposit are winchite or richterite (Fig. 2). Neither winchite asbestos nor richterite asbestos are listed as regulated asbestos minerals. Thus even though this mineral might meet the definition of asbestos from a mineralogical perspective, it does not from a legal one. The judge's argument does not even need to refer to morphology because these particular amphibole species were not listed as regulated materials. Clearly the issues surrounding these nonregulated amphibole species are of concern to the regulatory, legal, and mineralogical communities. The mineralogical community must first characterize these materials, then the legal and regulatory communities must establish laws and regulations to protect the public's health. When these nonregulated amphiboles were first discovered at the former mine, many in the geological community wanted to change the regulatory rules to include all amphiboles that met the morphological definition of asbestos. The problem with making that change is that determination of mineral species is very objective while determination of morphology can be very subjective.

The major issue with morphology as discussed in other sections of this chapter is that the methods used by the regulatory community were established to deal with asbestos in the industrial setting (i.e., the regulated and widely used asbestos minerals). When these same methods are applied to amphiboles in nonasbestos deposits, which are the great majority of amphiboles on the Earth, several issues arise which need to be resolved.

GEOLOGICAL OCCURRENCE

To those in the geological community, it seems redundant to make the statement that asbestos occurs in rocks naturally; however, as previously stated, many people believe that it is manufactured. Clearly asbestos is mined and it is associated with certain geological features. Amphiboles often form during mountain building events, and as such correlate to current or past tectonically active regions (e.g., Ross 1981; Ross and Nolan 2003). Figure 15 by Van Gosen (2006a) shows the geological distribution of asbestos occurrences in the eastern USA. Notice the correlation between the asbestos locations and the trend of the Appalachian Mountains. Van Gosen (2006b) produced a similar map for the central USA, and as one might expect, there are very few asbestos occurrences there. He is currently compiling a map for the western USA (Van Gosen personal communication). A similar map is currently being complied for all Italian occurrences (F. de Grisogono personal communication); it will complement and update the sketch maps published years ago only for the Piemontese Alps (Belluso et al. 1994, 1997).

In this section, we provide an overview of the formation of different types of amphibole in general and amphibole asbestos in particular, because (as we are aware in the geological community) there are orders-of-magnitude more amphibole than amphibole asbestos in the geologic environment. From the environmental-exposure concern, the weathered products from geological formations are presently more of an issue than the geological formations themselves. Thus we will spend some time discussing amphiboles in soils and other unconsolidated materials. The geological conditions that conspire to form amphibole asbestos and asbestiform amphiboles (i.e., some type of regional stress environment) will also form other types of fibrous minerals. Thus we also include a section discussing the occurrences of these amphiboles with other fibrous minerals.

Association with rock type

In a general sense, we must consider the major rock types containing amphiboles. Martin (2007, this volume) discusses the occurrence of amphiboles in igneous rocks and Schumacher (2007, this volume) discusses the occurrence of amphiboles in metamorphic rocks, so readers are referred to those chapters for more general discussions on amphibole occurrence. In this chapter we will limit our discussion to the formation of commercial amphibole-asbestos and to areas where asbestiform amphiboles may occur.

Recall that there are two major commercial amphibole asbestos minerals: crocidolite (asbestiform riebeckite), and amosite (asbestiform grunerite). Both occur in banded ironstones. The name "amosite" derives from the Asbestos Mines of South Africa Company, reminding us where it occurs and was mined. On the other hand, crocidolite has been mined in three areas: South Africa, Bolivia, and Australia. Figure 1a shows a photograph of Bolivian crocidolite which appears as a bundle of blue fibers over six inches long; there is no question that the material is fibrous, looking more like human hair than a mineral.

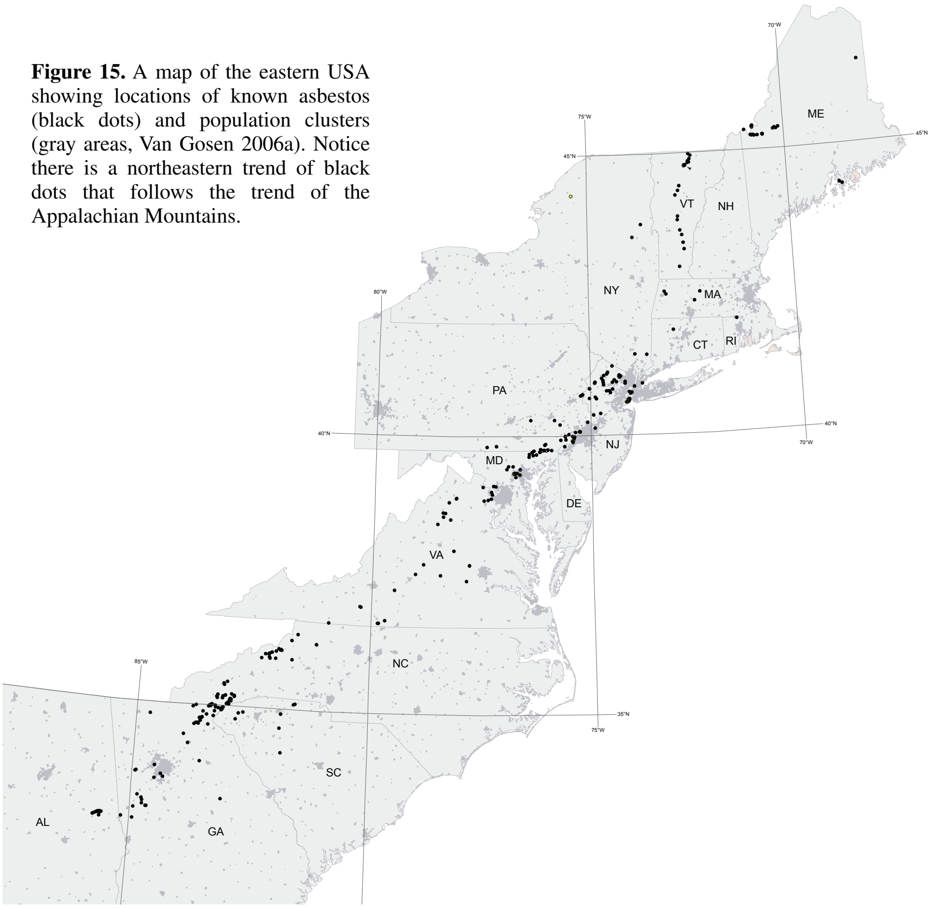


Figure 15. A map of the eastern USA showing locations of known asbestos (black dots) and population clusters (gray areas, Van Gosen 2006a). Notice there is a northeastern trend of black dots that follows the trend of the Appalachian Mountains.

Other amphiboles, most notably anthophyllite, tremolite, and actinolite, will sometimes occur in an asbestiform habit. For these amphiboles to form in this habit, a nonhydrostatic stress field is necessary. Ophiolite complexes favor the formation of asbestos minerals, especially Mg-rich ones, based on the original composition of the parent rock, P and T conditions, and stress fields. It is in these ophiolite complexes where much of this chrysotile asbestos also occurs. Thus, actinolite, tremolite, and anthophyllite can occur as accessory minerals in association with chrysotile asbestos. For an in-depth discussion of chrysotile deposits and associated amphiboles, see Ross and Nolan (2003) and Ross (1981, 1984), also Veblen and Wylie (1993) provide overviews of the formation of amphiboles.

Amphiboles can also form as low-temperature alteration products of pyroxenes, as at the now closed vermiculite mine in Libby, Montana. The amphiboles in this deposit occur in different morphologies (Figs. 1B, 4D, 5, 6, 12, 14). While some of the amphiboles in the deposit are pyroxene alteration products, amphiboles also occur between the layers of sheet silicates from the deposit. The latter was noted on a macroscale by Clark et al. (2003) and recently on a microscale by Gunter et al. (2006). One interesting aspect of the amphiboles between the sheet-silicate layers is the amphibole dimensions and aspect ratios are similar to those of asbestiform asbestos, but they do not meet the definition of asbestiform morphology (i.e., they were not formed by length-wise separation of amphiboles into fibers). Figure 6 shows examples of amphibole particles occurring as small single crystals between the sheets; this mode of formation is discussed in a following section dealing with Libby.

Association with other fibrous minerals

Amphibole fibers can occur both with mineral fibers of the same species and, as often occurs, with different species to form: (1) bundles of tightly packaged fibers, with fiber axes lying parallel or sub-parallel to the length of the bundle, and (2) aggregates of randomly oriented fibers. The former type of intergrowths have been known for a long time (e.g., the oriented association of tremolite fibers with talc fibers and anthophyllite fibers with talc fibers, Stemple and Brindley 1960; Virta 1985). In this kind of association, the fibers are usually crystallographically rotated with respect to each other and not correlated by twinning operations.

An investigation whose purpose was to determine which types of amphibole occur in vermiculite showed that fibrous bundles are made up of tremolite and actinolite with variable quantities of asbestiform anthophyllite, winchite, and richterite, fibers of diopside, hornblende and talc, vermiculite, calcite, and quartz with an apparently fibrous habit (Atkinson et al. 1982; Wylie and Verkourteren 2000). Tremolite fibers are present as accessory minerals in many talc deposits, and in some, tremolite is associated with asbestiform winchite and richterite (Van Gosen et al. 2004).

In the serpentinitic rocks of the Piedmont Zone of the Western Alps, fibers of asbestos occur in association with fibrous antigorite (Belluso et al. 1994). Talc lamellae develop from the grain boundaries, as with anthophyllite (Fig. 16). It is not uncommon to see asbestos fibers associated with crystals of the same (but not asbestiform) species, such as fibrils of anthophyllite surrounding coarse-grained anthophyllite crystals (Veblen 1980). This feature is shown in Figure 14 where fibrous amphibole occurs surrounding single crystals of amphibole.

In some samples, the boundaries between anthophyllite fibers are partially filled with talc, antigorite, chrysotile, and chlorite. These minerals replace amphibole during a retrograde metamorphic hydration reaction (Veblen 1980). These species develop along the entire length of the amphibole fibers, so they too are fibrous; however, they are only identifiable at the

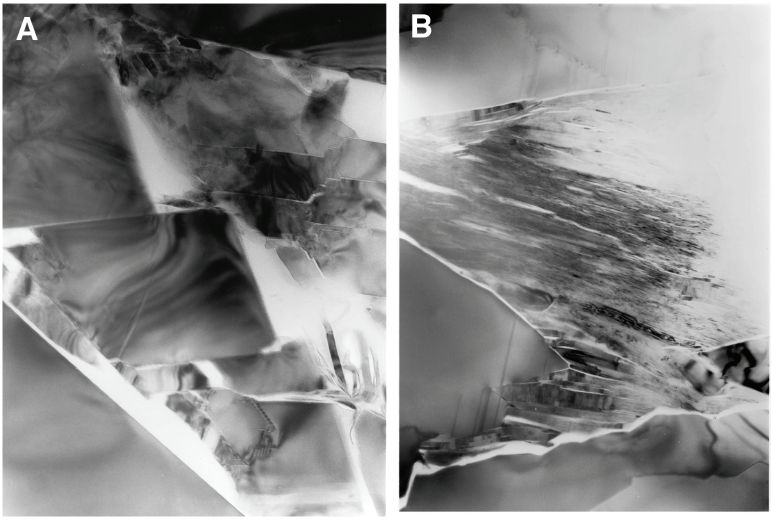


Figure 16. HRTEM image of tremolite fibers as seen along the fiber bundle elongation (c-axis): A) fibrils of different sizes showing typical 120° interfacial angles and transformation into talc (on the right); B) laths of talc replacing fibers of tremolite.

HRTEM scale owing to their small extension in the perpendicular plane. In these associations, chrysotile, which forms from amphibole, gives rise to fascinating textures (as seen in the plane normal to fiber axis). Partially or totally rolled or S-shaped wavy serpentine "moustaches" form along boundaries with the anthophyllite fiber. Figures of eight are also present, made of two intergrown rolls of chrysotile (Veblen et al. 1977). Talc fibers have been found in intimate association with ferromagnesian pyriboles through replacement by sheet silicates. Some fibers, where replacement is not complete, are composed of both pyriboles and talc (Veblen and Buseck 1980). Fibers of crocidolite have been found only in association with mica at grain boundaries between amphibole fibers and have a fibrous morphology (Ahn and Buseck 1991).

Asbestos fiber may also occur in association with other fibrous minerals because of chain width disordering. Chain-width faults may occur in amphibole and develop along the *b* axis. These faults can prevent the classification of fibers into a particular silicate subclass (i.e., sheet vs. double or single chain). In some cases, the fiber should, strictly speaking, be classified as several different species. Indeed, sometimes the chain-width faults become ordered and extend for wide domains, producing pyribole portions with triple-silicate chains or with alternating double and triple chains; these pyriboles are respectively known as jimthompsonite and chesterite. When fibers are almost entirely composed of these kinds of pyriboles, they could be classified as one of two species since these minerals are also fibrous (Veblen et al. 1977). Because of the possibility of such ambiguities, Veblen et al. (1977) suggested using the term pyribole asbestos for all amphibole asbestos, as this term enables all possibilities to be included without preventing them from being distinguished from chrysotile.

Amphiboles in soils and unconsolidated material

In many areas of the world, soils contain mineral fibers that are mostly amphibole. Soils derived from rocks containing asbestiform amphiboles also contain fibers that may potentially become airborne. Some of these rocks are very susceptible to weathering and also very rich in magnesium (e.g., those containing asbestos) and hamper the development of vegetation, inhibiting soil formation. Chrysotile is more soluble in the presence of H_2O and at low pH, and acid leaching removes magnesium from the fibers fairly rapidly, leading to their disintegration. Amphiboles are more resistant, and amphibole fibers are more frequently found in soils (Trescases 1997; Hillerdal 2003). Moreover, soils can become enriched in amphiboles as other minerals in the soil weather away.

Investigation on the presence of asbestos fibers in soils began after the identification of asbestos-related pathologies in human populations not occupationally exposed to asbestos. These soils may expose local populations because they contain amphibole fibers that were easily dispersed in air due to dry climate. The respirable dimensions of amphibole fibers have been related to the formation of calcified pleural plaques in humans and in animals (Abrahams 2002) and some mesothelioma cases (Browne and Wagner 2001). Soils containing less than 1% asbestos fibers can release large quantities of fibers into the air and may constitute health risks (CDPHE 2006). The fibers contained in soils become airborne when the soils are disturbed either by natural processes (mainly wind) or by human activities (such as agriculture, planting trees or bushes) or a combination of the two.

The above scenario occurs in rural areas of southwestern China were the soil is covered by scattered, clay-like, bluish patches (termed "blue clay") that contain short, rigid crocidolite fibers (Luo et al. 2003). On dry and windy days, the mineral particles are airborne and later settle, covering the villages with bluish dust. The blue-clay was used locally to make building blocks, stoves, plaster, and paint for house interiors. The inhabitants are therefore subject to both natural and anthropogenic exposure. Situations like this have been observed in areas of Cyprus, Greece, Turkey, and New Caledonia where tremolite is present in soils. In these cases, the better-developed soils tend to release fewer tremolite fibers into the air than the Chinese case; nevertheless, the exposures of the inhabitants is high because the local rock was widely used as whitewash, stucco, or plaster for houses (Browne and Wagner 2001). Tremolite-asbestos fibers were also detected in the soils of an area in Basilicata (southern Italy), and they derive from the natural weathering and erosion of serpentinite (Burragato et al. 2006). Asbestiform tremolite occurs in the soils of some Balkan areas; various activities cause them to split into fibers, which then subdivide into respirable fibers (Wagner 1980).

Abundant quantities of asbestiform amphiboles, including fluoro-edenite, are present in portions of brecciated lavas in a local quarry in Biancavilla, Sicily. Detrital fine-grained accumulation occurs in this area because of the incoherence and friability of the volcanic rock. Even though the quarry has been closed as a consequence of the identification of airborne fiber-related pathologies, the fibers continue to spread easily in the air and settle on agricultural soil because of the dry, windy climate and the fact the quarry has not been revegetated (Mazziotti Tagliani 2006).

Some soils are originally asbestos-free and then are subsequently contaminated by commercial amphibole-asbestos (and also by chrysotile) owing to human activities. An example of this is the demolition of buildings in which there are various materials containing asbestos. This necessarily causes dispersion of the fibers into the air, many of which fall to the ground, thus becoming constituents of the soil. Further instances are the land-based disposal of waste asbestos materials (e.g., Mangano et al. 2006) and the disposal or abandonment of asbestos that is not properly stored and contains debris that undergoes degradation. Over time, these asbestos fibers penetrate both the soil surface and the subsurface (CDPHE 2006). Fortunately, while disposal of asbestos waste to landfills was a common practice in the past, current regulations restrict this practice.

In Nature, many soils contain asbestos (mainly amphibole) either because (1) they derive from rock material containing asbestos or (2) through proximity to natural or anthropogenic sources of easily airborne asbestos contaminants. In the case of cultivated soils, farmers working these soils may be exposed to high doses of fibers. For example, asbestiform amphibole fibers occur in the soils of Libby, Montana. These fibers are released into the air during routine residential activities (USEPA 2001a); however, to date no one has determined the quantity of fibers that are anthropogenic vs. those that are nonanthropogenic. There are few detailed studies on the chemical and mineralogical composition of soils and the asbestos fibers contained in them. Even so, we know that amphiboles occur in many unconsolidated materials in the western USA associated with various mountain terrains (Gunter and Lee 2006).

In populated areas where soils are heavily contaminated with amphibole fibers, risk assessment is particularly useful and, if necessary, provisions should be adopted to contain air dispersion or to remediate the ground in question. The Colorado Department of Public Health and Environment (CDPHE 2006) has recently published a detailed guideline of modalities for the characterization of asbestos contaminated sites (ACS) and for the management of ACS related to partial or total remediation (involving the excavation, removal and burial of the soil to a suitable depth).

OCCUPATIONAL VS. NONOCCUPATIONAL EXPOSURE

Occupational exposure to asbestos has been covered in past RIM volumes. Ross (1981) did an excellent job discussing mortalities based on different populations in chrysotile and amphibole asbestos exposures. His early work clearly showed that amphibole asbestos exposure induced more disease than chrysotile exposure. In the early 1980’s, the nonoccupational exposures often involved the wives of miners, and their exposure roots was from husbands’ clothing. In 2007, we focus on nonoccupational exposure to asbestiform amphiboles in their natural setting. The distinction here should also be made that, in general, the term asbestos should be reserved for the commercial product (refer to Fig. 1A for the inch-length fibers of tremolite and chrysotile). The term asbestiform should be reserved for amphiboles that split lengthwise (as shown in Fig. 1B). These particles, while being separable fibers on a very small scale, would tend to not be used as commercial asbestos because they are too short. Thus we would propose to use the expression nonanthropogenic exposure to asbestiform amphibole to replace the commonly used expression of exposure to "naturally occurring asbestos."

Asbestosis, silicosis, and lung carcinoma are widely agreed to be related mostly, if not exclusively, to exposure to dusts and fibers that are other than amphibole, namely chrysotile, quartz and various other minerals. By contrast, pleural mesothelioma has almost invariably been related to exposure to amphibole fibers, with erionite, a zeolite, being the only other mineral of possible cause (Metintas et al. 1999). Attention to mesothelioma is particularly acute in Italy after the general public was made aware of the Biancavilla, Sicily, cluster of disease (Comba et al. 2003, 2005; Fano et al. 2005). A much worse case occurred at Casale Monferrato, Piedmont, where nearly 200 mesothelioma cases were diagnosed between 1983 and 2002, and in the year 2003 alone there were 32 new findings of the disease. Indeed, both pleural and peritoneal mesotheliomas are such interesting exposure-related diseases that they have attracted world-wide attention (e.g., Roggli et al. 2002; Dodson et al. 2005).

As for Italy, Table 4 shows the overall mortality rate (defined as mortality rate = number of deaths / total population × 100,000) due to pleural mesothelioma from 1995 to 2002 (the last year for which full statistical information is available). Also, Table 5 gives mesothelioma death-rates for different regions of Italy. Based on these data, Montanaro et al. (2004) and Marinaccio et al. (2005) made a reasonable estimation of future development of the disease (Fig. 17). They related it to the total consumption of asbestos and found that the peak for mortality should occur in 2015, lagging behind the peak of the 1976 date for the peak of asbestos consumption. However, their statistics may be misleading because they note total consumption and not consumption of only amphiboles, which by consensus is the inferred cause of mesothelioma. Therefore, the statistics may be strongly biased by the fact that most asbestos-containing materials used in Italy until 1989, after which it was forbidden, were chrysotile.

Mesothelioma mortality can best be studied by comparing the data from four provinces of Italy having asbestos quarries with two where no quarries are present and where other sources of exposure can be assessed. Balangero is a village located in the province of Turin and contains the largest asbestos mine in Italy (1918-1979). The now-closed mine is still surrounded by over 65 million m^3 of waste hosting an estimated 800,000 m^3 of fibers. Most of it is short-fiber chrysotile, but there is an estimated 10% tremolite in the tailings. Figure 18A shows that with steadily decreasing population in Turin province, the mortality rate fluctuated but substantially increased after 20 years of Balangero closure, implying that nonoccupational exposure is a major problem. However, this statistic may be biased by several joint-causes

Table 4. Mortality rate in Italy for pleura mesothelioma

Year	Average Population	Total Deaths	Rate cause specific
1995	56,844,408	925	1.6272
1996	56,844,197	1014	1.7838
1997	56,876,364	972	1.7090
1998	56,904,379	978	1.7187
1999	56,909,109	1096	1.9259
2000	56,923,524	1141	2.0044
2001	56,960,692	1193	2.0944
2002	56,993,742	1203	2.1108

Table 5. Pleura mesothelioma deaths for different regions of Italy.

Region	Men		Women		Total	
	Cases	Rate st.	Cases	Rate st.	Cases	Rate st.
Piemonte	800	3.42	510	2.00	1310	2.68
Valle d'Aosta	6	1.00	7	1.11	13	1,05
Liguria	831	7.81	251	2.07	1082	4.77
Lombardia	1034	2.59	753	1.64	1787	2.07
Trentino-Alto Adige	57	1.45	45	0.99	102	1.20
Veneto	426	2.10	240	1.05	666	1.54
Friuli-Venezia Giulia	274	4.18	74	0.97	348	2.44
Emilia Romagna	403	1.74	207	0.83	610	1.28
Marche	132	1.60	70	0.83	202	1.22
Toscana	397	1.90	197	0.87	594	1.38
Umbria	50	1.03	27	0.56	77	0.80
Lazio	206	0.88	124	0.51	330	0.69
Campania	344	1.65	185	0.84	529	1.24
Abruzzo	67	0.99	41	0.62	108	0.81
Molise	10	0.52	5	0.26	15	0.39
Basilicata	19	0.63	29	0.75	39	0.69
Puglia	321	1.93	125	0.78	446	1.36
Calabria	79	0.87	53	0.60	132	0.75
Sicilia	367	1.63	170	0.78	537	1.22
Sardegna	119	1.69	48	0.71	167	1.21
Italy	5942	2.17	3152	1.09	9094	1.61

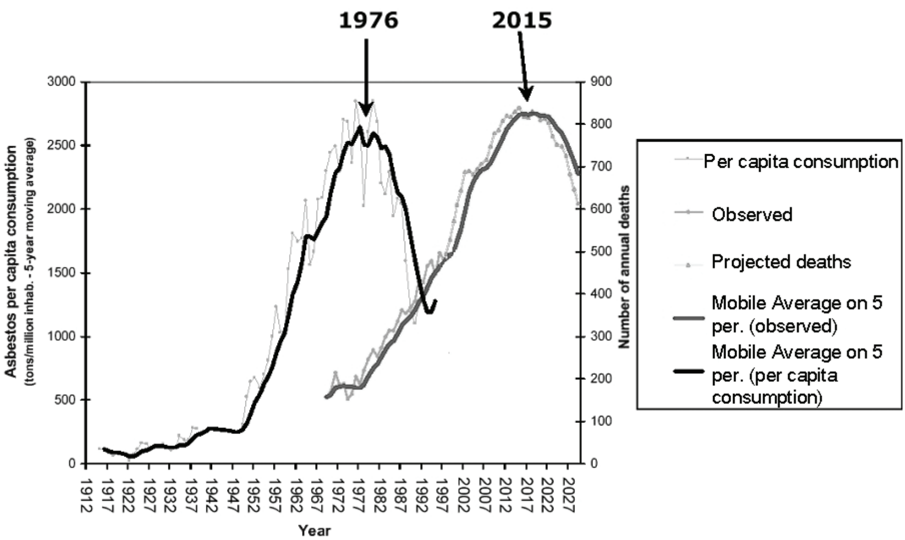


Figure 17. A plot showing the usage of asbestos (left curve) and yearly death rates from mesothelioma (right curve; actual deaths to 1997, then projected deaths to 2032). Note the graph shows offset from the usage to the onset of disease.

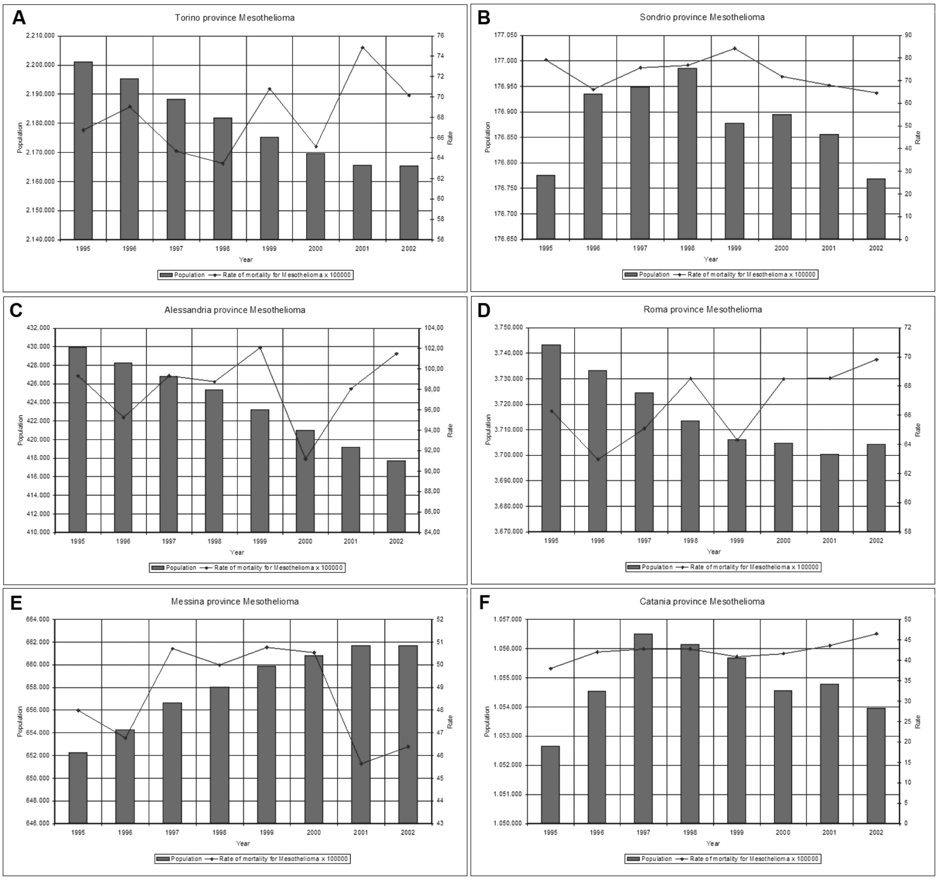


Figure 18. Death rates for mesothelioma in the different regions of Italy from 1995 to 2002. Bars represent the populations (shown on the left axis) and dots connected by lines represent deaths from mesothelioma (shown on right axis).

because Turin is a large city with major factories where asbestos was used (and still is, although exposures will be much lower because of safety regulations). The overall mortality rate may be the sum of occupational and nonoccupational exposure.

The province of Sondrio (Fig. 18B) stretches over a valley in the Alps removed from asbestos plants of any kind, where greenstones have been handcrafted from the time of Pliny, and the first mining license for asbestos (long-fiber chrysotile) in Italy was granted in 1866. The mortality rate can be related to occupational activity, as chrysotile occurs as long fibers coating cracks in serpentinites, together with white, almost visibility indistinguishable tremolite. The provincial population and mortality rate are constant, and the latter is higher than in Turin (Fig. 18A); in fact, it is the highest in Italy.

The province of Alessandria (Fig. 18C), on the lower right corner of Piemonte (i.e., the same region where Turin), has no significant outcrops of asbestos-bearing rocks, but it hosts the largest asbestos-treating manufacturing plant of Italy (now closed) at Casale Monferrato, in the middle of the Po plain. Despite decreasing in total population, Alessandria maintains a high and increasing mesothelioma rate, obviously related to occupational reasons. However, in Rome

(Fig. 18D), a city where there are no asbestos occurrences, but where there was widespread use of all types of asbestos for building, industrial and home applications, show mortality rates that are especially high and are increasing, even though the number of inhabitants is steadily decreasing.

The mortality rate is higher in Messina (Fig. 18E) than Catania (Fig. 18F). Messina is a neighboring Sicilian province to Catania where there are no known occurrences of fluoro-edenite or greenstones, but where both shipyard and railroad industries existed (i.e., industries where asbestos was widely used in the past). Thus, occupational exposure was high in Messina. Catania is the province in Sicily where Biancavilla is located. Mortality rates are not especially high, as most geological occurrences are asbestos-free (sediments and the Etna volcano); however, the rate is increasing, possibly because of the nonoccupational exposure of the inhabitants in the areas contaminated by fibrous fluoro-edenite.

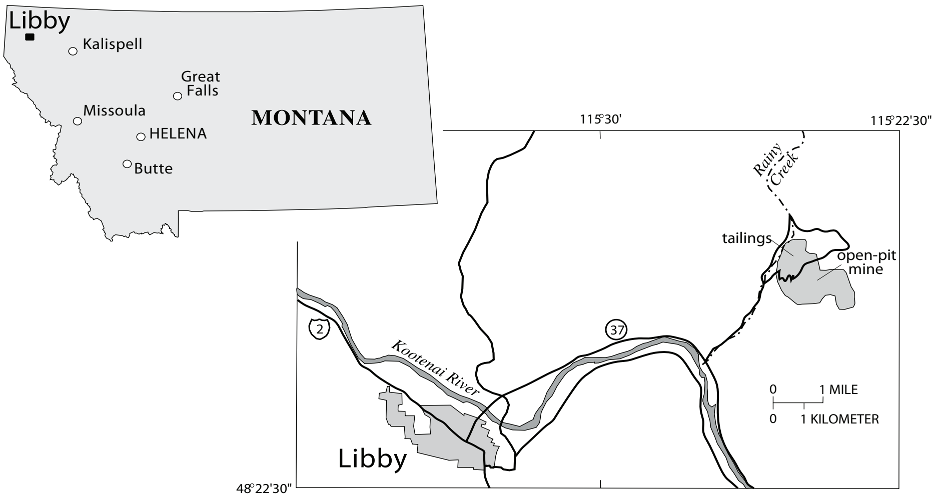
In summary, there are no definitive statistical indicators suggesting that low-level exposure to amphiboles in the natural setting are a direct cause of mesothelioma, as widely believed in the medical circles, but exposure to amphibole fibers may be a contributing factor. What is certain is that mortality due to mesothelioma has not yet reached its peak in Italy.

CURRENT EXAMPLES OF AMPHIBOLE EXPOSURE

A retired colleague recently commented, “asbestos has been a backwater of concern in America until Libby, Montana, made the national news.” Libby re-awoke not only interest in, but also the fear of asbestos exposure. Following closely on the heels of Libby was the issue of dust generated from the collapse of the World Trade Center Towers in 2001. Some of the same individuals who worked on the issues surrounding Libby, Montana, also became involved with the issues surrounding the dust from the World Trade Centers. Fortunately, the dust from the World Trade Centers was more-or-less asbestos-free and of such size as to not be respired into the lung. However, there are other respiratory diseases associated with that dust; they are beyond the scope of issues surrounding asbestos and will not be discussed herein. Contemporaneous with Libby and the World Trade Center were issues surrounding asbestos in El Dorado Hills, California. In this area asbestos was never mined; in fact, much of the current debate is whether the amphiboles in El Dorado Hills are actually fibers or fragments. Regardless, issues surrounding El Dorado Hills cause us to focus our concern on nonoccupational exposure to amphiboles. While the exposure might lead to a health risk, the fear of risk might also be detrimental to human health. In Italy, the village of Biancavilla on the flanks of Mount Etna has gained international attention because of higher incidence of mesothelioma and geological occurrences of both fibrous and nonfibrous fluoro-edenite.

Libby, Montana, USA

Issues surrounding the now-closed vermiculite mine near the small town of Libby, Montana, (Fig. 19) brought concerns over asbestos exposure back to public attention, beginning with a series of newspaper articles in the fall of 1999. The ore deposit, the articles reported, contained small amounts of amphiboles, some of which had asbestiform habit. Within days of these articles, the EPA arrived in Libby and is still there today, dealing with asbestos-contamination issues. Even though most of the world had never heard of Libby (or the vermiculite mine) until that fall, health studies had already been performed on the workers (McDonald et al. 1986a,b, 1988; Amandus and Wheeler 1987; Amandus et al. 1987a,b), showing that rates of lung cancer, asbestosis, and mesothelioma are about 2.5 times higher in the miners than expected. Ross et al. (1993) discussed several issues surrounding the amphibole content of the vermiculite ores. A follow-up study by McDonald et al. (2004) showed that out of 406 men who had worked at the mine for at least one year before January 1, 1963, 285 died by January 1999. Out of that group, 107 of the deaths had been from respiratory diseases: 51 deaths from asbestosis, 44



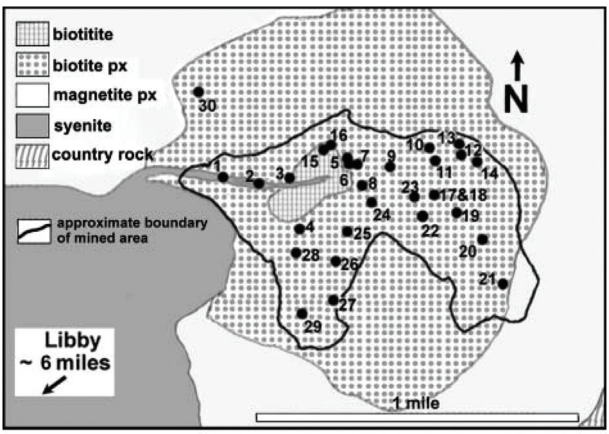


Figure 19. The location of Libby, Montana, with an inset showing the town's location with respect to the former vermiculite mine (from Van Gosen 2005) and a geologic map of the mine showing the locations for samples collected and analyzed by Meeker et al (2003).

from lung cancer, and 12 from mesothelioma. This study again confirmed that death rates are about 2.5 times the expected rates.

Concern spread from the miners to the general population in Libby and the surrounding area, about 8,000 past and current residents. Peipins et al. (2003) found higher rates of pleural plaques in the residents of Libby, which indicates that the residents were exposed to asbestos. However, their study was disputed (see Environmental Health Perspectives, Feb. 2004, Correspondence section) based upon the claims that Piepens et al. did not follow appropriate experimental procedures for reading the lung X-ray films (i.e., the readers were told which films were from Libby residents). Moreover, the study did not correctly adjust for obesity. Regardless, the popular media has used this study to state that the local population suffers from asbestos-related diseases.

One of the main uses of the vermiculite ore mined at Libby was for attic insulation. A product called Zonolite was produced from "popping" the mined vermiculite: the vermiculite was heated for a few seconds at approximately 1000 °C. Zonolite ore was then shipped nation-wide and used as attic insulation; thus, there could be a much larger cohort of individuals exposed to amphibole-contaminated vermiculite than just those in Libby. The popular press has estimated that from 15-35 million homes in the USA contain this material. These sorts of numbers seem unreasonable given the population of the USA and the fact that there are only 65 million homes in America. Gunter et al. (2005) reviewed these estimates, and along with help from EPA personnel, estimated that there are close to 1,000,000 homes in the USA that may contain this product. The issue now is two-fold: (1) what is the asbestiform amphibole content of this material and (2) what are the risks homeowners face? A legal opinion recently issued by Fitzgerald (2006) stated that there was no reliable evidence indicating that Zonolite attic insulation poses an unreasonable risk of harm. Although some scientists may disagree with this legal view, yet again this points out the interconnectedness of science and legal issues involved in issues surrounding amphiboles.

Figure 19 shows a geological map of the former mine, and the location of samples collected by USGS, discussed by Meeker et al. (2003), and plotted in Figure 2. These data, along with those of Bandli et al. (2003), Gunter et al. (2003), and Sanchez (2007), show that the majority of the amphiboles at the mine are winchite and richterite, which as discussed above, are nonregulated. Also, Brown and Gunter (2003) pointed out that approximately 1/3 of the amphiboles occur in the asbestiform habit. These mineralogical characterizations have been important in legal decisions and play a major role as the issues are debated on what amphiboles should be regulated based on composition and morphology.

Figure 20 shows a series of photographs taken at the mine in the fall of 1999. Briefly, the deposit was an ultramafic intrusion composed mainly of biotite and pyroxene which later underwent partial alteration of pyroxene to amphibole and biotite to vermiculite (Boettcher 1967). Figure 21A shows an intergrown amphibole/pyroxene particle in a near refractive index-matching fluid for the amphibole. Figure 21B shows another recently found occurrence of the amphiboles (Gunter et al. 2006; Harris et al. 2007), where the amphiboles are growing on and into a sheet silicate. The images of air samples collected in Libby (Fig. 6) show these particles after they have been liberated from the sheets.

Sanchez and Gunter (2006) developed a powder XRD method to determine the amount of amphiboles in bulk Zonolite samples. Figure 22A shows a series of standards they made and shows a detection limit of approximately 1000 ppm. In Figure 22B, a series of Zonolite attic samples are plotted with a 1% spiked sample. From this figure, it appears that the amphibole content of these attic samples is below 1% total amphibole. Moreover, because around 1/3 of the amphiboles from Libby appear to be asbestiform (Brown and Gunter 2003), the amphibole-fiber content of this product would be less than 1/3 of the total amphibole content. In a related study, Gunter et al. (2005) showed that the trace elements of Libby vermiculite can be used to differentiate it from other commercial vermiculite products (Fig. 23).

From a risk and worker safety perspective, it is important to understand the dose received by the mine workers. Bandli and Gunter (2006) reviewed the exposure data for 1960 doses ranging from 10.7 to 168.4 f/cc, with the highest value occurring in miners that worked in the dry mill. Doses decrease to less than 1 f/cc in 1980. To date no one has determined a safe level of exposure to amphibole-asbestos; detailed studies of the miners, townspeople, and occupants of Zonolite insulated houses may help answer this question. Regardless, issues surrounding Libby will continue for years.

Last, it is interesting to note that Ross (1981) stated "Epidemiological evidence does not exist to assess the health effects of tremolite." Ten years later, a series of papers by Case (1991), Nolan et al. (1991), and Weill et al. (1990) all concluded that tremolite-asbestos is the most harmful type of asbestos. At the time, much of the evidence to support this came from studies on the Libby miners. Ironically, we now know that several different species of amphiboles occur in that deposit, with tremolite being less than 10% of the total amphibole population (Meeker et al. 2003, Gunter et al. 2005).

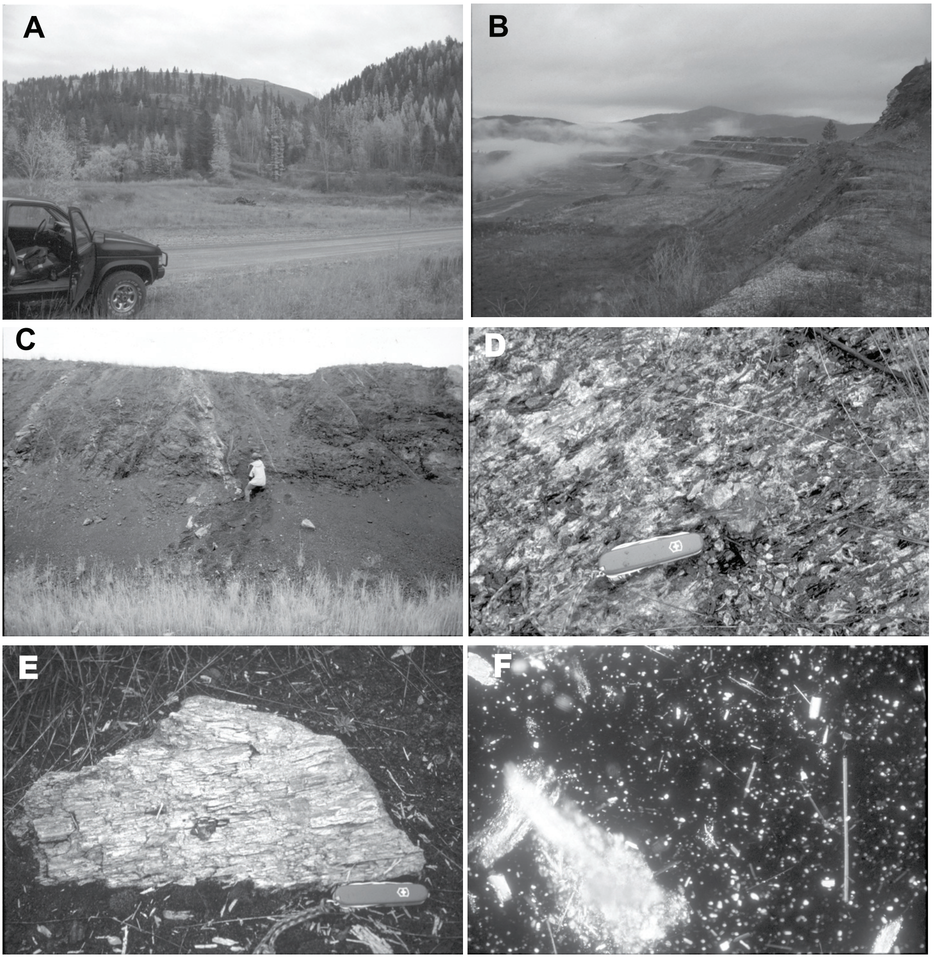


Figure 20. A series of photographs from large to small scale of the former mining operation near Libby, Montana. A) A photograph taken on Rainy Creek road, looking directly east to the top of what is termed locally as Vermiculite Mountain, the location of the former mine. B) A photograph looking west from the eastern side of the mine, showing the mined portion of the mountain top with the individual mined benches. C) A photograph of an individual bench with veins cross-cutting it. D) A close-up photograph of the bedrock at the mine. The lighter color minerals are amphibole, the dark minerals vermiculite or biotite, and the intermediate colors pyroxenes. E) A boulder-sized piece of amphibole on the surface. F) A photomicrograph of amphiboles collected from the mine. The blob in the lower left is a fibrous mass, while the vertical particle on the right is a single crystal of amphibole (modified from Bandli and Gunter 2006).

El Dorado Hills, California, USA

Housing developments in El Dorado Hills have grown over the past few years. The area serves as a bedroom community for Sacramento (Fig. 24). During the development of this area, amphiboles were discovered in the soils near a local school. Early remediation efforts at the school led the EPA (Ecology and Environment 2005) to conduct activity-based sampling to ascertain what exposure the students might be subjected, and the highest level was 0.0019 f/cc. This study was called into question by the National Stone Association (NSA), and a subsequent study funded by them was carried out by the RJ Lee Group (RJ Lee 2005), which examined

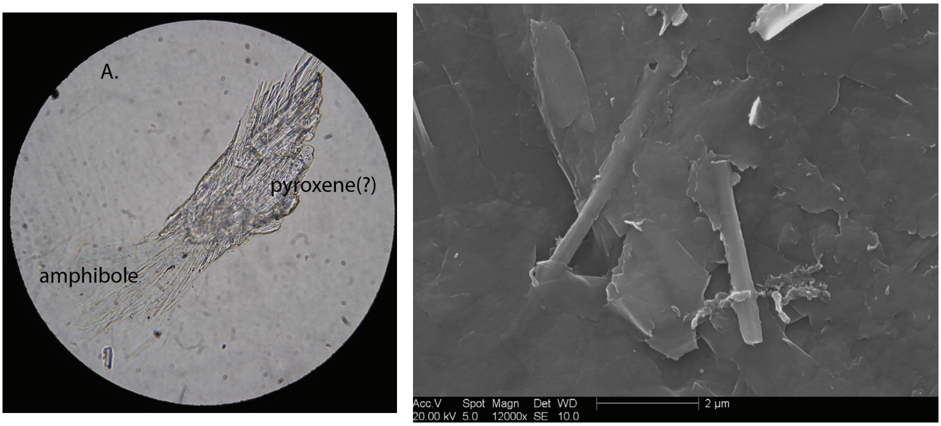


Figure 21. A) PLM photograph of an intergrown pyroxene/amphibole particle in a near refractive index-matching fluid for amphibole. The lower left portion of the particle matches the refractive index of the liquid, while the upper right exceeds it (FOV = 360 µm). B) An FESEM image from the Libby vermiculite deposit, showing amphiboles intergrown with layers of a sheet silicate. (Gunter et al. 2006, image courtesy of the RJ Lee Group Inc., Monroeville, Pennsylvania, USA).

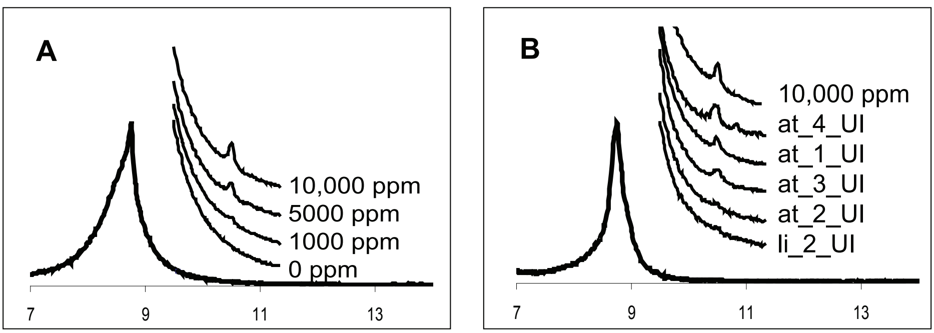


Figure 22. Powder X-ray diffraction scans of K-exchanged vermiculite samples. The long 2θ scan (7-14°) was collected at 0.02° step size and count times of 9 s. The shorter 2θ regions (8.5-11.5°) were collected at 0.02° step size and 180 s count times. A) This set of scans shows an amphibole-free sample and three amphibole-spiked samples. Notice the correlation in the size of the 110 peak for amphibole and the amount of added amphibole. B) This set of scans is vermiculite attic samples with a known Libby source with the 10,000 ppm spiked sample added; by observation, all samples have less than 1% amphibole (modified from Sanchez and Gunter 2006).

the same material as did the EPA. A third study (Meeker et al. 2006, (funded by the EPA) addressed some issues from the earlier studies. At the heart of the El Dorado Hills controversy is: (1) how do we deal with amphiboles that might pose a risk to humans in their natural setting and (2) what methods are appropriate to characterize amphiboles that are not associated with commercial asbestos products (i.e., can the standard methods developed to deal with asbestos in the workplace be used to deal with amphiboles in their natural settings?).

Figure 25A is a series of SEM photographs taken by the RJ Lee Group (2005) showing amphibole particles collected during the EPA-supported study (Ecology and Environment 2005). Even though these particles meet counting rules (i.e., the correct aspect-ratio) to be considered as fiber, they do not have the morphological character of asbestos. While the EPA-

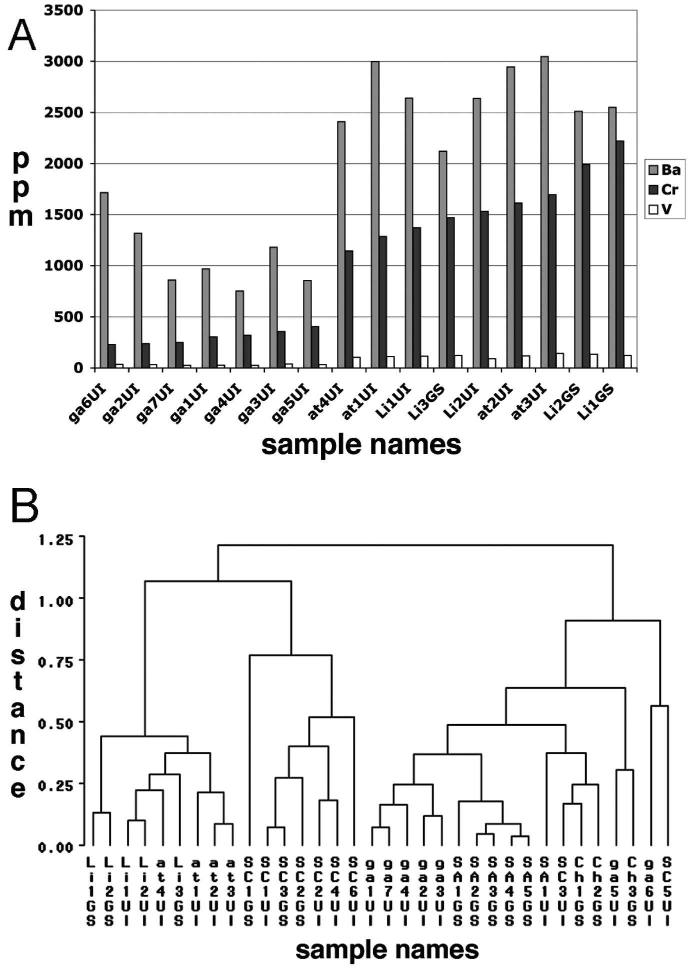
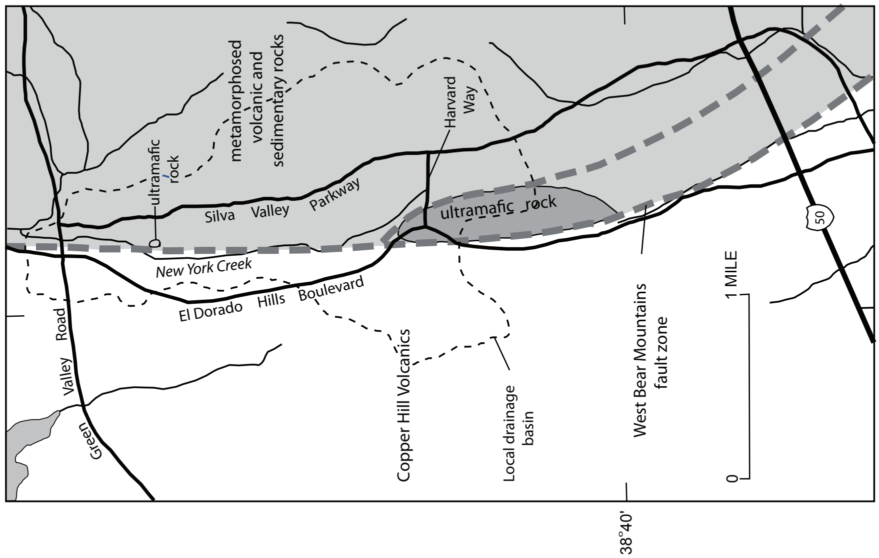


Figure 23. Chemical analysis of vermiculite ores can be used to determine their source. A) The trace element contents are plotted for 14 vermiculite samples. Those starting with "ga" are from commercial garden samples, "at" were obtained from attics, and "Li" are samples from Libby. Note how the "at" samples group with the Libby ones. B) Here, 34 samples are shown and 18 major, minor, and trace elements are used to group the samples. For these samples, "SC" refers to South Carolina and "SA" to South Africa. Note how the "ga" samples group with the "SA" samples (for more details see Gunter et al. 2005).

funded study found amphiboles they considered as asbestos, the RJ Lee Group (2005) found significantly less what they considered asbestos. Figure 25B is a series of photos from Meeker et al. (2006) that seem to show an asbestiform habit for another set of samples collected in the El Dorado Hills area. It is important to note that regardless of whether there are asbestiform amphiboles in the area, dosage is the most important thing to consider when dealing with mineral exposure. In the EPA's activity-based sampling, the highest value they obtained was 0.0019 f/cc, which is one order of magnitude above ambient air levels (Table 2).

The USGS (United States Geologic Survey) has taken on the challenge first in Libby, then the World Trade Center, and now in the El Dorado Hills to aid in characterization of minerals in their natural setting. During the last 5-6 years, they have assisted local communities and



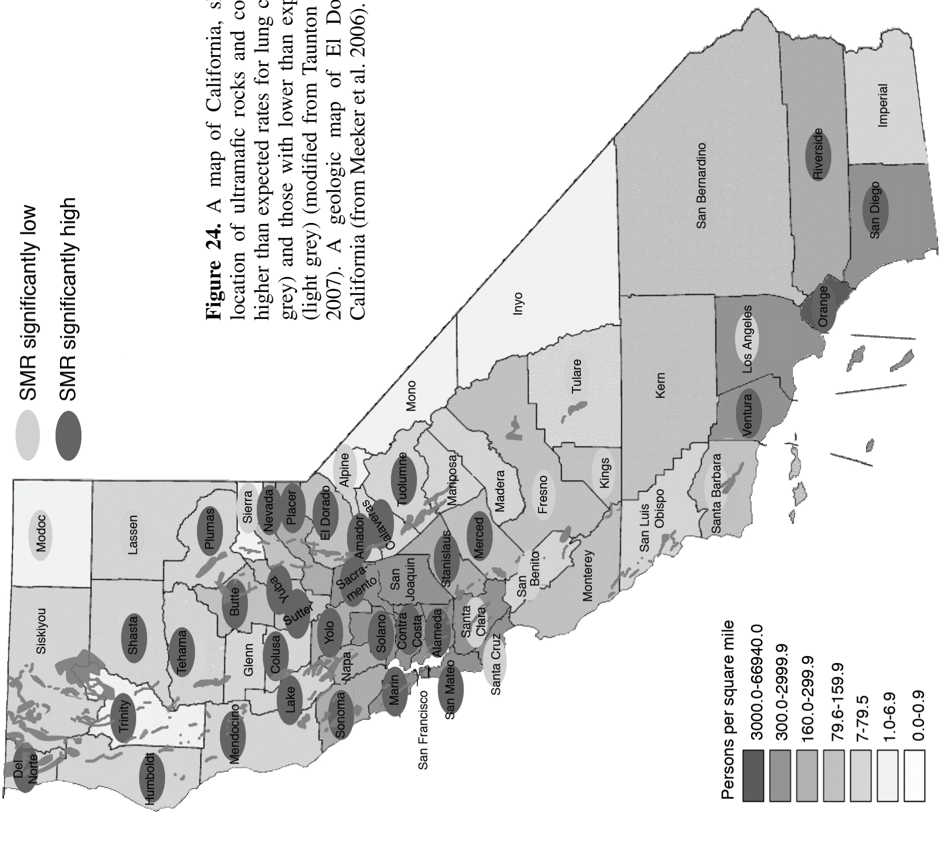
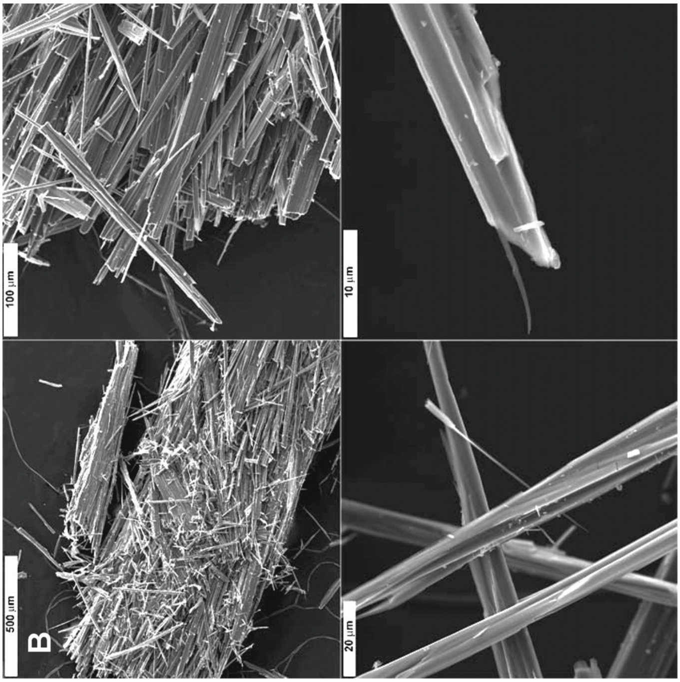


Figure 24. A map of California, showing the location of ultramafic rocks and counties with higher than expected rates for lung cancer (dark grey) and those with lower than expected rates (light grey) (modified from Taunton and Gunter 2007). A geologic map of El Dorado Hills, California (from Meeker et al. 2006).



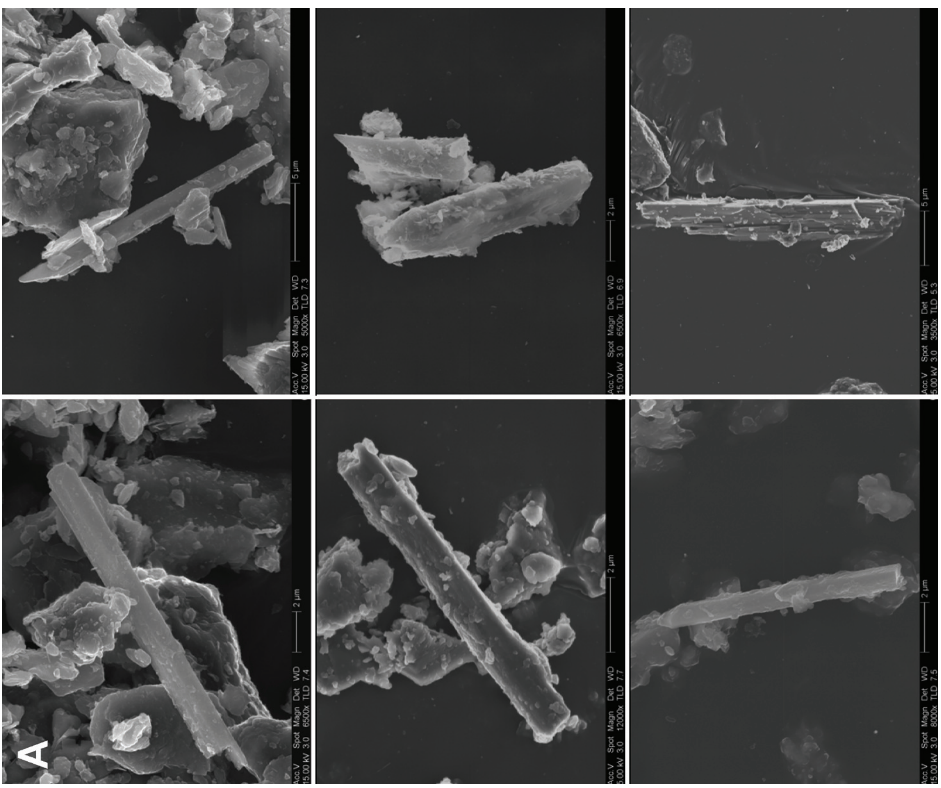


Figure 25. Example SEM photos of amphiboles collected in the El Dorado Hills area. A) Taken from RJ Lee (2005). B) Taken from Meeker et al. (2006).

regulatory agencies in dealing with the issues surrounding these natural exposures. They have brought to bear everything from their analytical experience, as shown in Figure 2, for the characterization of the Libby samples to remote sensing to help locate areas that might contain amphibole-bearing rocks (such as the spectroscopic analysis from a low-flying airplane, Fig. 26).

Unfortunately, some of the asbestos issues become polarized as they are played out in the public media, and no doubt the so-called "naturally occurring asbestos" is one of these issues. It is creating considerable fear not only in this area of California, but in much of the state. And it is not really all that new. Ross (1994) was already speaking of it, yet 13 years later, little has been resolved. What seems to be happening is the fear of nonoccupational exposure is spreading from El Dorado Hills to the rest of the USA (e.g., Dusek et al. 2002 in Virginia) and

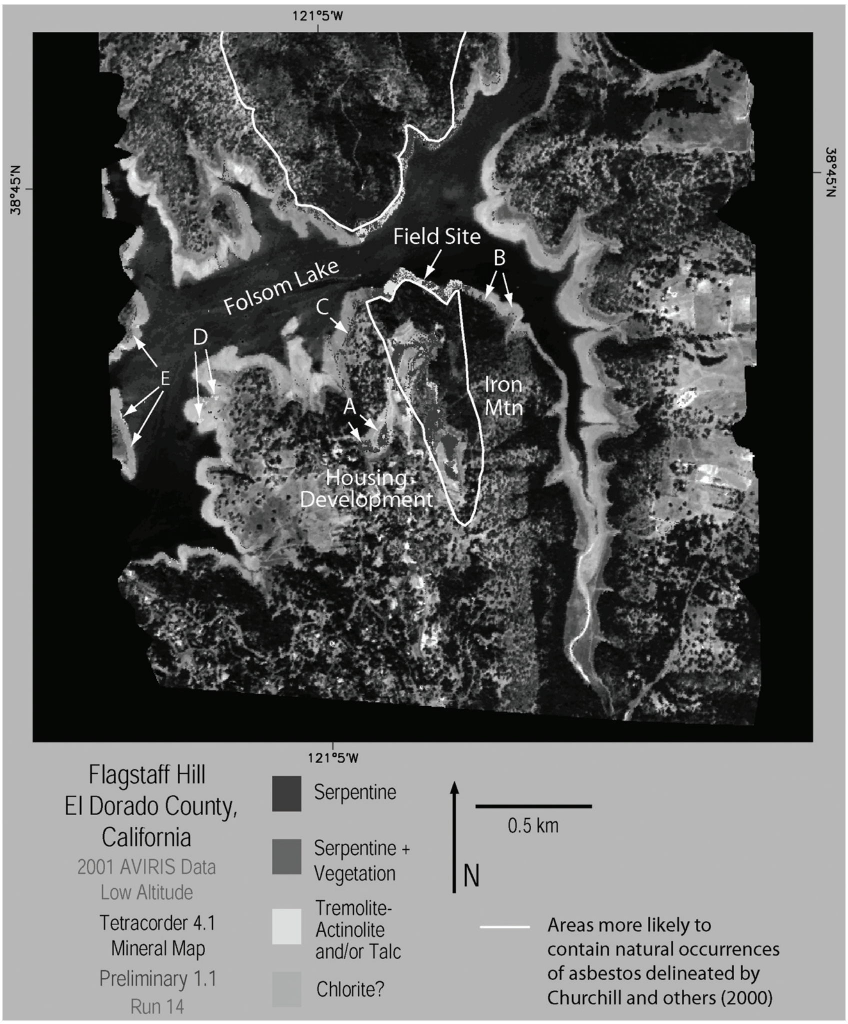


Figure 26. An aerial photograph of the area in and around El Dorado County, California. The different shadings on the map represent different rock types as determined by spectroscopic data obtained from an aircraft (Swayze et al. 2004). (Please see color version of this map at *pubs.usgs.gov/of/2004/1304*.)

it will be our role as mineralogists and geologists to try to assist industry, State and Federal agencies, and citizens as they grapple with this issue.

Biancavilla, Sicily, Italy

The small community of Biancavilla on the southern slope of Etna volcano in Sicily (Fig. 27) fell into the international spotlight (much like Libby, Montana) due to a positive anomaly for pleural mesothelioma detected in sanitary maps (Paoletti et al. 2000; Burragato et al. 2005). Biancavilla is now well-known as the first example of amphibole-fiber occurrence in a volcanic

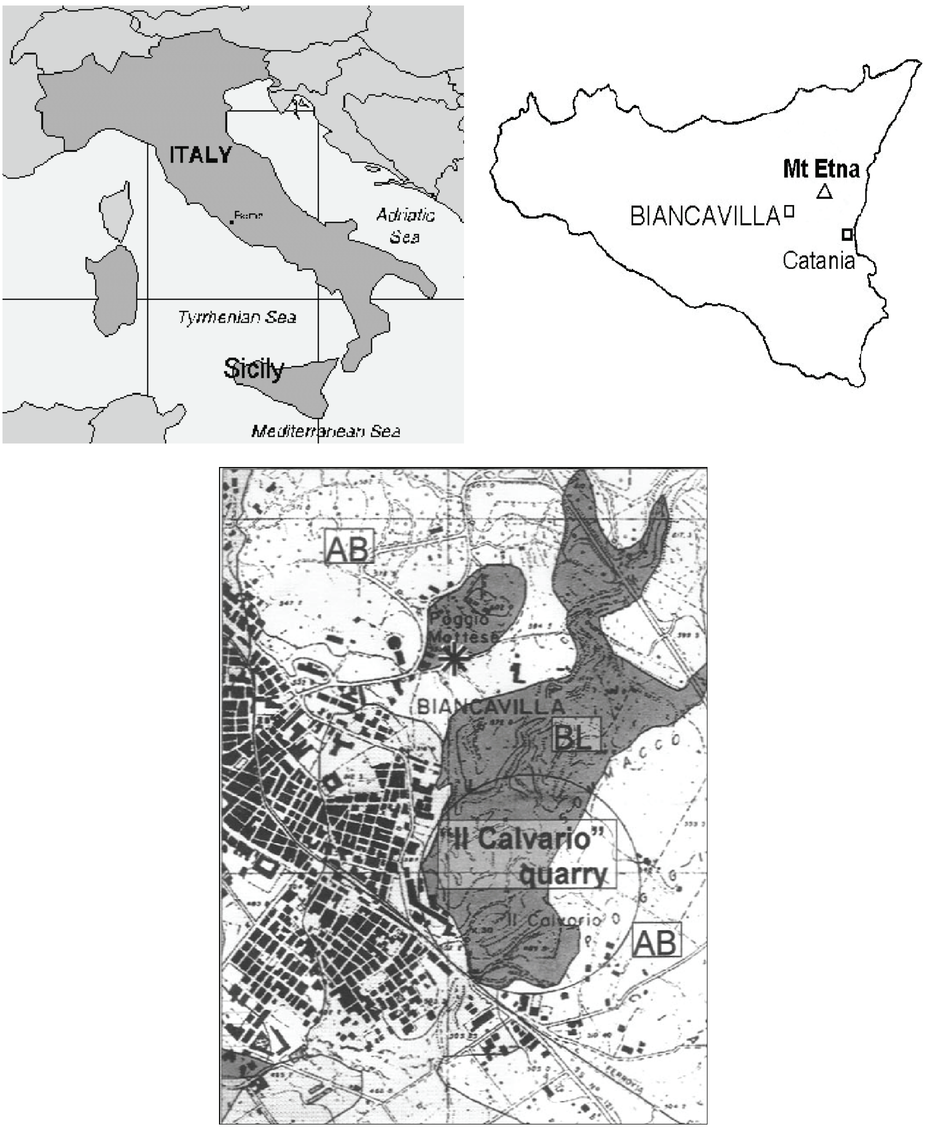


Figure 27. A location and geologic map of the Mt. Etna Biancavilla region. Biancavilla is at the very southern end of the map and the quarry containing fluoro-edenite is located northeast of the village. AB = alkali basalts and BL = benmoreitic lavas. (From Gianfagna et al. 2007.)

context. These fibers have an uncommon composition and are classified as the amphibole species fluoro-edenite (Gianfagna and Oberti 2001). Moreover, they seem to be oncogenic (cancer-causing) minerals. The latter finding of fibers with similar characteristics in human- and sheep-lung parenchyma is strong evidence that environmental exposure produces mesothelioma, especially when associated with exposure to building materials such as those produced from the Biancavilla Il Calvario quarries (Pasetto et al. 2004a; Burragato et al. 2005).

The stratigraphic succession exposed in the Biancavilla area comprises (from top to bottom):

Recent and present-day lava debris;

Lava flows of the Recent Mongibello (i.e., present Etna) activity stage (alkali-basalts, hawaiites and mafic mugearites);

Massive and stratified ash and scoria flow-deposits of the Biancavilla-Montalto ignimbrite (De Rita et al. 1991), which is benmoreitic in composition. This major explosive event, which deposited a tephra marker layer (Y-1) to be found elsewhere around the Mediterranean Sea at distances as great as 1000 km, is dated radiometrically at 14,500 ± 5,000 (Gillot et al. 1994), thus constraining the age of the underlying Biancavilla lava complex;

Lava flows, domes, dikes, and autoclastic breccias of the Ellittico center (Ancient Mongibello stage), mainly hawaiites, mugearites, and benmoreites; they include the autoclastic benmoreite lava body, reported as "lava autobrecciata" in the geological map of Mt. Etna, which hosts the fluoro-edenite fibers; the contact with the overlying ignimbrite deposits is well-exposed along the gorge Vallone di S. Filippo, and it is marked by a 10-cm thick reddish-brown palaeosoil;

Lava flows erupted from early alkaline eruptive centers: mainly alkali-basalts, hawaiites and mafic mugearites;

Tholeiite basalt lava flows of the earliest sub-alkaline period of Palaeo-Etna activity;

Clayish marls with interbedded sandstones of the pre-Etna sedimentary basement (Pliocene to Quaternary).

The severe and widespread environmental contamination of the entire Biancavilla community area by fluoro-edenite fibers is related to the volcanic materials present in the local quarries at the Il Calvario hill (Comba et al. 2003; Gianfagna et al. 2003). Fluoro-edenite occurrences are scattered in and around Il Calvario quarries throughout an area of about 2 km^2. The outcrops where fluoro-edenite occurs are in a benmoreitic lava dome and dike complex with the associated autoclastic breccias; all are metasomatized in places. The fluoro-edenite crystals occur within a friable material in the altered lava, in fractures, and in the breccias. However, fluoro-edenite is not the only amphibole present; a mixture of fibrous minerals containing a different asbestiform amphibole (described below) was found in a stone quarry to the north of Il Calvario hill that had been used extensively for local building activities under the name "azolo." These loose products contain fibrous amphiboles which were first identified as tremolite or actinolite, but which turned out to be partly fluoro-edenite.

Fluoro-edenite typically occurs either as prismatic or acicular millimeter-scale crystals or as fibers with asbestiform morphology (Fig. 28) in the cavities of the altered gray reddish benmoreitic lavas. Fluoro-edenite is generally associated with feldspars, quartz, clino-, and orthopyroxene, F–Cl-apatite, ilmenite and hematite, and probably crystallized from high-temperature volcanic fluids. The other type of fibrous amphibole in Biancavilla is yellowish and whitish in color and shows a strongly asymmetric morphology. This amphibole fills the pores of the altered volcanic rock (metasomatic benmoreitic lavas and pyroclastic rocks). Rietveld analysis shows it as a mixture of 24% amphibole-asbestos, 73% feldspar, and 3%

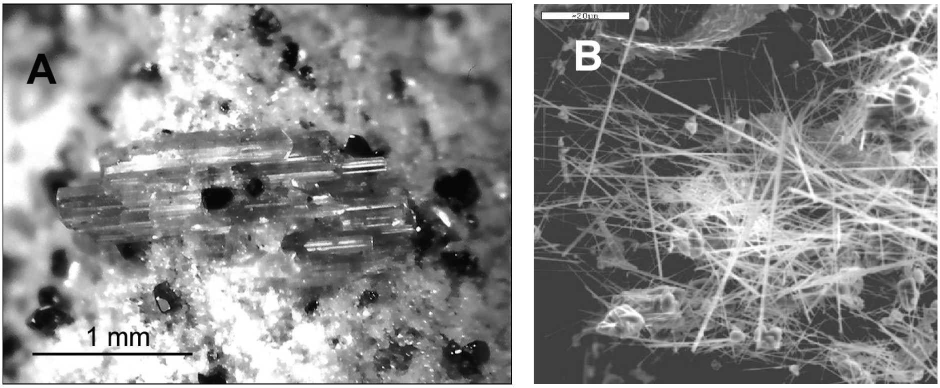


Figure 28. Photographs of fluoro-edenite from Biancavilla. A) Fluoro-edenite crystal exhibiting a blocky texture. B) Fluoro-edenite exhibiting a fibrous texture at a much finer scale. (From Gianfagna et al. 2007.)

hematite. Crystal size and morphology of these amphibole fibers do not allow quantitative EPMA analysis, but they are generally low in Ca and Mg, although both morphologies seem to have the same high fluorine content (Gianfagna et al. 2003). The high F content of all volatile-bearing minerals in the Biancavilla rocks is worth noting, not only in fluoro-edenite but also in fluorophlogopite (A. Gianfagna, personal communication). Also, as shown in Figure 29, Gianfagna et al. (2007) found different $Fe^{3+}/\Sigma Fe$ values for prismatic and fibrous fluoro-edenite in this deposit. To our knowledge, this is the first chemical difference ever determined between fibers and fragments of amphiboles.

AMPHIBOLES IN BIOLOGICAL MATERIALS AND ASSOCIATED BIO-MARKERS

In 1914, (otherwise undefined) crystals were observed in lung tissue during the autopsy of an asbestos worker who had died of pleuro-pneumonia. For many years, the recognition of minerals in the lungs of asbestos workers occurred essentially through correlation between the cause of death and the subject's occupation. It was only with the use of electron microscopy in

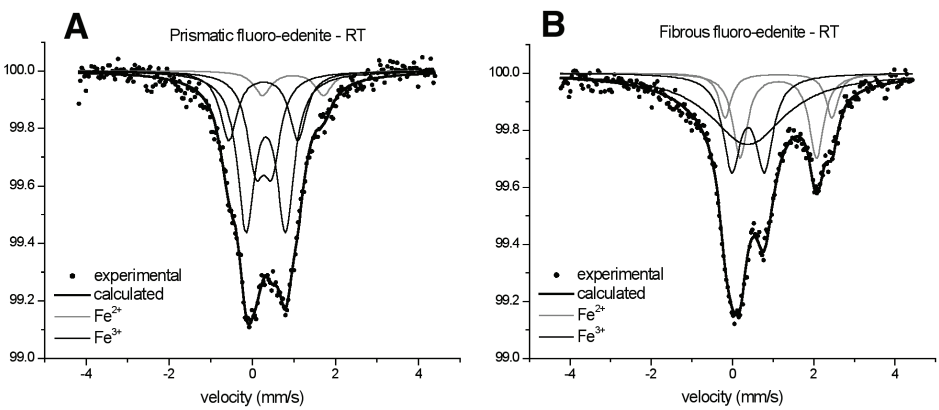


Figure 29. Mössbauer spectrum of fluoro-edenite (A) and fibrous fluoro-edenite (B); note the differing amounts of $Fe^{3+}/\Sigma Fe$. (From Gianfagna et al. 2007.)

the 1970s that it became possible to unequivocally identify asbestos amphiboles (in the lungs), to determine their burden in the lung tissue, and to understand that other inorganic fibrous species can enter the body (Roggli and Sharma 2004). Because fibers are inhaled, the lungs and the surrounding tissues were the first biological materials to be examined, and amphibole asbestos was commonly found in them.

At present it seems certain that the main repository of asbestos fibers in the human body is the lung parenchyma. However, fibers of amphibole asbestos have been found at high levels (both in the presence and absence of pathologies) in various other organs and tissues: in the visceral and parietal pleura (Tossavainen et al. 1994), in the larynx (Griffits and Malony 2003), in ovaric and intratesticular mesothelium (Attanos and Gibbs 2000), in omentum and mesentery (Dodson et al. 2000a), in lymph nodes (Dodson et al. 2000b), in the urothelium and the bladder wall (Pollice et al. 1995), in the intestinal mucosa (Storeygard et al. 1977), in the kidneys (Holt 1981), in the placenta (Haque et al. 1998), and in the liver and muscles of stillborn (Haque et al. 1998). Amphibole asbestos has been found also in biological fluids: in sputum (e.g., Putzu et al. 2006) and in bronchoalveolar lavage fluid – *BALF* (e.g., Sartorelli et al. 2001). To the authors' knowledge, there do not seem to have been any studies on amphibole asbestos (and chrysotile) in the blood. However, it is reasonable to think that the finest fibrils may pass into the blood circulation system after being inhaled. Indeed, the experiment by Nemmar et al. (2002) has shown that ^{99m}Tc-labeled ultrafine (5 to 10 nm in diameter) carbon particles inhaled by volunteers pass into the blood in one minute. Also, an experiment with hamsters has shown that a substantial fraction of intratracheally instilled particles with a diameter < 100 nm diffuse rapidly from the lung into the circulation system (Nemmar et al. 2001). Amphibole asbestos, as well as other fibrous minerals and synthetic inorganic fibers, have also been found in urine (e.g., Battaglia et al. 2005).

Amphibole in human lungs

There is a large body of scientific literature on the presence of amphibole asbestos and chrysotile in the human lungs (e.g., Chrug 1993; Roggli 2004). Many of the studies were done to correlate the cause of death with the subject's occupation (cases of occupational and paraoccupational exposure). Recently, investigations have been aimed at assessing the possible correlation between pathologies of the respiratory system and anthropogenic or natural environmental exposure, and to ascertain whether it is possible to determine the threshold value below which there is no risk of disease.

Asbestos fibers found in the lungs must have been respired. Thus an excellent way of assessing lifelong exposure to airborne and respirable fibers is to investigate fibers contained in the lungs. After fiber inhalation, a portion of the fiber burden is eliminated (by clearance) from the lungs. Both the clearance-persistence ratio and the difference in clearance mechanisms among individuals are unknown, so the dose-response relation between exposure and fiber burden in the lung is unclear. Nevertheless, this type of study is useful for classifying exposure, especially when information about the subject's activities is lacking. This type of study is also useful for assessing the type and relative quantities of asbestos fibers to which individuals were exposed with respect to respirable sizes and biopersistence characteristics (Roggli and Sharma 2004). If the examination of the fiber burden is done on biologic material, the data obtained provide useful information for assessing the risk of subsequent disease (Roggli 1990).

The finding of amphiboles in human lungs, like other minerals and toxicants in general, can be attributed to three kinds of exposure: occupational (and paraoccupational), anthropogenic in the environment, and natural environmental. Nevertheless, it is not rare for exposure to be of mixed origin and variable quantities. The finding of amphibole asbestos in the lungs proves that the subject has been exposed in some way to these minerals. The respired amphiboles can be airborne from an anthropogenic and/or natural source. We know that only crocidolite and amosite have been used in large quantities and in thousands of products by industry. The use of anthophyllite has been undoubtedly far less and not widespread worldwide, essentially because of the scarcity of the economically exploitable deposits. Tremolite and actinolite have not been industrially exploited because their technological properties are not particularly useful, and as for anthophyllite, economically exploitable deposits are lacking.

While the distribution of crocidolite and amosite is high in the anthropogenic environment because of their widespread use, tremolite and actinolite are commonly only found in the natural environment. Indeed, these two calcic amphiboles are ubiquitous in ophiolite complexes and greenstones in many areas of the world (e.g., Ross and Nolan 2003). In areas where there are outcropping rocks bearing only tremolite and actinolite as amphibole asbestos, their presence in the air can be reasonably related to a natural source. If in the same air environment, crocidolite fibers are also present, the source must necessarily be anthropogenic, such as an asbestos-cement roofing (Fornero 2005). For example, if tremolite and actinolite fibers are the only types found in the lungs of a subject, it is possible to exclude professional exposure to commercial amphibole asbestos (i.e., crocidolite and amosite). The presence of different kinds of asbestos fibers in the air depends on their presence in different matrices. Obviously, asbestos inhalation is possible only if the minerals are airborne. In distinguishing occupational, anthropogenic, or natural fiber sources, the situation may become more complicated because: (1) there are no physical barriers limiting fiber distribution, (2) asbestos fibers are spread worldwide due to occupational, anthropogenic, and natural occurrences, (3) for reasons of work, residence and lifestyle, human beings are exposed to very different environments, and (4) humans respire fibers regardless of the sources.

In order to have a general view of the various situations leading to amphibole asbestos in the lungs, some case studies regarding different types of exposure are briefly illustrated below. In some cases, the fiber concentrations found in humans are reported in Table 6, together with information about the presence or absence of asbestos-related pathologies in the subjects. The fiber concentration is indicated as the number of fibers $\times 10^6$ *per gram of dried tissue* (ff $\times 10^6$ /gdt), as most commonly indicated in the literature.

The determination of the fiber burden in the lungs and in other biological materials requires the fibers' identification and quantification by SEM-EDS and/or TEM-EDS; however, there is a possibility to use powder XRD. The means of acquiring, treating, and investigating biological samples by SEM and/or TEM with EDS and the type and quantification of the inorganic fibers are discussed by Roggli (2004), Roggli and Sharma (2004), and Belluso et al. (2006a). However, it is necessary to bear in mind that an internationally adopted protocol for studying fiber burden in biological samples does not exist, and various laboratories use slightly different techniques (Tossavainen et al. 2001). Therefore, the data reported in Table 6 have to be viewed with some caution. To be able to make an interlaboratory comparison, it is international practice to indicate the fiber concentration (i.e., mineralogical burden) as fibers per gram of dry tissue (ff/gdt).

High quantities of crocidolite and amosite amphiboles in the lungs are common not only in miners of the material but also in subjects professionally exposed to asbestos. Different species of amphibole have been found in the lungs of workers exposed to various kinds of fibers. This is the case for workers from a factory producing insulation boards predominantly using amosite (occupational exposure). In the workers' lungs, high quantities of amosite fibers and lesser amounts of crocidolite, chrysotile, mullite, and anthophyllite were detected (Gibbs et al. 1994). Also, the same kinds of fibers as used in an asbestos-cement factory were found in the lungs of inhabitants who lived near the factory (i.e., anthropogenic environmental exposure). In addition to crocidolite, amosite, and anthophyllite (the fibers present at the asbestos-cement factory), a small quantity of tremolite was also present in the neighbors' lungs (e.g., Magnani et al. 1998; Table 6). Similarly, for people who lived in the proximity of amosite or crocidolite mines and subjected to anthropogenic environmental exposure, amphiboles deposited and accumulated in their lungs (e.g., Roggli et al. 2002).

Table 6. Amphibole asbestos fiber burden (ff × 10^6/gdt) found in human lungs.

	Tremolite	Actinolite	Anthophyllite	Amosite	Crocidolite
general population (not professionally exposed - no pathologies asbestos correlated)					
Vancouver (Churg 1993)[2]	0.4	0	0	0.001*	
East Texas (Dodson et al. 2000a)[2]	0.002	0.002	0.002	0.002	0.002
hSV north-western Italy (Belluso et al. 2006b,c; Fornero 2005)[1]	0.327	0.030	0	0	0
lSV north-western Italy (Belluso et al. 2006b,c; Fornero 2005)[1]	0.053	0.007	0	0.006	0.002
LV north-western Italy (Belluso et al. 2006b,c; Fornero 2005)[1]	0.026	0.005	0	0	0
professional exposition, talc mine workers (with pathologies asbestos correlated)					
New York talc mine (Hull et al. 2002) no mesothelioma	0.1*		22.4	0	0
New York talc mine (Hull et al. 2002) with mesothelioma	556*		2.5	0	0
professional exposition, chrysotile mine workers (no pathologies asbestos correlated)					
South African mine (Rees et al. 2001)	0.33	0	0	0.14	0.13
professional exposition, chrysotile mine workers (no pathologies asbestos correlated)					
Churg 1983	50.0	0	0	0	0
professional exposition, vermiculite plant workers (no pathologies asbestos correlated)					
Libby (Wright et al. 2002)	5.94	1.78	0.05	0	0
professional exposition, asbestos-cement workers (unselected cases)					
Casale Monferrato, Italy (Magnani et al. 1998)	0.045	0	0.281*		0.706
anthropic environmental exposition near asbestos-cement factory (unselected cases)					
Casale Monferrato, Italy (Magnani et al. 1998)	0.006	0	0.004*		0.010
environmental exposition (with pathologies asbestos correlated)					
Corsica (Rey et al. 1993)[1]	21.0	0	0	0	0
Cyprus (Mc Connochie et al. 1987, 1989)[3]	220.0	0	0	0	0

[1] natural environmental exposition to rocks bearing tremolite; [2] general population; [3] anthropic-domestic environmental exposition; *not elsewhere specified
hSV = high Susa Valley - Piedmont, north-western Italy, cow lungs; lSV = low Susa Valley - Piedmont, north-western Italy, cow lungs; LV = Lanzo Valley -Piedmont, north-western Italy, cow lungs; AT = control group, Asti - Piedmont, north-western Italy, cow lungs; gdt = gram of dried tissue

Amphiboles used industrially are also present in the lungs of the general population (i.e., not professionally exposed), because the materials that contain and release asbestos are extremely widespread where humans live (e.g., Churg 1993; Dodson et al. 2000a; Table 6). Nevertheless, their fiber burden is generally much lower than the quantities found in the lungs of those professionally exposed. Also, in the general population, small quantities of other types of asbestos can be present. Crocidolite fibers in significant quantities have been found in the lungs of subjects professionally exposed to it in an almost unique way - crocidolite was used in the manufacture of cigarette filters (Dodson et al. 2002).

Tremolite and actinolite are commonly found in human lungs because they are widespread in the geological environment. The quantities are usually low, except in cases of indirect professional exposure, such as in people working in talc mines (together with anthophyllite asbestos: Hull et al. 2002; Table 6), chrysotile mines (e.g., Churg 1983; Table 6), and dolomite mines (with acicular wollastonite: Selden et al. 2001), where calcic amphiboles are naturally present at trace levels in the deposit. But there are also cases in which the contamination in the ore body is very low, so the same kind of professional activity (chrysotile mine workers) produces a far lower presence of tremolite asbestos in the lungs (e.g., Rees et al. 2001; Table 6). Even so, the amphiboles are very biopersistent, and with continuing exposure, amphiboles accumulate and remain unaltered in the lung. This behavior is different from that of chrysotile fibers; the chrysotile fibers are fragmented at their ends, and to a large extent they start to dissolve much more rapidly than amphiboles (e.g., Gibbons 1998; Bernstein 2005).

The quantity of amphibole present in human lungs through anthropogenic environmental exposure is generally low. However, in particular cases of exposure defined as domestic (i.e., in a household environment), the burden can be very high and comparable to occupational exposure. Tremolite fibers (usually with actinolite in smaller quantities) have been discovered in high quantities in the lungs of residents in Cyprus (McConnochie et al. 1987, 1989; Table 6), Greece (Constantopoulos et al. 1987), Turkey (Yazicioglu et al. 1980), New Caledonia (Luce et al. 1994, 2000; Browne and Wagner 2001), and Afghanistan (Voisin et al. 1994). The presence of abundant quantities of these types of asbestos in lungs has been attributed to anthropogenic environmental exposure (mainly of the domestic kind). These people lived in villages where houses were whitewashed and plastered using materials from local rock deposits that contained tremolite, and where streets were covered with materials containing amphibole asbestos. Interestingly, exposures in Turkey also include the use of baby-powder containing tremolite. Considerable quantities of amphibole asbestos have been seen in the lungs of the inhabitants of some areas in Corsica, France because they live in areas with outcropping rocks bearing a very high quantity of asbestiform tremolite (Magee et al. 1986; Rey et al. 1993; Table 1). However, in the lungs of inhabitants of Basilicata (southern Italy) with similar exposure routes to those in Corsica, lower quantities of these minerals have been found (Pasetto et al. 2004b).

It is common to find amphiboles in the lungs of the general population when they live near asbestos-bearing rock outcrops (e.g., in Piedmont, Belluso et al. 2006b,c; Fornero 2005; Table 6). Table 6 lists the lung burdens of subjects who lived in three different areas of Piedmont with actinolite- and tremolite-bearing rock outcrops and various levels of industrialization: the upper part (hSV) of the Susa Valley, which is industrialized to a limited extent; the lower part (lSV) of the Susa Valley, which is highly developed; and the Lanzo Valley (LV), which is moderately developed. On the basis of the geologic characteristics of these three areas, the presence of two calcic amphiboles is correctly attributable to release from a natural source.

Asbestos fibers of anthophyllite are not frequently found in the lungs because its deposits are not very widespread, occurring in only a few places in the world where it was produced economically. Nevertheless, in Finland, this asbestos has commonly been used (with chrysotile) in the manufacture of insulation materials. Anthophyllite fibers have been detected in construction workers' lungs in variable quantities with crocidolite and lesser quantities of tremolite and amosite (Anttila et al. 1993). Abundant quantities of anthophyllite fibers have been detected in the lungs of talc-mine workers, because anthophyllite is naturally associated with talc (Hull et al. 2002). High and almost equal quantities of anthophyllite and tremolite have been seen in the lungs of workers of an asbestos plant using rocks from chrysotile mines as raw material (Tossavainen et al. 2001). Much higher quantities have been found in an unusual case of mixed-dust exposure of a worker in an iron pipe foundry (Dodson and Levin 2001).

In recent years, in addition to regulated amphibole asbestos species, three other species of amphiboles have been found in human lungs and related to pathologies analogous to those that have traditionally been linked to commercial asbestos exposure. Fibers of an amphibole species recently discovered in Sicily, fluoro-edenite, have been found in the lungs of a subject nonoccupationally exposed to fibrous minerals who lived in an environment contaminated by this kind of fibers (anthropogenic and domestic environmental exposure). This is similar to what happened in Greece with regard to tremolite and actinolite (Paoletti et al. 2000). Winchite and richterite fibers, historically identified as tremolite and occurring in the former vermiculite mine near Libby, Montana (Bandli et al. 2003; Gunter et al. 2003; Meeker et al. 2003), have been detected in high quantities in workers at an expansion plant using vermiculite from this deposit (Wright et al. 2002).

Biomarkers

There exists the possibility of using asbestos biomarkers to determine possible asbestos exposure to an individual human or a human population. (See ATSDR (2006) for a review of the use of asbestos biomarkers.) These can be, for example, agents or their metabolites that in particular conditions are present and detectable in the body. To have an indication of the level of exposure to a contaminant, selective markers of exposure are based on the direct measurement of the chemical substance or its metabolites. Amphibole asbestos particles are altered to only a small extent on inhalation, thus they are suitable for use as biomarkers to evaluate exposure. One kind of exposure assessment is based on counting peculiar biomarkers that are golden brown elongated objects, beaded or segmented, and clearly visible with the light microscope. In 1929, these formations were recognized as structures that had formed around asbestos fibers, and they were named "asbestos bodies" (ABs). Their identification was related to the pathology causing death and attributed to professional exposure to asbestos. Afterward, however, *in vivo* animal experiments observed similar structures forming around inorganic dusts of nonelongated habit (such as cosmetic talc intratracheally instilled into the lungs; Roggli 2004) as well as asbestos, so a new term was used to describe them: pseudoasbestos body (Churg et al. 1979; Roggli 2004). It has now been verified that these bodies form around inorganic fibrous material of any chemical nature whatsoever (e.g., fibers of TiO_2; Bologna et al. 2005) and refractory ceramic fibers (Dumortier at al. 2001)), the generic term "ferruginous bodies" (FB) is preferred when the precise nature of the core is not known (Roggli 2004).

The formation of these structures seems related to the dimensions of the inorganic particle inhaled and deposited in the lung parenchyma. The smallest particles are phagocytized by the macrophages. Fibers with a significantly greater length than the size of the macrophages (whose diameter is about 15-20 μm) are instead covered, partially or totally, by iron-protein-mucopolysaccharide material (Roggli 2004). It seems that this coating can reduce the cytotoxicity of fibers. On the basis of the considerable scientific literature on this subject, it is possible to state that the majority of ferruginous bodies isolated from human lungs and morphologically identifiable as ABs possess an amphibole core (Fig. 30), suggesting a preferential protective mechanism toward these mineralogical species. The amphibole species covered are not limited to the regulated amphiboles, and this would seem logical. Indeed, the study by Paoletti et al. (2000) reports the post-mortem finding of FB with a fluoro-edenite amphibole core in the lung of a subject who lived in Biancavilla.

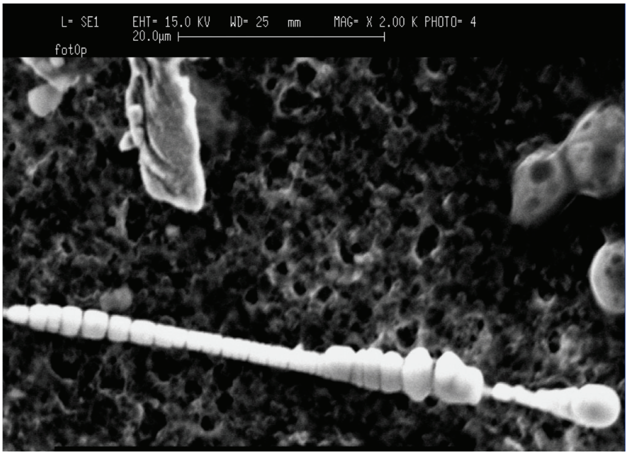


Figure 30. A secondary-electron image of an asbestos body with a tremolite fiber core, extracted from autopsy lung tissue.

FBs are used as biomarkers of internal dose, and specifically as selective biomarkers of exposure, because their presence in the various biological samples in any case indicates exposure to respirable inorganic fibers. If the core is identified as asbestos (and therefore they are true ABs), it follows that the subject has been exposed to asbestos. AB counting in BALF or in lung tissue may be used as a valid biomarker, on condition that the core is undeniably identified as asbestos. The AB quantities internationally established by the International Expert Meeting on Asbestos, Asbestosis and Cancer of Helsinki (Tossavainen 1997) and made official by the European Respiratory Society guidelines exposition (De Vuyst et al. 1998) to indicate high probabilities of professional exposure to asbestos are:

ABs burden in lung tissue more than 1×10^3 / gdt (gram of dried tissue);

ABs burden in lung tissue more than 1×10^2 / gwt (gram of wet tissue);

ABs concentration in the BALF more than 1 / ml.

The AB concentrations in the BALF and in the lungs are correlated (De Vuyst et al. 1998). Knowledge of the AB burden is also useful when the exact type of asbestos exposure is not available. Similarly to the ABs, the concentration of fibers is used as an exposure biomarker. Indeed, their presence in biological material is indicative of exposure. The evaluation of the fiber presence in BALF (e.g., De Vuyst et al. 1997) and in sputum (e.g., McDonald et al. 1992) is more suitable as a qualitative biomarker, while the detection and fiber counts in autopsied or surgically resected lung tissue samples supply more representative data (e.g., Dodson et al. 1999). To determine the effective kind of exposure, it is also possible to use fibers detectable in urine as a biomarker, but this marker does not reflect the quantity accumulated and it is not predictive of health effects.

Generally speaking, high quantities of fibers indicate exposure in an occupational setting. The quantities internationally established by the International Expert Meeting on Asbestos, Asbestosis, and Cancer of Helsinki (Tossavainen 1997) and made official by the European Respiratory Society guidelines exposition (De Vuyst et al. 1998) as indicative of significant asbestos exposure are:

amphibole fiber burden with a length of > 5 µm more than 1×10^5 / gdt,

amphibole fiber burden with a length of > 1 µm more than 1×10^6 / gdt.

Some studies have concluded that AB concentrations over 250 ABs/gdt and chrysotile or tremolite fiber concentrations greater than 1×10^5 / gdt are "robust indicators of mining-area residence" (Case 1994). For an accurate assessment of past asbestos exposure, it is considered that an analysis of the concentration of ABs or asbestos fibers in lung tissue samples may be better than the analysis of BALF or sputum. However, investigations of fiber burden and relation to asbestos exposure are not without difficulties and present both advantages and disadvantages owing to the presence of many variables (ATSDR 2006).

The concentration of retained amphibole asbestos in lung-tissue samples has also been used to try to determine potential dose-response relation for asbestos-induced pathologies and to attribute risk to specific fiber-types and dimension classes. The medical risks are higher in relation to the dimensions of the fibers (the most dangerous fibers are very thin with a high length-width ratio), surface structure and interactions (ion exchange, acid-base catalysis, oxidation-reduction), duration of exposure, quantity of fibers breathed, fiber biodurability, and fiber Fe-content, with the latter being the least important factor (Van Oss et al. 1999; Committee on Asbestos 2006). On the basis of these factors, the pathogenicity of amphibole asbestos seems to be: crocidolite, tremolite asbestos, and amosite (Van Oss et al. 1999).

When discussing biomarkers for asbestos in general, the term "biomarker" means some pathological formation indicating the presence of asbestos-related pathologies, such as the ferruginous bodies described above or pleural plaques as markers of asbestos exposure (e.g., Churg 1983). However more recently, biological alterations, such as differences in modulation in DNA-adduct formation between people exposed to asbestos and those without exposure (Committee on Asbestos 2006), are being used as biomarkers. Even so, to date there is not an ideal biomarker for asbestos (ATSDR 2006).

Amphiboles in animal lungs

After the discovery of the pathogenicity of asbestos in humans, *in vivo* experiments began and continue today on various kinds of animals in an attempt to understand the mechanisms that lead to disease (i.e., where the fibers are deposited in the lung, the fate of the inhaled fibers, biopersistence and clearance, toxicity mechanisms provoked by fibers, comparison between responses to various types of asbestos and other kinds of fibers, etc.). These experiments have also shown the high biopersistence and biodurability of amphibole asbestos in the lungs (e.g., Bernstein et al. 2005) and that chrysotile is much less so (e.g., Hume and Rimstidt 1992). While these experiments provide valuable information for high-dose exposure, comparable to occupational levels, they do not address the question that is more recently become of greater concern - the health effects from long-term, low-dose exposure that occurs in the natural environment. Investigations into this kind of exposure have been done on animal populations, defined as the "animal sentinel system" (ASS), which are exposed to various airborne and potentially toxic pollutants, among which is asbestos, to evaluate their possible health effects. The concept of using animals as sentinel markers is not new: canaries were used for a long time in mines to detect the presence of carbon monoxide (van der Schalie 1999). However, it was much easier to see when the canary died (because it was very susceptible to oxygen level in the mine) than to relate the lung contents of an animal to the health risk of a human.

Regardless, ASS shows some promise because: (1) the reactions of animal bodies to various kinds of exposure are comparable to that of humans; (2) in animals the latency period for the development of some diseases is shorter; and, (3) animals do not have confounders such as possible occupational or paraoccupational exposure or lifestyle (e.g., smoking cigarettes). One limit of ASS is that the anatomy of the respiratory system and the clearance mechanisms are different from humans, and there are anatomical and physiological differences among the various animal species. Therefore, fiber deposition in the lungs does not occur in the same way (Backer et al. 2001). Nevertheless, the advantages of the ASS may be extremely useful for the purposes of the indirect evaluation of the kind and quantity of airborne fibers of breathable dimensions in the environment. For instance, animals in isolated parts of the world could be used to obtain ambient, nonanthropogenic levels of minerals. The animals in question would act as a biological sampler and could be used to map natural environmental risk of asbestos exposure (Belluso et al. 2006b). Pets, especially dogs, are particularly useful in predicting the health risk of their owners. For example, this is the case for dogs who have died of mesothelioma; the dog's pathology permitted the recognition of domestic environmental pollution of high doses of amphibole asbestos (Glickman et al. 1983).

At present, there are very few studies on natural environmental evaluation based on ASS. Moreover, each study has too few animals to obtain a statistically reliable assessment of environmental risk. Tremolite fibers have been detected in the parietal pleura of one dog and two goats that lived in some areas of Corsica where there are outcropping serpentinitic rocks bearing this material (Rey et al. 1993). Comparable results have been obtained from goats that lived in areas contiguous to those described above (Dumortier et al. 2005). The concentrations are lower than those detected in occupationally exposed humans. A recent study reports a high burden of tremolite and actinolite fibers in the lungs of cats and dogs from El Dorado Hills, California (Abraham et al. 2005). Fluoro-edenite fibers have been detected in the lungs of sheep near Biancavilla in Sicily, where this asbestiform amphibole was discovered after the detection of a mesothelioma cluster (De Nardo et al. 2004).

Table 7 shows the tremolite fiber burden in 11 animal groups at three different locations (California, Corsica, Piedmont). Nine groups had environmental exposure to amphibole. The remaining two groups were used as controls because they live in areas where amphiboles do not occur. Fibers of tremolite and actinolite were detected in the lungs of all exposed animals, whereas none were observed in the control groups. The concentrations are low in Italian animals, and from low to high, depending on the zone, in Corsican and Californian animals. Commercial asbestos fibers (amosite and crocidolite) have been detected in the lungs of two groups of

Table 7. Amphibole asbestos fiber burden (ff × 10^6/gdt) in animal lungs.

Location/Group	Tremolite	Actinolite	Anthophyllite	Amosite	Crocidolite
hSV	0.007	0.006	0	0	0
lSV	0.050	0.011	0	0.003	0.002
LV	0.034	0.008	0	0.001	0
SVVC	0.002	0	0	0	0
ATcg	0	0	0	0	0
COa	0.405	0	0	0	0
COb	3.350	0	0	0	0
COc	0.141	0	0	0	0
CAa	0.121		0	0	0
CAb	2.976		0	0	0
CAcg	0		0	0	0

hSV = High Susa Valley - Piedmont, north-western Italy, cow lungs (Belluso et al. 2006b,c)
lSV = Low Susa Valley - Piedmont, north-western Italy, cow lungs (Belluso et al. 2006b,c)
LV = Lanzo Valley -Piedmont, north-western Italy, cow lungs (Belluso et al, 2006b,c)
SVVC = Sesia Valley Vercelli - Piedmont, north-western Italy, cow lungs (Battaglia 2006)
ATcg = control group, Asti - Piedmont, north-western Italy, cow lungs (Belluso et al. 2006b,c)
COa = north-eastern Corsica, dog parietal pleural (Rey et al. 1993)
COb = north-eastern Corsica, goats parietal pleural (Rey et al. 1993)
COc = north-eastern Corsica, goat lungs (Dumortier et al. 2005)
CAa = El Dorado, California, cat lung (Abraham et al. 2005)
CAb = El Dorado, California, dog lung (Abraham et al. 2005)
CAcg = control group, California, cat lung (Abraham et al. 2005)
gdt = gram of dried tissue

animals from Italy (Piedmont Region). Their presence is compatible with the considerable industrialization of the area and the use of asbestos containing materials.

Amphiboles in human urine

Once the possibility of detecting amphibole asbestos fibers in the urine (Cook and Olson 1979) was verified, the few studies done since then have shown that the quantity of fibers expelled with urine is not related to the concentration of fibers present in the air or in the ingested drinking water (Boatman et al. 1983; Finn and Hallenbeck 1985). Nevertheless, it is evident that the presence and concentrations of asbestos in urine can be used as biomarkers of exposure both for individuals occupationally exposed and the general public. Indeed, high concentrations are indicative of exposure to high doses, while low quantities are indicative of normal environmental exposure, like those found in the general population. However, the presence of asbestos fibers in urine is only an indicator of recent exposure, from a few days to a few months before the sample was taken (Cook and Olson 1979; ATSDR 2006). This is because the fibers enter the digestive system as they are rapidly cleared from the respiratory system, and the residence time in the digestive system is short. The detection of fibers in urine is therefore not suitable for biomonitoring of chronic exposure to asbestos, but it is particularly useful for monitoring, almost "in real time," the presence of respirable fibers. These data enable evaluation of both environmental background of fibers and those from anthropogenic sources. Also for these investigations, the distinction between natural and anthropogenic source for the detected fibers may be made when knowledge is available about the minerals of the local geological environment.

Table 8 shows the types and quantities of amphibole fibers detected in the urine of people living in five areas of the Piedmont Region of northwestern Italy. Four of the areas have rock outcrops bearing tremolite and actinolite, and have various levels of industrialization. The areas have been divided into the upper part (HSV, not very industrialized), the lower part (lSV, very highly industrialized), the Lanzo Valley (LV, moderate industrialization), and the Sesia Valley (SVVC), a mountain area with low industrialization and few rocks bearing tremolite and actinolite. The latter is a control group from an area in which tremolite and actinolite are geologically lacking.

The data are shown as the number of fibers per 1 cc (ff/1 cc), the internationally accepted unit system, to indicate the urine-fiber concentration for inter-laboratory comparison. Asbestos fibers classifiable as from the natural source (i.e., tremolite and actinolite) have been detected in two areas, and their quantity is higher than in the control group (ATcg). This result shows that the subjects have been exposed to these fibers, that these fibers were airborne, and that their quantity is higher than in the control area. Changes in exposure can be evaluated only if the tests are repeated for the same area at regular intervals. The fact that other types of fibers have

Table 8. Types and quantities (ff/1 cc) of amphibole fibers detected in the urine of people living in five areas of the Piedmont Region of northwestern Italy.

<table>
<tr><th>Location/Group</th><th>Tremolite</th><th>Actinolite</th><th>Anthophyllite</th><th>Amosite</th><th>Crocidolite</th></tr>
<tr><td>hSV</td><td>2.7</td><td>0</td><td>0</td><td>0</td><td>0</td></tr>
<tr><td>lSV</td><td>1.6</td><td>0</td><td>0</td><td>0</td><td>0</td></tr>
<tr><td>LV</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td></tr>
<tr><td>SVVC</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td></tr>
<tr><td>ATcg</td><td colspan="2">1</td><td>0</td><td>0</td><td>0</td></tr>
</table>

hSV = High Susa Valley - Piedmont, north-western Italy (Belluso et al. 2006b,c)
lSV = Low Susa Valley - Piedmont, north-western Italy (Belluso et al. 2006b,c)
LV = Lanzo Valley -Piedmont, north-western Italy (Belluso et al. 2006b,c)
SVVC = Sesia Valley Vercelli - Piedmont, north-western Italy (Battaglia 2006)
ATcg = control group, Asti - Piedmont, north-western Italy (Belluso et al. 2006b,c)

not been detected in these samples cannot be interpreted as their absence in the environment. To have more certain data, more sampling tests are needed. Also, it is necessary to consider what minerals might dissolve in the low pH environment of the stomach.

Conclusion for humans and animals

Today, nearly all scientific papers on the identification of pathologies and pathological symptoms (e.g., pleural plaques) attribute their formation to fibrous species to which the subject has been exposed in his or her living or working environment - without any research into mineral identification and quantification of fibers in the tissues involved. This failure may give rise to assessment errors in the medical investigations (and some medical researchers like Governa et al. 2006, have begun to consider it important) and certainly does not supply any information about the quantity of fibers, per individual species, that were inhaled and biopersisted. The quantity of airborne fibers that may be inhaled and respired from the environment of the various areas has not been assessed. Therefore, information about the fibrous respirable fraction constituting the environmental background of various areas of the world is not known, and neither is the amount of fibers that have been placed into the air by human activities.

In the attempt to understand whether it is possible to approximately quantify an accumulation *threshold value* above which clearance is no longer active and cancer pathologies develop for these types of asbestos, it may be useful: (1) to examine the mineralogical burden of human lungs for nonoccupational individuals and the lungs of animals that lived in areas with outcropping rocks bearing crocidolite and amosite asbestos (this investigation would provide the natural background of respirable asbestos fibers, for these areas, as well as the other minerals that occur in the lungs), and (2) to compare the values of the local natural background with the asbestos fiber burden in the lungs of subjects occupationally exposed to this type of asbestos and of those who died of mesothelioma (Belluso et al. 2005).

For a correct evaluation of the amphibole (and also chrysotile) asbestos risk for each area of interest, the following procedures are necessary:

1. Investigation and identification of the mineral fibers that may be present in the outcropping rocks and soils;
2. Environmental-background evaluation, including mineralogical studies of the type, quantity, and dimensions of airborne fibers and the distinction between asbestos from natural and from anthropogenic sources;
3. Assessment of the mineralogical burden in ASS to determine the respirable fraction of amphibole fibers present in the environmental background;
4. Assessment of the mineralogical burden in the lungs of people with asbestos-related pathologies who lived or are living in these areas.

In the areas assessed as being of amphibole asbestos risk by these investigations, periodic investigation of and identification of mineral fibers in urine would enable the environmental situation to be monitored almost in "real time" and, when necessary, it would make it possible to activate suitable measures of medical prevention. In the areas where the mineralogical investigations have shown the presence (in the outcropping rocks) of noncommercial asbestos (e.g., tremolite and actinolite) and the anemometric characteristics exclude transportation of these from other areas, the above-mentioned types of asbestos can be used as biomarkers of natural environmental exposure insofar as it is airborne from a natural source.

STABILITY OF AMPHIBOLES

It comes as no surprise to the geological community that amphiboles can and do alter in the geological environment to other minerals. However, this often comes as a major surprise to those outside of our community. For example, once when mentioned that an amphibole can convert to a pyroxene by heating, non-geological colleagues commonly insist that it is a mineral and will not change! However, in the fields relating to amphiboles many geologists would think about amphibole stability in terms of varying metamorphic conditions (i.e., that is to say the formation of amphiboles during metamorphic events), while others would think of their stability during formation in igneous rocks and yet others their occurrence in sediments. What we would like to do in this section is to turn our attention to the formation of amphiboles from other minerals or the alteration of amphiboles into other minerals that may occur in the arena of human exposures or the human body itself.

Temperature conversions

It is well known in the geological community that amphibole will convert to pyroxene with increasing temperature. Figure 31 shows two powder X-ray diffraction patterns: one of an unheated sample of amphibole from Libby, Montana, and the other of the same sample heated to 1,000 °C for 10 minutes. Note that the amphibole peaks have disappeared and have been replaced by pyroxene peaks. Thus in any industrial setting where temperatures were above approximately 900 °C, the amphibole could convert to pyroxene if the kinetics of reaction were fast enough. Based on our knowledge of geologic conditions, we can predict when some of these conditions will occur, and then verify them experimentally. These temperature conversions could be significant for the Libby amphiboles in two separate conditions: (1) during the expansion

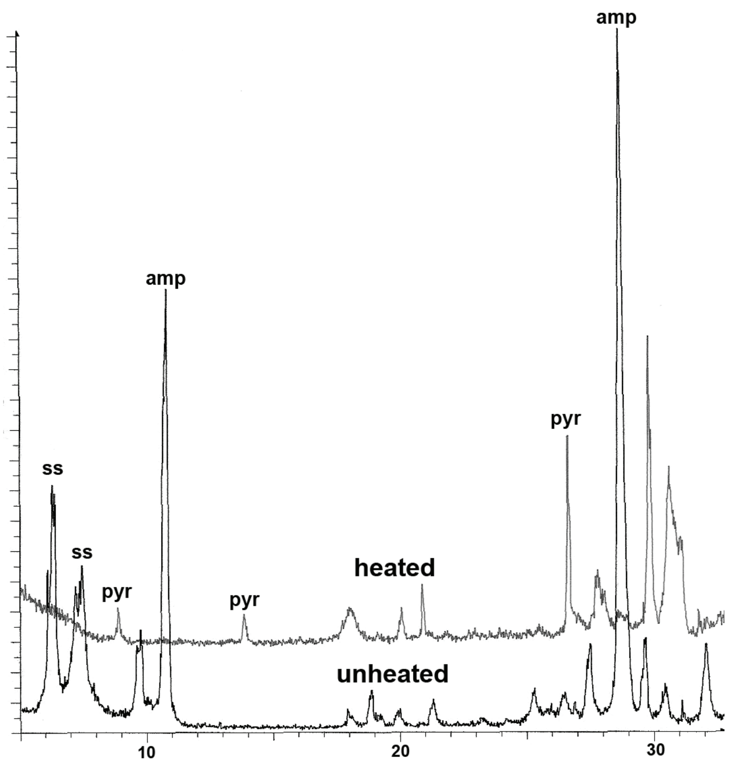


Figure 31. The lower powder diffraction pattern is of an amphibole (amp) sample from Libby that contains some sheet silicates (ss). The upper pattern is of the same sample after heating for 10 minutes at 1,000 °C; note how the amphibole has converted to pyroxene (pyr).

process (popping) of the Libby vermiculite during which the samples are heated to over 1,000 °C for a few seconds; (2) in a woodstove in which temperature can reach upwards of 900 °C. The issue here is that fibers of amphibole have been found in the bark of trees near Libby and burning this wood might disperse the fibers. Even though (to our knowledge) no converted amphiboles have been found in either setting, it is this sort of thought process that the geological community needs to make more widely known to the regulatory and health communities.

In the lung

The conditions in the human lung are somewhat similar to the conditions at the surface of the Earth: 37 °C with pH 7.35, and lung fluid has a known composition. Thus we can use our knowledge of mineral reactions on the surface of the Earth to help understand mineral reactions in the lung. The impetus for this line of research comes from basic observations of the mineral content of chrysotile-asbestos workers on autopsy. It was noted by Wagner et al. (1987) that the chrysotile-miners' lung loads are typically very high in tremolite with only a low content of chrysotile. However, Figures 9 and 10 show that the amphibole content of these ores is very small (i.e., <1%). In Wagner's study, they said that they could find no tremolite in chrysotile ores from Canada unless they put the material into a rat lung and waited for six months. Clearly, something happens to the chrysotile:tremolite ratio in the lung. Based upon the work of several researchers (e.g., Hume and Rimstidt 1992), chrysotile dissolves in the lung at a fairly rapid rate. Thus we are seeing the chemical weathering (i.e., dissolution) of a mineral in the lung in a manner similar to that at the Earth's surface. Figure 32 shows calculations for a mixture of quartz, tremolite, and chrysotile in lung fluid (Wood et al. 2006). The diagram shows that quartz does not dissolve, and that tremolite starts to dissolve (but only after a long period of time), and chrysotile dissolves in less than one year. Interestingly, two other minerals form: dolomite and hydroxylapatite. Dolomite forms as chrysotile dissolves, whereas hydroxylapatite appears to form at the expense of none of the dissolving minerals. This makes sense from a human physiology perspective in that a body is in near equilibrium with hydroxylapatite. As part of our ongoing research, we are attempting to model more mineral reactions in the lungs and to study materials that occur in the lung. Figure 33 shows a large solid particle with the approximate chemical formula of hydroxylapatite observed in autopsied lung tissue. This particle could not have been respired because it is too large; thus, it grew in place in the lung.

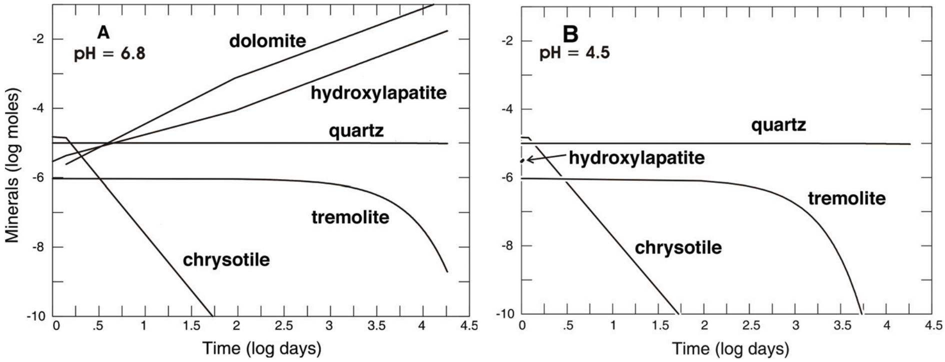


Figure 32. Two calculated reaction paths for a mixture of chrysotile, tremolite, and quartz placed in a simulated lung fluid at 37 °C and pH = 6.8 (A) and pH = 4.5 (B), the former representing lung fluid and the latter representing lysosome fluid in a macrophage. In both cases, chrysotile dissolves in about 60 days, while quartz is stable. Tremolite starts to dissolve in about eight years (A) and six years (B). Also note that hydrolxyapatite forms under both pH conditions, but remains only in the higher pH run (modified from Wood et al. 2006).

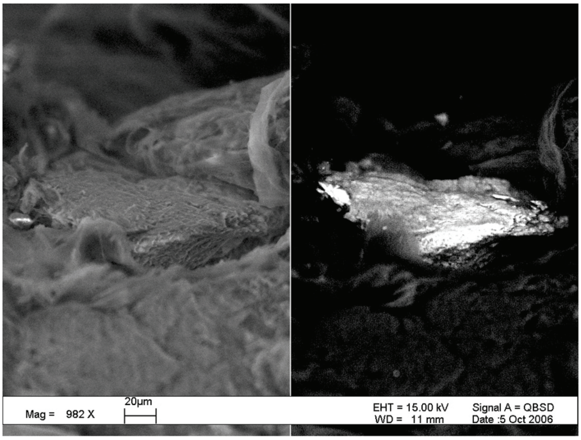


Figure 33. FESEM images of a lung tissue sample of a human pleural plaque, post autopsy. The particle in (A) is almost 100 µm long, too big to be respired; it formed in the lung. B) A backscattered-electron image of the same particle.

Based on previous discussion, we know that minerals may: (1) persist in the lung (i.e., quartz), (2) dissolve (i.e., chrysotile), or (3) form (e.g., hydroxylapatite). A fourth possibility is one mineral could alter to another mineral; this occurs often in the geological environment. Our original idea that sent us down the research path for calculating mineral stabilities in the lung, was the possibility that chrysotile might alter to tremolite; this would help explain the large amounts of tremolite in the lungs of chrysotile miners. Preliminary calculations indicated this transformation might occur (Taunton et al. 2002) whereas later more refined calculations indicate that it will not occur (Wood et al. 2006). However, this does not preclude the possibility of other mineral reactions occurring in the lung. Along with our calculations, we have also placed chrysotile ore in simulated lung fluid. To date, these experiments are only of one-year duration, and we have seen no conversion of chrysotile to tremolite. However, we have seen formation of hydroxylapatite as predicted from the calculations.

FUTURE AREAS OF RESEARCH

What seems like the most important issue for the mineralogical community is to assist the regulatory community in distinguishing between fibers and fragments of amphiboles. However, the single most important area for future research is to determine if there are significant differences between the health effects of fibers and fragments of amphiboles. To do this will require collaborative efforts between mineralogists and the medical community for both *in vivo* and *in vitro* experiments. Probably the largest single role of the mineralogy community will be to provide well-characterized suites of these samples to the medical community [e.g., the preliminary work of Bellamy and Gunter (2006) on the Libby material and more thorough studies of Guthrie (1992, 1997) which reviewed several mineral groups]. Another major contribution for mineralogists and geochemists is to predict how minerals behave in the lung by modeling the lung as a low-temperature aqueous system (see the recent work of Taunton et al. 2002, Plumlee et al. 2006, Wood et al. 2006 for examples).

Other major contributions from the geologic community would be to help determine environmental exposure to minerals based on dust sampling, geological mapping, and integrated epidemiological studies. For example, Norton and Gunter (1999) examined the relation between respiratory disease and quartz content of dust in Idaho. Such studies go in concert with the recommendations made at the end of the section on amphiboles in biological materials. Currently in California, Pan et al. (2005) proposed a relation between mesothelioma and proximity to ultramafic rock bodies. More of these types of studies are needed to confirm or disprove these types of geological relations. Also, the geologic community can aid in educating the public and teaching students on the risks associated with exposure to minerals in the environment. One example of this was discussed by Gunter (1994) using the general issues of asbestos, another by Gunter (1999) for issues dealing with quartz as a "known human carcinogen." A classroom exercise is given by Taunton and Gunter (2007) for correlation (or lack thereof) of lung cancer and breast cancer with geologic maps.

There are many areas outside the fields of Mineralogy and Geochemistry that are in need of more research. One of the main areas is in the determination of other causes of mesothelioma. Recently, Dogan et al. (2006) showed that mesothelioma cases caused by erionite in Turkey is also related to genetics. It seems that there is a genetic predisposition for those who succumb to the disease if the parents also had the disease (Dogan et al. 2006). There is still another concern that SV-40 may be a cofactor causing mesothelioma (Baldi et al. 2001). As we have seen in this chapter, the mesothelioma rate in Italy is increasing; can this increase be related solely to amphibole-asbestos exposure?

SUMMARY

Throughout history, humans have been exposed to dust. Yet for all such dust exposure, the case of asbestos has received the most attention, probably because more people have been afflicted with asbestos-related disease than for any other mineral. Why is this? Clearly, the dose is the most important single criteria for contracting a disease. Increased dose resulting from asbestos exposure might relate to the fact that asbestos fibers are very small and, in turn, more respirable than other minerals. Thus the property of asbestos, becoming thinner and thinner as it is mined and processed, will cause it to produce many more respirable particles than any other mineral (i.e., the asbestiform habit lends itself to producing very small particles with only a minimum amount of applied force). The fact that asbestos minerals may be the only minerals in Nature that can easily be reduced to respirable size, coupled with high doses of these minerals for workers and the fact that the asbestos minerals are more biopersistent than other minerals such as calcite, might explain why workers suffer from asbestos-related diseases.

Four concluding points on the discussion of human health, environmental concerns, and amphiboles are: (1) the health impact of inhalation of amphibole asbestos is worse than that of chrysotile asbestos, (2) occupational exposure to amphibole asbestos is much more harmful than nonoccupational exposure to amphibole asbestos, (3) it is not clear whether low-level environmental exposure to amphibole is a significant health risk, and (4) there is still considerable research needed to understand how minerals behave in the lung. Also, in the USA, there needs to be a coming together of the different groups (i.e., mineralogist, geochemist, geologist, medical, legal, regulatory, and industrial communities) to try and educate the public to reduce the fear of exposure to minerals in their natural environment.

ACKNOWLEDGMENTS

MEG would like to thank his past students who have worked with him in this area, as well as Nicole Bellino for her efforts in assisting with the references and formatting of this chapter, and Anne Taunton for reading and editing an earlier draft. EB would like to thank pathologist Donata Bellis, collaborator Silvana Capella, and Professor Giovanni Ferraris for useful medical information, data to build tables, and critical incitement respectively. AM would like to thank his student F. de Grisogono for his assistance in preparing this chapter. Last we would like to thank Frank Hawthorne for a meticulous job of editing this chapter, and Jodi Rosso for the wonderful layout of this chapter and its many figures.

REFERENCES

Abraham JL, Case BW, Burnett BR, Trent T (2005) Lung-retained fiber in pets confirms environmental exposure to naturally-occurring asbestos in Western El Dorado County, California. Proc Am Thoracic Soc 2:A818

Abrahams PW (2002) Soils: their implications to human health. Sci Tot Environ 291:1-32

Addison J, Davies LST (1990) Analysis of amphibole asbestos in chrysotile and other minerals. Ann Occup Hygiene 34:159-175

Ahn JH, Buseck PR (1991) Microstructures and fiber formation mechanisms of crocidolite asbestos. Am Mineral 76:1467-1478

Amandus HE, Wheeler R (1987) The morbidity and mortality of vermiculite miners and millers exposed to tremolite-actinolite: Part II. Mortality. Am J Ind Med 11:15-26

Amandus HE, Wheeler R, Jankovic J, Tucker J (1987a) The morbidity and mortality of vermiculite miners and millers exposed to tremolite-actinolite: Part I. Exposure estimates. Am J Ind Med 11:1-14

Amandus HE, Althouse R, Morgan WKC, Sargent EN, Jones R (1987b) The morbidity and mortality of vermiculite miners and millers exposed to tremolite-actinolite: Part III. Radiographic findings. Am J Ind Med 11:27-37

Anttila S, Karjalainen A, Taikin-Aho O, Kyyrönen P, Vainio H (1993) Lung cancer in the lower lobe is associated with pulmonary asbestos fiber count and fiber size. Environ Health Perspect 101:166-170

Atkinson GR, Rose D, Thomas K, Jones D, Chatfield E, Going J (1982) Collection, analysis and characterization of vermiculite samples for fiber content and asbestos contamination. Midwest Research Institute Report to EPA, Project 4901-A32, Contract No 68-01-5915, Washington DC

ATSDR (2000) Health consultation, Libby asbestos site, Libby, Lincoln County, Montana. Mortality from asbestosis in Libby, Montana, 1979-1998, December 12, 2000. Agency for Toxic Substances and Disease Registry, Atlanta, Georgia

ATSDR (2001) Medical testing of individuals potentially exposed to asbestiform minerals associated with vermiculite in Libby, Montana. A report to the community. Division of Health Studies, US Dep of Health and Human Services, Atlanta, Georgia

ATSDR (2006) Report on the expert panel on biomarkers of asbestos exposure and disease. ERG contract 2006

Attanos RL, Gibbs AR (2000) Primary malignant gonadal mesotheliomas and asbestos. Histopathol 37:150-159

Backer LC, Grindem CB, Corbett WT, Cullins L, Unter JL (2001) Pet dogs as sentinels for environmental contamination. Sci Total Environ 274:61-169

Baldi F, Baldi A, Giordano G, Giordano A (2001) p53 and the retinoblastoma gene family in human mesothelioma: the SV40 hypothesis. *In:* The Health Effects of Chrysotile Asbestos. Can Mineral Spec Publ 5:141-144

Bandli BR, Gunter ME (2001) Identification and characterization of mineral and asbestos particles using the spindle stage and the scanning electron microscope: The Libby, Montana, USA. amphibole-asbestos as an example. The Microscope 49:191-199

Bandli BR, Gunter ME (2006) A review of scientific literature examining the mining history, geology, mineralogy, and amphibole asbestos health effects of the Rainy Creek Igneous Complex, Libby, Montana USA. Inhal Toxicl 18:949-962

Bandli BR, Gunter ME, Twamley B, Foit FF Jr, Cornelius SB (2003) Optical, compositional, morphological, and X-ray data on eleven particles of amphibole from Libby, Montana, USA. Can Mineral 41:1241-1253

Battaglia T (2006) Valutazione indiretta dell'inquinamento ambientale da amianto e fibre asbestiformi nel territorio della Valsesia tramite indagine di campioni biologici animali, Report, Torino University

Battaglia T, Belluso E, Capella S, Fornero E, Ferraris G, Bellis D, Biagini G, Pugnaloni A, Panico AM, Cardile V (2005) Monitoring of respirable mineral fibres in the Biancavilla area (Sicily) by SEM-EDS analysis of urine. *In:* Proc Int Conf Asbestos Monitoring and Analytical Methods, p 68-69

Bellamy JM, Gunter ME (2006) Morphological characterization of amphiboles used in *in vivo* studies. Geological Society of America Abstracts with Programs, vol. 38, #7, p 366

Belluso E, Bellis D, Fornero E, Capella S, Ferraris G, Coverlizza S (2006a) Assessment of inorganic fibres burden in biological samples by SEM-EDS. Microc Acta 155:95-100, doi:10.1007/s00604-006-0524-y

Belluso E, Bellis D, Bruni BM, Capella S, Coverlizza S, Ferraris G, Fornero E, Paoletti E, Rinaudo C (2006b) Studio preliminare sulla valutazione indiretta delle fibre inorganiche respirabili aerodisperse in Valle di Susa (Piemonte – Alpi Occidentali). Rend Soc Geol Ital 3:41-45

Belluso E, Bellis D, Capella S, Fornero E, Battaglia T, Rinaudo C, Coverlizza S, Ferraris G, Pelissero F, Rey C, Benedetto F, Colzani A, Curti PC, Gobetto M, Graziano E (2006c) Indirect assessment of breathable inorganic fibres by sentinel animals of Piedmont areas (N-W Italy). *In:* Proc Int Conf Asbestos Monitoring and Analytical Methods, p 209

Belluso E, Compagnoni R, Ferraris G (1994) Occurrence of asbestiform minerals in the serpentinites of the Piemonte Zone, Western Alps. *In:* Giornata di studio in ricordo del Prof. Stefano Zucchetti, Politecnico di Torino (ed), p 57-64

Belluso E, Ferraris G, Alberico A (1997) Amianto, la componente ambientale: dove, quali e come sono gli amianti nelle Alpi Occidentali? *In:* L'amianto: dall'ambiente di lavoro all'ambiente di vita. Nuovi indicatori per futuri effetti. Minoia C, Scansetti G, Piolatto G, Massola A (eds) Fondazione Salvatore Maugeri, IRCCS, Pavia 1997 - I Documenti 12, p 167-174

Bernstein DM (2005) Understanding chrysotile asbestos: a new perspective based upon current data. *In:* Proc IOHA 2005 Pilanesberg, J3:1-10

Bernstein DM, Rogers R, Smith P (2005) The biopersistence of Canadian chrysotile asbestos following inhalation. Final results through 1 year after cessation of exposure. Inhal Toxicol 17:1-14

Boatman ES, Merril T, O'Neill A, Polissar L, Millette JR (1983) Use of quantitative analysis of urine to assess exposure to asbestos fibers in drinking water in the Puget sound region. Environ Health Perspect 53:131-139

Boettcher AL (1967) The Rainy Creek alkaline-ultramafic igneous complex near Libby, Montana. I: Ultramafic rocks and fenite, J Geol 75:526-553

Bologna L, Ferri A, Lauria E, Wojtowicz M (2005) The necessity of SEM analysis in outdoor environment monitoring of airborne asbestos fibres. *In:* Proc Int Conf Asbestos Monitoring and Analytical Methods, p 22-23

Brown BM, Gunter ME (2003) Morphological and optical characterization of amphiboles from Libby, Montana USA, by spindle stage assisted polarized light microscopy. The Microscope 51:121-140

Browne K, Wagner JC (2001) Environmental exposure to amphibole-asbestos and mesothelioma. *In:* The health effects of chrysotile asbestos. Contributions of Science to Risk-Management Decisions, Nolan RP, Langer AM, Ross M, Wicks FJ, Martin RF (eds) Can Mineral Special Pub 5:21-28

Burragato F, Comba P, Baiocchi V, Palladino DM, Simei S, Gianfagna A, Paletti, Pasetto R (2005) Geo-volcanological, mineralogical and environmental aspects of quarry materials related to pleural neoplasm in the area of Biancavilla, Mount Etna (Eastern Sicily, Italy). Environ Geol 47:855-868

Burragato F, Crispino M, Montangano G, Monti A, Monti F, Papacchini L, Rossigni F, Schettino B, Sperduto B (2006) Environmental pollution from airborne asbestiform fibres: development of fibre propagation maps. Abstracts of the European Conference on Asbestos Risks and Management, p 85-90

Case BW (1991) Health effects of tremolite. *In:* The third wave of asbestos disease: Exposure to asbestos in place. Landrigan PJ, Kazemi H (eds) Annals of the New York Academy of Sciences 643:491-504

Case BW (1994) Biological indicators of chrysotile exposure. Ann Occup Hyg 38:503-518

CDPHE: Colorado Department of Public Health and Environment (2006) Asbestos-contaminated soil. Guidance document. Hazardous Materials and Waste Management Division, Colorado Dept. of Public Health and Environment (303) 692-3300

Clark RN, Hoefen TM, Sawyze GA, Livo KE, Meeker GP, Sutley S, Wilson S, Brownfield I, Vance JS (2003) Reflectance spectroscopy as a rapid assessment tool for the detection of amphiboles from the Libby, Montana region. USGS OFR 03-128.

Churg A (1983) Asbestos fiber content of the lungs in patients with and without asbestos airways disease. Am Rev Respir Dis 127:470-473

Churg A (1993) Asbestos lung patterns and disease patterns in man. Rev Mineral 28:410-426

Churg A, Warnock ML, Green N (1979) Analysis of the cores of ferruginous (asbestos) bodies from the general population: II. True asbestos bodies and pseudoasbestos bodies. Lab Invest 40:31-38

Comba P, Gianfagna A, Paoletti L (2003) The pleural mesothelioma cases in Biancavilla are related to the new fibrous amphibole fluoro-edenite. Arch Environ Health 58:229-232

Comba P, Merler E, Pasetto R (2005) Asbestos-related diseases in Italy: Epidemiologic evidences and public health issues. Int J Occup Environ Health 11:36-44

Committee on Asbestos (2006) Asbestos: selected cancers. Institute of Medicine, The National Academies Press, Washington, DC

Constantopoulos SH, Saratzis N, Kontogiannis D, Karantanas A, Goudevenos JA, Katsiotis P (1987) Tremolite whitewashing and pleural calcifications. Chest 92:709-712

Cook PM, Olson GF (1979) Ingested mineral fibers: elimination in human urine. Science 294:195-198

Davis JMG, Addison J, McIntosh C, Miller BG, Niven K (1991) Variations in the carcinogenicity of tremolite dust samples of differing morphology. *In:* The third wave of asbestos disease: Exposure to asbestos in place. Landrigan PJ, Kazemi H (eds) Annals of the New York Academy of Sciences 643:473-490

De Nardo P, Bruni B, Paoletti L, Pasetto R, Sirianni B (2004) Pulmonary fibre burden in sheep living in the Biancavilla area (Sicily): preliminary results. Science Tot Environ 325:51-58

De Rita D, Frazzetta G, Romano R (1991) The Biancavilla–Montalto ignimbrite (Etna, Sicily). Bull Volcanol 53:121-131

De Vuyst P, Dumortier P, Gevenois PA (1997) Analysis of asbestos bodies in BAL from subjects with particular exposures. Am J Ind Med 31:699-704

De Vuyst P, Karjalainen A, Dumortier P, Pairon JC, Monso E, Brochard P, Teschelr H, Tossavainen A, Gibs A (1998) Guidelines for mineral fibre analyses in biological samples: report of the ERS Working Group. Eur Respir J 11:1416-1426

Dodson RF, Graef R, Shepherd S, O'Sullivan M, Levin J (2005) Asbestos burden in cases of mesothelioma from individuals from various regions of the United States. Ultrastructural Pathology 29:415-433
Dodson RF, Levin JL (2001) An unusual case of mixed-dust exposure involving a "non commercial" asbestos. Environ Health Perspect 109:199-203
Dodson RF, O'Sullivan M, Huang J, Holiday DB, Hammer SP (2000a) Asbestos in extrapulmonary sites Omentum and mesentery. Chest 117:486-493
Dodson RF, Huang J, Bruce JR (2000b) Asbestos content in the lymph nodes of nonoccupationally exposed individuals. Am J Ind Med 37:169-174
Dodson RF, Williams MG, Huang J, Bruce JR (1999) Tissue burden of asbestos in nonoccupationally exposed individuals from East Texas. Am J Ind Med 35:281-286
Dodson RF, Williams MG, Satterley JD (2002) Asbestos burden in two cases of mesothelioma where the work history included manufacturing of cigarette filters. J Toxic Environ Health Part A 65:1109-1120
Dogan AU, Baris YI, Dogan M, Emri S, Steele I, Elmishad AG, Carbone M (2006) Genetic predisposition to fiber carcinogenesis causes a mesothelioma epidemic in Turkey. Cancer Res 66:1-6
Dorling M, Zussman J (1987) Characteristics of asbestiform and non-asbestiform calcic amphiboles. Lithos 20:469-489
Dumortier P, Göcmen A, Laurent K, Manço A, De Vuyst P (2001) The role of environmental and occupational exposures in Turkish immigrants with fibre-related disease. Eur Resp J 17:922-927
Dumortier P, Rey F, Viallat JR, Broucke I, Boutin C, De Vuyst P (2005) Chrysotile and tremolite asbestos fibres in the lungs and parietal pleura of Corsican goats. Occup Environ Med 59:643-646
Dusek CJ, Yetman JM (2002) Control and prevention of asbestos exposure from construction in naturally occurring asbestos: Fairfax County Health Department, Fairfax, Virginia, 6, *http://www.co.fairfax.va.us/service/hd/docs/TBRDPUBFIN.doc*
Ecology and Environment (2005) El Dorado Hills naturally occurring asbestos multimedia exposure assessment, El Dorado Hills, California: Preliminary assessment and site inspection report, Interim final, Contract No. 68-W-01-012
Fano V, Cernigliaro A, Scondotto S, Pollina Addario S, Caruso S, Mira A, Forastiere F, Perucci CA (2005) Stato di salute della popolazione residente nelle aree ad elevato rischio ambientale e nei siti di interesse nazionale della Sicilia. ESA Regione Sicilia, Dipartimento di Epidemiologia, ASL RME, Palermo p 118
Finn MB, Hallenbeck WH (1985) Detection of chrysotile in workers' urine. Ann Ind Hyg Ass J 46:162-169
Fitzgerald JK (2006) WR Grace vs Debtors. Bankruptcy No. 01-011139 (JKF)
Fornero E (2005) Asbestos hazard in Western Alps. Mineral burden investigation in humans and animals to assess the environmental exposure in the Susa and Lanzo Valleys. PhD thesis, Università degli Studi di Torino, Torino
Gianfagna A, Andreozzi GB, Ballirano P, Mazziotti-Tagliani S, Bruni BM (2007) Structural and chemical contrasts between prismatic and fibrous fluoro-edenite from Biancavilla, Sicily, Italy. Can Mineral 45:249-262
Gianfagna A, Ballirano P, Bellatreccia F, Bruni B, Paoletti L, Oberti R (2003) Characterization of amphibole fibres linked to mesothelioma in the area of Biancavilla, Eastern Sicily, Italy. Mineral Mag 67:1221-1229
Gianfagna A, Oberti R (2001) Fluoro-edenite from Biancavilla (Catania, Sicily, Italy): crystal chemistry of a new amphibole end-member. Am Mineral 86:1489-1493
Gibbons W (1998) The exploitation and environmental legacy of amphibole asbestos: a late 20th century overview. Environ Geochem Health 20:213-230
Gibbs AR, Gardner MJ, Pooley FD, Griffiths DM, Blight B, Wagner JC (1994) Fiber levels and disease in workers from a factory predominantly using amosite. Environ Health Perspect Suppl 102:261-263
Gillot PY, Kieffer G, Romano R (1994) The evolution of Mount Etna in the light of potassium-argon dating. Acta Vulcanol 5:81-87
Glickman LT, Domanski LM, Maguire TG, Dubielzig RR, Churg A (1983) Mesothelioma in pet dogs associated with exposure of their owners to asbestos. Environ Res 32:305-313
Governa M, Amati M, Bellis D, Bichisecchi E, Santarelli L (2006) Diagnosis of asbestos-related pleuropolmonary diseases. Med Lav 97:463-474
Griffits H, Malony NC (2003) Does asbestos cause laryngeal cancer? Clin Otolaryngol 28:177-182
Gunter ME (1994) Asbestos as a metaphor for teaching risk perception. J Geol Ed 42:17-24
Gunter ME (1999) Quartz - the most abundant mineral species in the earth's crust and a human carcinogen? J Geol Ed 47:341-349
Gunter ME, Dyar MD, Twamley B, Foit FF, Cornelius S (2003) Composition, $Fe^{3+}/\Sigma Fe$, and crystal structure of non-asbestiform and asbestiform amphiboles from Libby, Montana, USA. Am Mineral 88:1970-1978
Gunter ME, Lee RJ (2006) And we thought all minerals were naturally occurring: The need for a rational public policy dealing with so-called naturally occurring asbestos. Geological Society of America Abstracts with Programs, vol. 38, #7, p 123

Gunter ME, Singleton E, Bandli BR, Lowers, HA, Meeker GP (2005) Differentiation of commercial vermiculite based on statistical analysis of bulk chemical data: Fingerprinting vermiculite from Libby, Montana USA. Am Mineral 90:749-754

Gunter ME, Williams TJ, Sanchez MS, Harris KE, Bunker KL, Wyss RK, Lee RJ (2006) Amphiboles between the sheets: An interesting occurrence with even more interesting morphologies. Geological Society of America Abstracts with Programs, vol. 38, #7, p 114

Gunter ME, Sanchez MS, Williams TJ (2007) Characterization of chrysotile samples for the presence of amphiboles: the Carey Canadian deposit, southeastern Quebec, Canada. Can Mineral 45:263-280

Guthrie GD Jr (1992) Biological effects of inhaled minerals. Am Mineral 77:225-243

Guthrie GD Jr (1993) Mineralogical characterization in biological studies. Rev Mineral 28:251-274

Guthrie GD Jr (1997) Mineral properties and their contributions to particle toxicity. Environ Health Perspect 105:1003-1011

Guthrie GD Jr, Mossman BT (1993) Health Effects of Mineral Dusts. Reviews in Mineralogy, Volume 28. Mineralogical Society of America, Washington DC

Haque AK, Vrazel DM, Uchida T (1998) Assessment of asbestos burden in the placenta and tissue digests of stillborn in South Texas. Arch Environ Contam Toxicol 35:532-538

Harris KE, Bunker KL, Strohmeier BR, Hoch R, Lee RJ (2007) Discovering the true morphology of amphibole minerals: complementary TEM and FESEM characterization of particles in mixed mineral dust. *In:* Modern Research and Educational Topics in Microscopy, Formatex Microscopy Book Series, No. III. Méndez-Vilas A, Díaz J (eds) Formatex Research Center, Badajoz, Spain, 2007 (accepted)

Hawthorne FC, Oberti R (2007) Classification of the amphiboles. Rev Mineral Geochem 67:55-88

Hillerdal G (2003) Health problems related to environmental fibrous minerals. *In:* Geology and Health: Closing the Gap. Skinner HCW, Berger AR (eds) Oxford University Press, New York, p 113-118

Holt PF (1981) Transport of inhaled dust to extrapulmonary sites. J Pathol 133:123-129

Hume LA, Rimstidt JD (1992) The biodurability of chrysotile asbestos. Am Mineral 77:1125-1128

Hull MJ, Abraham JL, Case BW (2002) Mesothelioma among workers in asbestiform fiber-bearing talc mines in New York State. Ann Occup Hyg 46:132-135

Langer AM, Nolan RP, Addison J (1991) Distinguishing between amphibole asbestos fibers and elongate cleavage fragments of their non-asbestos analogues. *In:* Mechanisms in fibre carcinogenesis, Brown RC, Hoskins J, Johnson N (eds) Plenum Press, New York, p 252-267

Leake BE, Woolley AR, Arps CES, Birch WD, Gilbert MC, Grice JD, Hawthorne FC, Kato A, Kisch HJ, Krivovichev VG, Linthout K, Laird J, Mandarino JA, Maresch WV, Nickel EH, Rock NMS, Schumacher JC, Smith DC, Stephenson NCN, Ungaretti L, Whittaker EJW, Youzhi G (1997) Nomenclature of the amphiboles: Report of the subcommittee on amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names. Can Mineral 35:219-246

Lockey JE, Brooks SM, Jarabek AM, Khoury PR, McKay RT, Carson A, Morrison JA, Woit JF, Spitz HB (1984) Pulmonary changes after exposure to vermiculite contaminated with fibrous tremolite. Am Rev Respir Dis 129:952-958

Luo S, Liu X, Mu S, Tsai SP, Wen CP (2003) Asbestos related diseases from environmental exposure to crocidolite in Da-yao, China. I. Review of exposure and epidemiological data. Occup Environ Med 60:35-42

Luce D, Brochard P, Quenel P, Salomon-Nekiriai C, Goldberg P, Billon-Galland MA, Gordberg M (1994) Malignant pleural mesothelioma associated with exposure to tremolite. Lancet 344:1777

Luce D, Bugel I, Goldberg P, Goldberg M, Solomon C, Billon-Galland MA, Nicolau J, Quénel P, Fevotte J, Brochard P (2000) Environmental exposure to tremolite and respiratory cancer in New Caledonia. A case-control study. Am J Epidem 151:259-265

Magee F, Wright JL, Chan N, Lawson L, Churg A (1986) Malignant mesothelioma caused by childhood exposure to long-fiber low aspect ratio tremolite. Am J Ind Med 9:529-533

Magnani C, Mollo F, Paoletti L, Bellis D, Bernardi P, Betta P, Botta M, Falchi M, Ivaldi C, Pavesi M (1998) Asbestos lung burden and asbestosis after occupational and environmental exposure in an asbestos cement facturing area: a necroscopy study. Occup Environ Med 55:840-846

Mangano D, Gualtieri AF, Torri G, Ferraris S, Ricchi A, Foresti E, Lesci G, Roveri N, Mariotti M, Pecchini G, Zapparoli M (2006) Asbestos monitoring in civil and industrial environments of selected Italian sites. The case of a ceramic factory. Abstracts of the European Conference on Asbestos Risks and Management, p 140-145

Marinaccio A, Montanaro F, Mastrantonio M, Uccelli R, Altavista P, Nesti M, Costantini AS, Gorini G (2005) Predictions of mortality from pleural mesothelioma in Italy: a model based on asbestos consumption figures supports results from age-period-cohort models. Int J Cancer 115:142-147

Martin RF (2007) Amphiboles in the igneous environment. Rev Mineral Geochem 67:323-358

Mazziotti Tagliani S (2006) Mineralogical, genetic and environmental aspects of the fluorine-rich amphiboles from Biancavilla (Mt. Etna, Sicily, Italy). PhD thesis, Università degli Studi La Sapienza, Roma

McConnochie K, Simonato L, Mavrides P, Christofides P, Pooley FD, Wagner JC (1987) Mesothelioma in Cyprus: the role of tremolite. Thorax 42:342-347

McConnochie K, Simonato L, Mavrides P, Christofides P, Mitha R, Griffiths DM, Wagner JC (1989) Mesothelioma in Cyprus. *In:* Non-occupational exposure to mineral fibres. Bignon J, Peto J, Saracci R (eds) IARC Scientific Publ 90:411-419

McDonald JC, Harris J, Armstrong B (2004) Mortality in a cohort of vermiculite miners exposed to fibrous amphibole in Libby, Montana. Occup Envrion Med 61:363-366

McDonald JC, McDonald AD, Armstrong B, Sebastien P (1986a) Cohort study of the mortality of vermiculite miners exposed to tremolite. Br J Ind Med 43:436-444

McDonald JC, McDonald AD, Armstrong B (1986b) Radiological survey of past and present vermiculite miners exposed to tremolite. Br J Ind Med 43: 445-449

McDonald, JC, McDonald AD, Sebastien P, Moy K (1988) Health of vermiculite miners exposed to trace amounts of fibrous tremolite. Br J Ind Med 45:630-634

McDonald JC, Sebastien P, Case B, McDonald AD, Dufresne A (1992) Ferruginous body counts in sputum as an index of past exposure to mineral fibres. British Occ Hyg Society 36:271-282

Meeker GP, Bern AM, Brownfield IK, Lowers HA, Sutley SJ, Hoefen TM, Vance JS (2003) The composition and morphology of amphiboles from the Rainy Creek Complex, near Libby, Montana. Am Mineral 88:1955-1969

Meeker GP, Lowers HA, Swayze BS, Van Gosen BS, Sutley SJ, Brownfield IK (2006) Mineralogy and morphology of amphiboles observed in soils and rocks in El Dorado Hills, California. USGS OFR 2006-1362

Metintas M, Hillerdal G, Metintas S (1999) Malignant mesothelioma due to environmental exposure to erionite: follow-up of a Turkish emigrant cohort. ERS Journal Ltd 13:523-526

Millette JR (2006) Asbestos analysis methods. *In:* Asbestos Risk Assessment, Epidemiology, and Health Effects. Dodson RF, Hammer SP (eds) Taylor & Francis, p 9-37

Millette JR, Bandli BR (2005) Asbestos identification using available standard methods. Microscope 53:179-185

Molly DW (2006) USA vs WR Grace, CR 05-07-M-DWM. US District Court, Missoula MT

Montanaro F, Marinaccio A, Gorini G, Silvestri S, Altavista P, Mastrantonio M, Uccelli R (2004) Stima dell'andamento della mortalità per mesotelioma pleurico in Italia nel prossimo futuro in relazione alla produzione ed al consumo di amianto grezzo *http://www.ti.ch/dss/IstCP/RCT/documenti/GRELL04_mesotelioma.ppt*

Mossman BT, Bignon J, Corn M, Seaton A, Gee JBL (1990) Asbestos: Scientific developments and implications for public policy. Science 247:294-301

Nemmar A, Hoet PHM, Vanquickenborne B, Dinsdale D, Thomer M, Hoylaerts MF, Vanbilloen H, Mortelmans L, Nemery B (2002) Passage of inhaled particles into the blood circulation in humans. Circulation 105:411-414

Nemmar A, Vanbilloen H, Hoylaerts MF, Hoet M, VerbruggenA, Nemery B (2001) Passage of intratracheally instilled ultrafine particles from the lung into the systemic circulation in hamster. Am J Respir Crit Care Med 164:1665-1668

Nolan RP, Langer AM, Oechsle GW, Addison J, Colflesh DE (1991) Association of tremolite habit with biological potential: Preliminary report. *In:* Mechanisms in Fibre Carcinogenesis. Brow RC, Hoskins JA, Johnson NF (eds) Plenum Press, New York, p 231-251

Norton MR, Gunter ME (1999) Relationships between respiratory diseases and quartz-rich dust in Idaho. Am Mineral 84:1009-1019

OSHA (1992) Occupational exposure to asbestos, tremolite, anthophyllite, and actinolite. Federal Register 1992, 57, 24310

Pan X, Day HW, Wang W, Beckett, LA, Shenker MB (2005) Residential proximity to naturally occurring asbestos and mesothelioma risk in California. Am J Respir Crit Care Med 172:1019-1025

Paoletti L, Batisti D, Bruno C, Di Paola M, Gianfagna A, Mastrantonio M, Nesti M, Comba N (2000) Unusually high incidence of malignant pleural mesothelioma in a town of eastern Sicily: an epidemiological and environmental study. Arch Environ Health 55:392-398

Pasetto R, Bruni B, Bruno C, D'Antona C, De Nardo P, Di Maria G, Di Stefano R, Fiorentini C, Gianfagna A, Marconi A, Paoletti L, Putzu MG, Soffritti M, Comba P (2004a) Problematiche sanitarie della fibra anfibolica di Biancavilla: aspetti epidemiologici, clinici e sperimentali. Not Ist Super Sanità 17:8-12

Pasetto R, Bruni B, Bruno C, Cauzillo G, Cavone D, Convertini L, De Mei B, Marconi A, Montavano G, Musti M, Paoletti L, Comba P (2004b) Mesotelioma pleurico ed esposizione ambientale a fibre minerali: il caso di n'area rurale in Basilicata. Ann Ist Super Sanità 40:251-265

Peipens LA, Lewin M, Campolucci S, Lyparger JA, Miller A, Middleton D, Weis C, Spence M, Black B, Kapil V (2003) Radiographic abnormalities and exposure to asbestos-contaminated vermiculite in the community of Libby, Montana, USA. Environ Health Perspect 111:1753-1759

Pollice L, Ferri GM, Paoletti L, Gentile A, Iacobellis U, Batisti D, Di Tonno P, Caruso G, Molinini R (1995) Concentrazione di fibre di asbesto nei tumori uroteliali e nella parete vescicale esente da neoplasia, G Ital Med Lav 17:11-15

Plumlee GS, Morman SA, Zeigler TL (2006) The toxicological geochemistry of earth materials: An overview of processes and the interdisciplinary methods used to understand them. Rev Mineral Geochem 64:5-274

Putzu MG, Bruno C, Zona A, Massiccio M, Pasetto R, Piolatto PG, Comba P (2006) Fluoro-edenitic fibres in the sputum of subjects from Biancavilla (Sicily): a pilot study. Environ Health, A Global Access Science Source 5:20

Rees D, Phillips JI, Garton E, Pooley FD (2001) Asbestos lung fibre concentration in South African chrysotile mine workers. Ann Occup Hyg 45:473-477

Rey F Viallat JR, Boutin C, Farisse P, Billon-Galland MA, Hereng P, Dumortier P, De Vuysts P (1993) Les mésothéliomes environnementaux an Corse du Nord-Est. Rev Mal Resp 10:339-345

RJ Lee (2005) Evaluation of EPA's analytical data from the El Dorado Hills asbestos evaluations project. RJ Lee Group, Monroeville, Pennsylvania, USA

Roggli VL (1990) Human disease consequences of fiber exposures: a review of human lung pathology and fiber burden data. Environ Health Perspect 88:295-303

Roggli VL (2004) Asbestos bodies and nonasbestos ferruginous bodies. *In:* Pathology of Asbestos-Associated Diseases. Roggli VL, Oury TD, Sporn TA (eds) Springer-Verlag New York, p 34-70

Roggli VL, Sharma A (2004) Analysis of tissue mineral fiber content. *In:* Pathology of Asbestos-Associated Diseases. Roggli VL, Oury TD, Sporn TA (eds) Springer, New York, p 309-354

Roggli VL, Sharma A, Butnor KJ, Sporn T, Vollmer RT (2002) Malignant mesothelioma and occupational exposure to asbestos: a clinicopathological correlation of 1445 cases. Ultrastruct Pathol 26:55-65

Ross M (1981) The geologic occurrences and health hazards of amphibole and serpentine asbestos. Rev Mineral 9A:279-323

Ross M (1984) A survey of asbestos-related disease in trades and mining occupations and factory and mining communities as a means of predicting health risks of nonoccupational exposure to fibrous minerals. *In:* Definitions for Asbestos and Other Health-related Silicate. Levadie B (ed), ASTM STP 834, American Society for Testing Materials, Philadelphia, Pennsylvania, p 51-104

Ross M (1994) The New Idria serpentinite of California: a toxic rock? Geological Society of America Abstracts with Programs, 1994 Annual Meeting, Seattle, Washington, October 24-27, No 7 26:A320

Ross M, Nolan RP (2003) History of asbestos discovery and use and asbestos-related disease in context with the occurrence of asbestos within ophiolite complexes. Geol Soc Am Special Paper 373:447-470

Ross M, Nolan RP, Langer AM, Cooper WC (1993) Health effects of mineral dusts other than asbestos. Rev Mineral 28:361-409

Sanchez MS (2007) Characterization methods for asbestiform minerals. MS Thesis, University of Idaho, Moscow, Idaho

Sanchez MS, Gunter ME (2006) Quantification of amphibole content in expanded vermiculite products from Libby, Montana USA. Am Mineral 91:1448-1501

Sanchez MS, Gunter ME, Dyar MD, Badger SR, Hobbs GC, Van Orden DR, Potter MS (2006) Characterization of historical amphibole samples from the former vermiculite mine near Libby, Montana USA. Geological Society of America Abstracts with Programs, vol 38, #7, p 293

Sartorelli P, Scancarello G, Romeo R, Marcianò G, Rotoli P, Arcangeli G, Palmi S (2001) Asbestos exposure assessment by mineralogical analysis of bronchoalveolar lavage fluid. J Occup Environ Med 43:872-881

Schumacher JC (2007) Metamorphic amphiboles: composition and coexistence. Rev Mineral Geochem 67:359-416

Selden AI, Berg NP, Lundgren EAL, Hillerdal G, Wik N-G, Ohlson C-G, Bodin LS (2001) Exposure to tremolite asbestos and respiratory health in Swedish dolomite workers. Occup Environ Med 58:670-677

Stemple IS, Brindley GW (1960) A structural study of talc and talc-tremolite reaction. J Am Ceram Soc 43:34-42

Storeygard AR, Brown AL Jr (1977) Penetration of the small intestinal mucosa by asbestos fibers. Mayo Clin Proc 52: 809-812

Su S, Bloss FD (1984) Extinction angels for monoclinic amphiboles or pyroxenes: a cautionary note. Am Mineral 69:399-403

Swayze GA, Higgins CT, Clinkenbeard JP, Kokaly RF, Clark, RN, Meeker GP, Sutley, SJ (2004) Preliminary report on using imaging spectroscopy to map ultramafic rocks, serpentinites, and tremolite-actinolite-bearing rocks in California. USGS OFR 2004-1304

Taunton AE, Gunter ME (2007) Introducing medical geology to undergraduates as a critical thinking and risk assessment tool. J Geol Ed 55:169-180

Taunton AE, Wood SA, Gunter ME (2002) The thermodynamics of asbestos mineral dissolution and conversion in the human lung. 12th Annual Goldschmidt Conference, Davos, Switzerland.

Tossavainen A (1997) Asbestos, asbestosis and cancer: the Helsinki criteria for diagnosis and attribution. Consensus Report Scand J Work Environ Health 23:211-216

Tossavainen A, Dumortier P, Billon-Galland MA, Burdett G, Mitha R, Monso E, Rödelsperger K, Taikin-Aho O, Tuomi T, Vanhala E, Maier EA (2001) The certification of the content of asbestos fibres in lung tissue. European Commission, BCR 665 and BCR 666, reference materials, Directorate-General for Research, EUR 19073 EN

Tossavainen A, Karjalainen A, Karhuenen PJ (1994) Retention of asbestos fibers in the human body. Environ Health Perspect 102:253-255

Trescases JJ (1997) The lateritic nickel-ore deposits. *In:* Soils and Sediments Mineralogy and Geochemistry. Paquet H, Clauer N (eds) Springer, Berlin, p 125-138

USEPA (2001a) Weis Memorandum to Paul Peronard: Re "Fibrous amphibole contamination in soil and dust at multiple locations in Libby, Montana." USEPA Region 8, July 2001

USEPA (2001b) EPA's actions concerning asbestos-contaminated vermiculite in Libby, Montana. EPA 744-R-00-010, United States Environmental Protection Agency, Washington

Van der Schalie WH, Gardner HS Jr., Bantle JA, De Rosa CT, Finch RA, Reif JS, Reuter RH, Backer LC, Burger J, Leroy CF, Stokes WS (1999) Animals as sentinels of human health hazards of environmental chemicals. Environ Health Perspect 107:309-315

Van Gosen BS, Lowers HA, Sutley SJ, Gent CA (2004) Using the geologic setting of talc deposits as an indicator of amphibole asbestos content. Environ Geol 45:920-939

Van Gosen BS, Lowers HA, Bush AL, Meeker GP, Plumlee GS, Brownfield IK, Sutley SJ (2005) Reconnaissance study of the geology of US vermiculite deposits – are asbestos minerals common constituents. USGS Bull 2192

Van Gosen BS (2006a) Reported historic asbestos miners, historic asbestos prospects, and natural asbestos occurrences in the Eastern United States. USGS OFR 2005-1189

Van Gosen BS (2006b) Reported historic asbestos miners, historic asbestos prospects, and natural asbestos occurrences in the Central United States. USGS OFR 2006-1211

Van Oss CJ, Naim JO, Costanzo PM, Giese RF Jr., Wu W, Sorling AF (1999) Impact of different asbestos species and other mineral particles on pulmonary pathogenesis. Clays Clay Mineral 47:697-707

Veblen DR (1980) Anthophyllite asbestos: microstructures, intergrown sheet silicates and mechanisms of fiber formation. Am Mineral 65:1075-1086

Veblen DR, Buseck PR (1980) Microstructures and reaction mechanisms in biopyriboles. Am Mineral 65:599-623

Veblen DR, Buseck PR, Burnham CW (1977) Asbestiform chain silicates: new minerals and structural groups. Science 198:359-365

Veblen DR, Wylie AG (1993) Mineralogy of amphiboles and 1:1 layer silicates. Rev Mineral 28:61-138

Verkouteren JR, Wylie AG (2000) The tremolite-actinolite-ferro-actinolite series: Systematic relationships among cell parameters, composition, optical properties, and habit, and evidence of discontinuities. Am Mineral 85:1239-1254

Verkouteren JR, Wylie AG (2002) Anomalous optical properties of fibrous, tremolite, actinolite, and ferro-actinolite. Am Mineral 87:1090-1095

Virta RL (1985) The phase relationship of talc and amphiboles in a fibrous talc sample. U.S. Bureau of Mines, Report of Investigations 8923

Wagner JC (1980) The pneumoconiosis due to mineral dusts. J Geol Soc London 137:537-545

Wagner JC, Griffiths DM, Munday DE (1987) Recent investigations in animals and humans. *In:* The Biological Effect of Chrysotile. Wagner JC (ed) 1:111-120

Wylie AG (1979) Optical properties of the fibrous amphiboles. *In:* Health Hazards of Asbestos Exposure. Selikoff IJ, Hammond EC (eds) Annals of the New York Academy of Sciences 330:611-619

Wylie AG, Huggins CW (1980) Characteristics of a potassian winchite-asbestos from the Allamoore Talc District Texas. Can Mineral 18:101-107

Wylie AG, Verkourteren JR (2000) Amphibole asbestos from Libby, Montana: aspects of nomenclature. Am Mineral 58:1540-1542

Weill H, Abraham JL, Balmes JR, Case B, Chrug A, Hughes J, Schenker M, Sebastien P (1990) Health effects of tremolite. Am Rev of Resp Dis 142:1453-1458

Williams-Jones AE, Normand C, Clark JR, Vali H, Martin RF, Dufresne A, Nayebzadeh A (2001) Controls of amphibole formation in chrysotile deposits: Evidence from the Jeffrey Mine, Asbestos, Quebec. *In:* The Health Effects of Chrysotile Asbestos. Can Mineral Spec Publ 5:89-104

Wood SA, Taunton AE, Normand C, Gunter ME (2006) Mineral-fluid interaction in the lungs: Insights from reaction-path modeling. Inhalation Toxicology 18:975-984

Wright RS, Abraham JL, Harber P, Burnett BR, Morris P, West P (2002) Fatal asbestosis 50 years after brief high intensity exposure in a vermiculite expansion plant. Am J Respir Crit Care Med 165:1145-1149

Yazicioglu S, Ilçayto R, Balci K, Sayli BS (1980) Plural calcification, pleural mesothelioma and bronchial cancers caused by tremolite dusts. Thorax 35:564-569

Zoltai T (1979) Asbestiform and acicular mineral fragments. *In:* Health Hazards of Asbestos Exposure. Selikoff IJ, Hammond EC (eds) Annals of the New York Academy of Sciences 330:621-643

Zoltai T (1981) Amphibole asbestos mineralogy. Rev Mineral 9A:237-278

Zoltai T, Wylie AG (1979) Definitions of asbestos-related mineralogical terminology. *In:* Health Hazards of Asbestos Exposure. Selikoff IJ, Hammond EC (eds) Annals of the New York Academy of Sciences 330:707-709