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Mineralogy of Asbestos Minerals

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Asbestos · Chrysotile · Actinolite · Tremolite · Anthophyllite · Amosite · Crocidolite

Abstract

Over the past fifty years the mineralogy and crystal chemistry of the materials called asbestos have been refined leading to better identification through new and more sensitive techniques. The health aspects of the exposure to fibrous inorganic species are also equally well determined from the anatomical to the biochemical levels. Integrating the efforts of many researchers from a diversity of disciplines from mineralogy and medicine, we can be more specific and detailed in the questions we raise. Coordinated research should add to our basic understanding of one area of disease induction and treatment: trauma related to inorganic materials.

Introduction

There is hardly a day that passes when the potential hazards of exposure to "asbestos" materials are not considered in some country around the globe. The term "asbestos" may be well known but the precise definition of these fibrous materials still raises questions, and often leads to differences of opinions, if not arguments, at least in the legal sense. It will be the purpose of this presentation to discuss a few of the issues from the perspective of a mineralogist as to possible lines of future research.

As part of discussions on the occupational and potential environmental health hazards related to asbestos exposure in the United States in the mid 1960s [1] some constructive responses took place. Several committees in different countries were convened to look into the issues. Reports from Great Britain, Canada and the US [2] produced the earliest views of the possible offending mineral species and described the range of potential disease states arising from exposure [3]. As with any problem submitted to such scrutiny, and especially involving the environment and human health, the contributing experts and investigators realised that there were not only differences of opinions among those who mined or utilized asbestos in their industries, but among those concerned with the possible diseases related to asbestos: they did not understand each other's areas and languages. To communicate effectively and constructively they had to meld together perhaps the widest range of scientific views than had heretofore existed. The disciplines spanned the biological to the geological communities, from practicing physicians and epidemiological researchers to the individuals involved with regulation in federal, state and local governments, attorneys, and, of course, those sick and suffering. These people were unused to seeking each other out much less focusing all their efforts and examinations on a particular technical question: how could fibrous materials be responsible for disease?

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It was imperative that a glossary of terms be generated that would allow communication. The efforts to do so, as might be anticipated to consider such disparate fields and needs, required education that included the scientists, as well as health practitioners. This educational process continues today. Asbestos materials, which may seem, because of their inorganic nature, to be well known and researched as to their physical and chemical characteristics, remain under investigation both by petrologists/mineralogists from the geological aspects and by pathologists/epidemiologists from the medical aspects.

The naturally occurring minerals that form fibres are legion, and the latest explosion of synthetic fibres needed for industrial, and especially telecommunications applications, add to the list. New fibres created by materials science investigations is a growth area for basic science, not only in how they can or could be used but how they might affect the health of humans [4]. We have a little knowledge gained over the past 50 years to guide us.

The ''Asbestos'' Materials

The earliest codified descriptions of the potentially offending fibres were the minerals called ''asbestos'' mined on many continents for hundreds of years. They were an industrial product, formed by earth processes, at sites well known to geologists. As a result of the health scare they were defined by the US governmental regulatory bodies, EPA, and OSHA, in the Federal Register in the 1970s. The definition was quite specific and listed six names, of which only three were bone fide mineral species. It identified: actinolite, tremolite, anthophylite, amosite and crocidolite, which were representatives of the amphibole group of minerals, and the sixth, chrysotile, from the serpentine mineral group. Chrysotile, or white asbestos and crocidolite, blue asbestos, are varietal names. Amosite, brown asbestos, is an industrial acronym for ''Asbestos Minerals of South Africa'' with the addition of the usual 'ite' to designate a mineral.

The amphibole group has the general chemical formula

$A_{0\text{-}1}\ B_2\ C_5\ T_8\ O_{22}\ (OH,F,Cl,O)_2$

where A, B, C, and T represent cation sites, each with distinctive geometries in the amphibole crystal structure.

For example in each formula unit of an amphibole mineral species, zero to one Na^{1+} or K^{1+} can be found in the A site, two ions of Mg^{2+}, Fe^{2+}, Mn^{2+}, Ca^{2+}, Na^{1+}, or Li^{1+} enter the B site, five ions of Mg^{2+}, Fe^{2+}, Mn^{2+} Al^{3+}, Fe^{3+}, Cr^{3+} or Ti^{4+} enter the C site and eight ions of Si^{4+} or Al^{3+} enter the T site. The remaining entry in the formula, (OH, Cl, O), indicates anions that occupy another site, i.e. three different anion species can potentially occupy that site. The crystal structure has been known for many years [5] but because of the variable chemistries of the different species specific site occupancies for a particular amphibole sample many not be available.

The 'ideal' formulae for the amphibole asbestos minerals are

Actinolite	$Ca_2\ (Mg, Fe^{2+})_5\ Si_8\ O_{22}\ (OH)_2$
Tremolite	$Ca_2\ Mg_5\ Si_8\ O_{22}\ (OH)_2$
Anthophyllite	$Mg_7\ Si_8\ O_{22}\ (OH)_2$
Amosite	$(Fe^{2+})_2\ (Fe^{2+}, Mg)_5\ Si_8\ O_{22}\ (OH)_2$ (minerals in the cummingtonite–grunerite series)
Crocidolite	$Na_2\ (Fe^{2+}, Mg)_3\ Fe^{3+}{}_2\ Si_8\ O_{22}\ (OH)_2$ (mineral name: riebeckite)

The serpentine mineral 'ideal' formula is

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

where R^{2+} is Fe^{2+}, Mn^{2+}, or Ni^{2+} and R^{3+} is Al^{3+} or Fe^{3+}.

The 'ideal' formula for chrysotile is

Chrysotile $Mg_3Si_2O_5(OH)_4$

The crystal structure of chrysotile, always in fibrous form, is discretely distinct from that of the amphiboles. The amphiboles are very common minerals in igneous and metamorphic rocks and often show an elongate or prismatic form that is directly related to the crystal structure [5,6]. In addition because of their peculiar structure the amphiboles have a distinctive cleavage that results in acicular or needle-like morphology when the minerals are crushed. A tiny oblong form often appears naturally in sedimentary deposits if the primary rocks are eroded, or when mined and milled as part of the extraction of other minerals. However, only when amphiboles form fibers, adopt an asbestiform habit, should they be classified as ''asbestos'' [7].

The formulae presented above show that the minerals are all hydrated silicates with the cations Ca, Fe, Mg and Na. There will also be some minor or trace elements present. All of these elements are common, indeed ubiquitous, in the geochemical environment. And therein lies one of the major problems in the definition of asbestos. There are many mineral species, especially silicates, that occur throughout the earth, which may be fibrous, or have needle-like forms [3]. It was not only the specific minerals or varieties that were designated in the regulatory definition of ''asbestos'' but the physical attributes: the

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shape and size of these fibres were stipulated. The fibres that needed regulation were to have an aspect ratio (length to width ratio) of at least 5:1, and be less than 10 μm in length. The physical attributes were critical for defining the health hazard as mineral materials of that size and shape could become airborne. Inhaled, and once inside the body such fibres could lodge in the lungs and potentially cause harm. The impact on the breathing apparatus, and specifically interference with the uptake and transfer of oxygen from the air by the lungs, would be compromised. The availability of oxygen to the tissues was essential for proper metabolism and functioning throughout the body and limiting it had dire consequences: disease and death would ensue.

Identification of 'Asbestos' and Related Diseases

The designation of the shape and size of fibrous materials can be relatively easily revealed by optical examination. Optics became the technique of choice to investigate the occurrence of inorganic fibrous air-borne particulates at occupational sites, in schools, or any building, and even outdoors where filters could be set up to obtain a representative aliquot sample of the air. Human beings exposed to dusty environments reacted. One symptom was 'shortness of breath' with a diagnosis 'pneumoconiosis', a group of diseases, which included asbestosis and silicosis. Both the specific names implicated mineral materials with the medical result scarring of the lung tissues. Another class of diseases were identified and related to the mineral particulate inhalation: lung cancer and mesothelioma. The latter is a cancer of the lining of the lung with no obvious cure. Mesothelioma was from asbestos inhalation and not the result of smoking, distinctly different from lung cancer. Patients with mesothelioma usually had a rapid demise (within a year in many cases), in spite of the fact that the exposure to asbestos may have been relatively mild and taken place over 30 years before [8].

Researchers into the potential causative effects of these diseases, and including exposure to fiberglass, suggested that the inorganic materials were 'foreign bodies' in the biological environment. Human anatomy already possessed some mechanisms to minimise the inhalation of particulates. Hairs in the nose, and ciliated cells in the upper bronchi could aid in the expulsion of at least part of the inhaled materials. Should the foreign materials reach deep within the lung a reaction ensued producing scar tissue, supposedly to encapsulate the non-normal additions to the normally soft tissue environment. The 'hard' particles initiated cellular responses to an unexpected trauma, and a normal repair mechanism was the deposition of a fibrous protein, collagen, in excessive concentrations at the site of trauma. This reaction is also encountered with the invasion of bacteria, for example, in the lung environment or when skin cut heal.

The physical rejection of air-borne fibrous particles can be envisioned, but the local reactions that led to scarring depend not only on the fibre reaching the delicate tissues of the alveoli deep within the lung but on local cell responses. Some individuals appeared to be more susceptible to asbestosis while others developed lung cancer with limited exposure. Because the two groups of mineral materials could be distinguished investigations into the factors related to disease concluded that small differences in the morphology of the particulates or in the chemical character of the particulates, and particularly the surfaces of the materials, as presented to the bio-environment were responsible. Investigators determined the chemical character of the asbestos materials. Scanning electron microscopy with chemical analytical capacities became the technique of choice to explore more fully the specific, and perhaps, the critical, offending characteristics. The mineral size and shape as obtained from mine sites, and from insulation were defined [9] and studies were undertaken on animal models to ascertain any differences between the various inorganic species, asbestiform and acicular. The body of evidence suggested that "white" asbestos (chrysotile) was less likely to induce trauma because of its curly morphology, than crocidolite, or blue asbestos, with its needle-like morphology. The amphiboles seemed to be the "bad actors" when the epidemiologists investigated the onset of mesothelioma in South Africa, in Turkey and in Australia. The details of the health issues in these countries was discussed by others at this conference. It did appear to some investigators that the amphiboles possessed some of the more devastating hazardous characteristics.

Investigating the Potentially Hazardous Minerals

Fibres and fibrous minerals are immediately noticeable and distinctive. As one addresses the problems presented by asbestos and other minerals, including the other silicates, for example erionite (one of the many natural and synthetic zeolite species), fiberglass, or other silica

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forms (diatoms) that have been shown to be extremely hazardous, one is forced to conclude that the airborne character is paramount. The specific gravity of the species, the size and an appropriate morphology that permits suspension is of primary consideration, provided the mineral material is relatively insoluble in the biological fluids. Reduction, if not prevention, of disease can be undertaken for anyone at occupational risk by wearing masks. By minimizing the amount of silicate-containing-foreign particles available one could obviate the likelihood of harm.

However, the identification of a particular hazardous species from areas where disease, such as mesothelioma, is endemic, showed that minerals other than those originally designated (asbestiform species of amphiboles and serpentines) could be present [10,11]. Investigators suggested mechanisms of disease induction that went beyond physical trauma. One of the hypotheses came with the investigations on crocidolite and focused on the distinctive elemental composition of this species. The presence of iron, in both Fe^{2+} and Fe^{3+} states in the amphibole could, perhaps, initiate a cascade of cell responses leading to an activated oxygen ligand thought to be a carcinogenic agent. There is some iron in many minerals but their precise composition is not usually investigated. Mineralogically there is a known relationship in the naturally occurring common amphibole species in the series tremolite–actinolite–ferroactinolite [12].

Discussion

The crystal chemical range of potentially hazardous inorganic and mineral species has been accurately identified [13]. The health responses are well documented [14]. We can now ask more precise questions based on data accumulated over the many years of scientific research.

Chemical and physical details on the range of potentially offending materials are increasingly accurate and sensitive with high resolution techniques (TEM, electron diffraction, spectroscopy). The information on the inorganic fibrous particulates can be matched with the equally high resolution techniques applied to analyses of tissues, with data gathered at the cellular and molecular levels. The advances in techniques increase the possibilities that we can test hypotheses and hopefully gain greater understanding (from the anatomic to the genetic) of the reactions that lead to induction of disease. Co-ordinating ultramicroscopic levels with the health and geological investigations for a particular geographic area should enable us to refine the possibilities.

It is important that we go beyond the classification of 'asbestos' and the health counterparts 'asbestosis' and cancer. An asbestiform species within the tremolite–ferroactinolite series is present at Libby, Montana, USA, where the mining of vermiculite has an accompanying fibrous Fe-containing amphibole species in the gangue. Since the Libby population has a high proportion of mesothelioma it seems reasonable that we follow on with at least one question: is iron an important element in the biochemical responses that lead to the destructive effects, scarring and cancer from asbestiform particulates? The body has multifactorial chemical cascades only partially understood. However, with the present knowledge on the production of proteins by cells in response to certain stimuli and with new analytical information available on inorganic materials we should be able to expand our knowledge of potential mechanisms of disease induction. The levels of sensitivity using the high resolution techniques now available mandate that we follow up the reactions thought to relate to particulates, and specifically mineral materials, interfering in the biologic environment.

In Libby, for example, Verkouteren and Wiley [12] have determined the chemical composition of the asbestiform amphibole (not one of the already named hazardous species listed above). By precisely identifying the mineral species as a small part (a maximum of 5% in the airborne particulates as it is only present in the gangue of this vermiculite mine) of the hazard where an entire town has been declared as potentially at risk, provides a geographic site for future investigations. The entire spectrum of research could be carried out from responses in the whole body down to those at a molecular level, including quantifying the range of the potentially hazardous transfers and biological impact of specific mineralogical samples, to the epidemiology of those affected. Libby could become a test case for treatment of patients and also for inquiring into mechanisms of induction that heretofore were not understood. This is an opportunity to question how precise one should be, both in showing the particular species that is involved at a specific location and the specific biochemical reactions that could be involved in the induction of disease.

The crossover of information between several disciplines will be needed to advance our knowledge. It is important that we go beyond the general classification of the mineral materials known as 'asbestos' and the potential hazardous health counterparts 'asbestosis' and cancer to solve the basic science and medical questions related to inorganic–biological interactions.

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