

Nature and Paragenesis of Asbestos Minerals [and **Discussion**]

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Nature and paragenesis of asbestos minerals

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The asbestos minerals fall into two groups of differing genetic, physical and chemical properties, their only common feature being their fibrous nature. Chrysotile is a sheet silicate, having a layered structure in the form of a scroll or ture, while the amphibole fibres are chain silicates with a lath-like structure.

The biological effects of asbestos depend firstly on its ability to form very small fibres capable of aerial suspension, inhalation and subsequent deposition in the minutest airways of the lung; secondly on the texture of these fibres and their ability to penetrate living tissue; and thirdly on their chemistry, not only considering their resistance to decomposition, but the way in which they may react with or adsorb other compounds.

This paper compares the physical and chemical properties of asbestos fibres insofar as these may influence biological activity and attempts to underline those contrasting features which may relate to the degrees of activity of the major types of asbestos.

ASBESTOS - THE RAW MATERIAL

Six species of asbestiform minerals are known, these being derived from two large groups of rock-forming minerals, the serpentines and the amphiboles. Chrysotile or white asbestos is the sole species classified in the serpentine group, but it is by far the most abundant kind of asbestos. The amphibole group includes the asbestiform types, crocidolite, amosite, anthophyllite, tremolite and actinolite. While the names of the last three types apply equally to the fibrous and crystalline forms of these minerals, the name crocidolite (blue asbestos) is given to the fibrous form of riebeckite and amosite to the fibrous form of grunerite. Figure 1 shows a classification of these minerals, together with their approximate chemical composition.

The bulk of the world's asbestos has developed as cross-fibre seams or veins in their host rocks. The seams contain fibres in extremely tightly packed parallel formation, seam width, which of course determines fibre length, generally being between 0.5 and 20 mm. Longer fibres are less abundant, but it is not uncommon to find chrysotile, crocidolite and tremolite fibres up to 100 mm long, and amosite fibres up to 250 mm long. Anthophyllite and certain forms of crocidolite in some deposits do not occur in cross-fibre development, but rather as fibrous masses containing randomly orientated cubic blocks of fibre up to 25 mm long. Within each block the fibres lie parallel as in a seam.

OCCURRENCE AND FORMATION OF ASBESTOS

All forms of asbestos are metamorphic minerals having a close association with their parent rocks. Most chrysotiles have formed in ultrabasic rocks in which olivines and pyroxenes have been altered by hydrothermal action to serpentine. Part of this serpentine has recrystallized as fibrous material in fissures and cracks which developed in the cooling of the original magma (Jenkins 1960). Fracturing appears to have taken place during the cooling of the original

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peridotites and dunites, soon after emplacement, and this stage was followed by the intrusion of acid magma resulting in partial or complete serpentinization of the rocks. Subsequently a final period of hydrothermal activity gave rise to fissure filling or wall rock-replacement along the routes of cracks by vein chrysotile. Talc and magnetite are prevailing impurities in many chrysotile deposits, and the magnetite may appear as banded margins to the fibre veins or be disseminated throughout both the wall rock and the fibre.

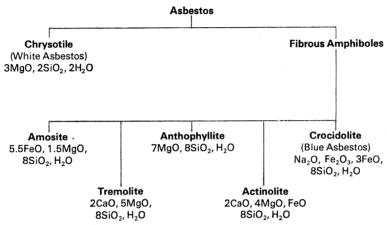


FIGURE 1. Classification chart of the asbestos minerals.

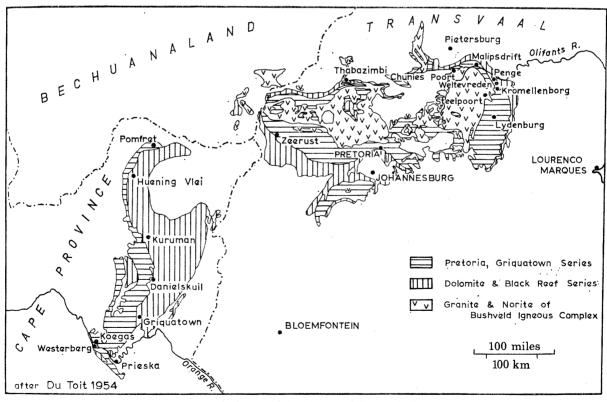


FIGURE 2. Geological map of the Transvaal System in South Africa.

A secondary source of chrysotile, though small, is mined from serpentinized dolomitic limestones. Such fibre is often of high quality and free of the magnetite associated with deposits where the host rock was of igneous origin.

Chrysotile deposits in the Northern Hemisphere are mid to late Palaeozoic in age. In contrast, the southern African chrysotiles are Precambrian as are also the amphibole asbestos deposits of South Africa, which latter are estimated to be some 2000 Ma old.

Such serpentine masses which contain chrysotile are usually extensive, both in plan and depth. The chrysotile veins form an irregular lattice work in the host rock and the winning of the fibre necessitates removal of the whole mass of rock for crushing and extraction at the refinery. Consequently, open-cast methods have proved to be the most economical way of working chrysotile deposits and the immense quarries in the asbestos fields of eastern Quebec province are typical of this development. There is some underground mining, particularly by block caving methods whereby ore is conveyed from the underside of an ore body while the superimposing rock collapses slowly downwards. There are extensive chrysotile deposits in Russia, China and in southern Africa, particularly in Southern Rhodesia where most of the exploitation is underground. There the ore bodies are generally tabular in shape with a pronounced dip. Underground development has been carried for several kilometres along strike and at depths of over 300 m.

The mining of amphibole asbestos is almost completely confined to South Africa (Du Toit 1945; Keep 1961). There, crocidolite and amosite asbestos occur in metamorphosed Precambrian sedimentary strata, the Banded Ironstones, which are included in the upper part of the Transvaal system. The Transvaal system, shown diagrammatically in figure 2, comprises:

in Transvaal

Pretoria System, shales quartzites with some instrusives and volcanics Dolomite, well-bedded magnesianlimestones with Banded Ironstone horizon at top

Black Reef, shales, flagstones and quartzites

in North Cape Province

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Griquatown Series, jaspers, quartzites volcanic beds with Banded Ironstone horizon at bottom Campbell Rand Series (Dolomite), both magnesian and calcareous limestones

Black Reef, shales, quartzites, some volcanic

The Transvaal type rocks are exposed on a broad arc extending some 1000 km from the Orange River in Cape Province northwards to south Botswana and thence east and south into Eastern Transvaal. Within the ironstone formations marker zones and potential asbestos horizons can be traced for hundreds of kilometres.

Despite the consistent nature of the strata there are notable differences in the origins of the two forms of asbestos found here (Cilliers & Genis 1964). Only crocidolite occurs in the Asbestos Hills of northern Cape Province. Its deposits are lensoid and appear to be dependent on structural changes in the host rock at intersections of successive folding and cross-folding. It is presupposed that the original sediments were the result of reaction between iron hydroxide gels and silica held in solution in an alkaline marine environment, and that these consolidated to form the banded ironstones. The banded nature of these rocks is evidence of cyclical changes of climate, temperature and probably atmosphere. Indeed the tight and thin nature of many of the individual bands is reminiscent of varved sediments and suggests annual changes in deposition. Provided that the chemical composition was right and that subsequent dynamic forces

were imposed in the right places, crocidolite asbestos formed as a cross vein fibre in thickness from 0.5 to 100 mm. There is evidence of seeding of fibre growth from magnetite or ankerite which often form thin layers at the interfaces between fibre veins and host rock. Barren rock in the crocidolite reefs has the same deep blue colour as the fibre and this blue colour is imparted by the dense formation of microscopic crocidolite fibres or riebeckite crystals set in a ground mass of ankerite and silica.

The amosite fields of eastern Transvaal have the same history of deposition as the blue asbestos fields of Cape Province. But there the comparison ends. The host rocks are a dense dark grey, the fibre seams an ash grey. Fibre seams are generally thicker and more abundant in the asbestos horizons here. There is little development of magnetite, but fibre/rock interfaces often have masses of large grunerite crystals generally disposed parallel to the interface. Such crystals often appear within the fibre seam, but without a preferred orientation. Graphite is an embarrassing contaminant of amosite fibre and occurs in thin seams both in the host rock and adjacent to fibre veins, with occasion al graphite screens running haphazardly through the veins.

While dynamic forces have contributed to some extent to the formation of amosite, there is almost no evidence of folding in the rocks in the Penge-Kromellenborg-Weltevreden area, where most of the amosite occurs. The strata is planar and dips at a constant 17° towards the west, and towards the core of the Bushveld Igneous Complex. Indeed all the evidence points to amosite being the product of thermal metamorphism, the excessive growth of some fibre veins, masses of grunerite crystals and graphite being sufficient to convince. But why amosite and not crocidolite? One reason is the lack of sodium. In fact the strata here generally lacks alkalis except that in places the host rock has an unusually high potassium contact. Another reason is the presence of graphite, which is conjunction with heat of the aureole of the Bushveld Igneous Complex, has maintained iron oxides in the reduced state. The iron in amosite is divalent, whereas in crocidolite there are similar proportions of divalent and trivalent iron.

About 80 km northwest of the Penge area, where the exposures of the banded ironstones trend east-west, in the Malipsdrift Pietersburg area, there lies a small elongated area along the Malips River, where both crocidolite and amosite occur and from whence the Transvaal crocidolite originates. Crocidolite here appears to have been a product of thermal metamorphism. Fibre seams have characteristic wall formations of large cuboid magnetite crystals, together with some riebeckite. While amosite and crocidolite occur in separate deposits, a curious and inexplicable feature of the fibre horizons is the frequent appearance of veins of both amosite and crocidolite within the same reef. Occasionally crocidolite may pass into amosite in the same vein, with a sharp interface between an upper layer of crocidolite and a lower one of amosite. There is no evidence of graphite or graphitic shale at Malipsdrift, as at Penge, and the chemistry of formation of the amphiboles in this area seems to show a preponderance of ferrous hydroxide gels in the early deposits.

The history of formation of the amphibole asbestos of South Africa has a marked biochemical background. Although the rocks of the Transvaal system are some 2000 Ma old there is evidence in the dolomite series of algal concretions indicating a life form. The banded ironstones in the upper part of the system were deposited in stagnant and anaerobic conditions, in which bacteria appear to have played a large part in determining the ratio of divalent to trivalent iron. Subsequent decomposition and dissipation of these organisms has left a secretion of minor amounts of primitive oils and waxes in the crocidolite fibre of northern Cape Province (Harington 1964). These do not occur in the Transvaal crocidolite or amosite, but the presence

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of considerable amounts of graphite in the Penge amosite fields indicates that the residues of primitive life were charred within the aureole of the Bushveld Igneous Complex shortly after the consolidation of the deposits of the Transvaal system.

Chrysotile, crocidolite and amosite are economically and technically the most important forms of asbestos. Of the remaining types of amphibole asbestos, anthophyllite is the most well known though its desposits are small. The Finnish anthophyllite of Paakkila, which ceased production in 1975, does not occur in cross-fibre development, but rather as fibrous masses containing randomly orientated cubic blocks of fibre up to 25 mm in length. Within each block the fibres lie parallel as in a seam. The Finnish deposit has a distinct igneous origin. Anthophyllite deposits are not uncommon throughout the world, but their economic importance is small. Similar remarks apply to tremolite, but it is available in Italy, Pakistan and Korea. Fibrous actinolite is rare, though there is a small production from Taiwan and a reef of such material has been found associated with crocidolite at Koegas, Cape Province.

Table 1. World asbestos production 1973

(From various sources)

| | 10³ tonne |
|---------------|-----------|
| Canada | 1677 |
| U.S.S.R. | 1279 |
| South Africa | 384 |
| China | 200 |
| Rhodesia | 140 |
| U.S.A. | 137 |
| Italy | 122 |
| Brazil | 39 |
| Australia | 37 |
| Swaziland | 33 |
| Cyprus | 30 |
| Japan | 20 |
| Yugoslavia | 8 |
| India | 8 |
| miscellaneous | 8 |
| | 4100 |

WORLD PRODUCTION AND APPLICATIONS OF ASBESTOS

Current production of raw asbestos fibre has approached or exceeded 4×10^6 tonnes per annum in recent years. The production of asbestos has increased dramatically since World War II and has doubled since 1960. In the past fifteen years, some 50 Mt of asbestos has been mined, distributed and used in its various applications on a world-wide scale. The annual proportions of chrysotile and the amphiboles have remained consistent, a little more than 93 % of the total being chrysotile, the remainder being as amosite and crocidolite. Looking to the future, the U.S. Bureau of Mines estimates that known reserves of asbestos stand at 87 Mt and that total resources may be of the order of 135 Mt.

World production country by country is a little imprecise because of lack of official mineral data from U.S.S.R., China and Rhodesia. Table 1 shows production data for 1973, which puts Canada at the top. Estimates given in Asbestos, December 1975, for last year's production indicate a large stride by U.S.S.R. to a volume of over 2 Mt with world production now standing at 4.6 Mt.

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Of the total asbestos produced annually, about 66 % is used in asbestos-cement products, mainly corrugated roofing sheets and pressure pipes. The average content of asbestos in these extremely hard wearing, weather proof and long-lasting materials is about 15%, indicating a world-wide production of asbestos-cement of some 17 Mt each year.

It would be impossible to tabulate the remaining varied applications of asbestos in global terms. Many of these are important, even crucial, though small in proportion, such as the use of chrysotile in brake linings and clutch facings, or the use of amosite in fireproof insulation products. In Western Europe and U.S.A., a considerable amount of short chrysotile is used in the manufacture of vinyl floor tiles, and next to asbestos-cement, this is probably the largest application of asbestos accounting for some 7% of total production.

Packings, gaskets, asbestos papers and millboards, spray insulations and decorative sprays, speciality paints, asphalt felts, acoustic insulations, corrosion and electrically resistant reinforced plastics are all examples of the varied applications of asbestos.

A most important application of long-fibred chrysotile and crocidolite is in the manufacture of asbestos textiles which are the basis of fire-fighting garments and innumerable fire proofing and insulation applications.

In the context of this paper it is relevant to emphasize the special rôle of crocidolite asbestos in the major outlet of asbestos of all types. Some 75 % of crocidolite production from its sole source in South Africa is used in the manufacture of asbestos-cement pressure pipes in conjunction with chrysotile for purposes of both reinforcement and speed of production. Asbestoscement pipes, despite competition from plastic and steel piping remain one of the most widely used forms of water transportation and are in enormous demand on a world scale. Indeed the demand for crocidolite in this application is considerably in excess of the availability of suitable grades at this present time.

STRUCTURE AND PROPERTIES OF ASBESTOS

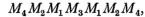
Since the turn of the century many words have been written about the properties of asbestos fibres, and lately three major international conferences on asbestos in 1967, 1971 and 1975 have by no means exhausted the search for knowledge of this extraordinary mineral. From this fund of information we need now to distill those facts which appear most relevant to the environmental emphasis, though indeed most of these are equally important when considering the reasons behind the uses of asbestos fibres.

First and foremost, while recognizing that all asbestos fibres have in common their delineation to fine filaments of immense strength, the chrysotiles on the one hand and the amphiboles on the other are opposed, but complimentary to one another in many of their properties. Additionally, the different types of amphiboles possess subtle differences which do not appear to be as well understood as they might.

Projections of the structures of the two major forms of asbestos are shown in figures 3 and 4, (Deer, Howie & Zussman 1962, 1963; Yada 1971, 1975). The fine structure of crystalline amphiboles as observed under the microscope is repeated on a superfine scale in fibrous amphiboles and the best possible electron-microphotographs of the cross section of a fibre bundle has shown structures akin to the basal cleavage lines in the crystal form. Beyond this point the amphiboles, fibrous or otherwise, differ only in the chemical composition of the cation layer sandwiched between the two silicate ribbons. The external surface of the amphiboles is a silicate layer,

having low surface potential and a degree of hydrophobicity. It will be seen that excepting at its edges, the cation layer is well protected.

The fundamental formula for the amphibole group is $X_7 Si_8 O_{22}(OH)_2$ where X represents cations. The cation sites are labelled in order from edge to edge of the ribbons:



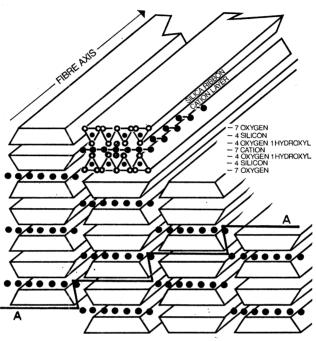


FIGURE 3. Schematic diagram of the crystal structure of an amphibole fibre, indicating the unit cell based on X₇Si₈O₂₂(OH)₂. The line A-A represents the edge of the preferred cleavage plane along which the fibres will split to form even smaller fibres.

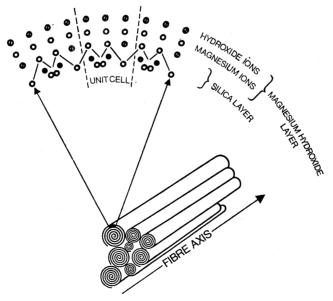


FIGURE 4. Schematic diagram of the structure of a chrysotile fibre formed of several scrolls of individual crystallites. Each scroll is formed from a closely connected double layer having magnesium hydroxide units on its external face and silica units on its inner face. The details of a small section of the scroll show the structure of the double layer and of the unit cell based on $\mathrm{Mg_3}(\mathrm{Si_2O_5})(\mathrm{OH})_4$.

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and the ordered occupancy of these sites determines the type of amphibole. In the monoclinic amphiboles M_4 sites may be occupied by one- or two-valent cations with large radius such as Na^+ , K^+ , Ca^{2+} , while the $M_2M_1M_3$ sites are filled with smaller radiused two- or three-valent cations such as Fc2+, Fe3+, Mg. In the orthorhombic amphibole, anthophyllite, all sites are preferentially filled with Mg, with some possible substitution by Fe^{2+} at M_1 and M_3 sites. Transition to monoclinic forms occurs with 4 Fe2+ which being the larger cations take precedence over $\mathrm{Mg^{2+}}$ in the M_4 and M_2 positions. The order of cation placing in the three most important amphibole fibres is:

| | M_4 | M_2 | M_1 | M_3 | M_1 | M_2 | M_4 |
|---------------|----------------|-----------|------------------|-------------------------|-------------------------|------------------|----------|
| anthophyllite | Mg+ | Mg^+ | ${ m Mg}^+$ | (Mg^+, Fe^{2+}) | Mg+ | Mg^+ | Mg+ |
| amosite | $Fe^{2\cdots}$ | Fc^{2+} | (Fe2+, Mg) | (Fc2+, Mg) | (Fe ²⁺ , Mg) | Fe2+ | Fe^{2} |
| crocidolite | Na+ | Fe^{2+} | Fe ²⁺ | (Fe ²⁺ , Mg) | Fe^2 | Fe ³⁺ | Na+ |

These differences in cation ordering are connected with differences in the properties of the three types of asbestos. Anthophyllite, which has the slightly smaller unit cell dimensions of the three, is a silky flexible fibre, with considerable resistance to chemical degradation. Amosite, in contrast, is a harsh relatively brittle fibre, easily oxidized and having less resistance to chemical degradation than either anthophyllite or crocidolite.

Crocidolite is also harsh, though not brittle, probably because the configuration of cations puts less strain and hence less defects in multiple lattices than is so for amosite. Crocidolite has good resistance to chemical attack, but in other respects has some unique chemical properties. Its unit cell contains two resonant pairs, $Fe^{2+} \longrightarrow Fe^{3+}$, which are held to be responsible for its blue colour, and this resonance is transmitted by electron oscillation to the central M_3 site to which two (OH) groups are attached. A number of thermal investigations in the early 1960s (Addison et al. 1962; Freeman & Taylor 1960) pointed to the existence of mobile protons the hydrogen ions of the hydroxyl groups – which may migrate to the surface of crystallite cells to combine with atmospheric oxygen, according to a redox reaction

$$4 \operatorname{Fc}^{2+} + 4 \operatorname{(OH)}^{-} + \operatorname{O}_{2} = 4 \operatorname{Fc}^{3+} + 4 \operatorname{O}^{2-} + 2 \operatorname{H}_{2} \operatorname{O}.$$

There is no structural change, and under normal pressures this is a sharp reaction at 400 °C, while at increased pressures the reaction proceeds slowly at ambient temperatures.

Other amphiboles display the phenomenon of proton mobility in varying degrees, and this appears to be linked with other properties:

crocidolite
$$\longrightarrow$$
 amosite \longrightarrow anthophyllite \longrightarrow tremolite decreasing proton mobility \longrightarrow increasing temperature of dehydroxylation \longrightarrow increasing temperature of structural breakdown \longrightarrow increasing Mg content at M_1 and M_3 sites \longrightarrow .

While all chrysotiles have similar chemical composition, their form bears little apparent relation to the platy elements of lizardite that are the main form of serpentine minerals. The basic structure is similar to that of the kaolinite group, with highly hydroxylated cation layers alternating with silicate layers. In the serpentines, the magnesium hydroxide (brucite) layer has slightly larger dimensions than the silicate (linked SiO₄) layer resulting in a mis-match, which resolves in chrysotile to a curvilinear structure of a scroll or coil form. The central axis ATHEMATICAL, HYSICAL ENGINEERING CIENCES

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of this form is the long axis of the fibre. Since the brucite layer forms the external surface of chrysotile, the fibre possesses strongly basic properties, exerts a high surface potential in water and has marked hydrophyllic tendencies. The surface layer may be leached out by water and the magnesium hydroxide content of chrysotile is rapidly removed by acids. The reactivity of the brucite layer is turned to good effect by linkage with polar organic compounds and surfactants (Fripiat et al. 1967, 1971).

The presence in asbestos of trace metals which may have biological effects has been investigated (Cralley et al. 1967, 1968). Traces of Ni, Cr, Co and Mn occur in all asbestos minerals, Ni and Cr being significant in chrysotile, and Mn in amosite, these metals being substitute cations for Mg and Fe in the respective unit cells. Extraction of these ions from asbestos by simple leaching is feasible with respect to chrysotile, but less so with the inactive amphiboles, particularly when consideration is given to their positions within cation ribbons. There is a problem in assessing the true significance of these trace metals as intrinsic components of the asbestos, because all are available in the free state from the many types of milling machinery, based on hard wearing NCM alloys, used in the refining of asbestos ores. Abrasion of machine parts by asbestos inevitably results in a proportion of the trace metal content of bagged asbestos originating from this source.

The identification of asbestos is itself an important subject. On the macro scale, the most useful methods are thermal analysis, infrared spectrometry and the mineralogical microscope. Some data on i.r. read-outs has been published (Parks 1971; Daykin 1971), but more recent identification and structural data based on wide range i.r. instruments remains unpublished. Typical thermal analysis data (Hodgson 1965, 1972; Monkman 1967) shows that each type of asbestos has a characteristic thermogram and that impurities can be quantitatively examined by thermogravimetric analysis. With experience it is possible, using combined data from these techniques, not only to identify an asbestos type with certainty, but to pin point its source, since marginal differences on thermal analysis or i.r. traces are characteristic of individual deposits of asbestos ores.

Both X-ray diffraction and i.r. methods are used quantitatively to assess microgram amounts of asbestos fibre collected by air sampling. There are obvious limits to sensitivity and the overall techniques presuppose a knowledge of the type of asbestos which is being sampled.

THE PHYSICAL PROPERTIES OF ASBESTOS FIBRES

The most important physical properties of asbestos fibres in the industrial context are strength, length, diameter and surface area. Equally so on the biological scale two of these parameters, length and diameter, are important within fairly well-defined limits. The ability of asbestos fibres to form airborne suspensions depends on their falling speeds which in turn depends on fibre diameter. In broad terms average diameters of fibres present in aerosols are 0.1-0.3 µm for chrysotiles and crocidolites and 0.3-0.5 µm for amosites (Gibbs & Hwang 1975; Timbrell et al. 1969). The length of respirable fibres is limited by the dimensions of the airways and alveoli of the lung wherein they may be trapped after inhalation, and this length range is generally accepted as 5 to 50 µm. The surface area of respirable fibres in these ranges is approximately 1.5 m²/g for amosite, 2 m²/g for crocidolite and 8 m²/g for chrysotile.

In comparison the length and diameter of refined and graded typical asbestos fibre as delivered into industrial applications is shown in table 2. Commerical grades of asbestos contain a 620

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high proportion of very short fibre, having correspondingly fine diameters less than 1 µm, which if improperly handled will give rise to aerosols of dust of respirable dimensions. Generally speaking commercial asbestos goes through some form or other of processing, before its application, with the object of increasing its degree of fiberization. This inevitably results in the reduction of the proportion of long fibres, an increase in short fibres and, of course, a considerable reduction in the upper limit of fibre diameter.

Table 2. Length and diameter relations for some grades of commercial asbestos

| | length | | diameter | |
|----------------------------|------------|---------------------|-----------|--|
| | | | | |
| | proportion | proportion | range | |
| | > 6 mm | $<75~\mu\mathrm{m}$ | μm | |
| | % | % | | |
| chrysotile, medium length | 25 | 25 | 0.1-100 | |
| chrysotile, short | 5 | 60 | 0.1 - 100 | |
| crocidolite, medium length | 50 | 25 | 0.2-100 | |
| crocidolite, short | 15 | 40 | 0.2-100 | |
| amosite, medium length | 25 | 35 | 0.5 - 100 | |
| amosite, short | 10 | 45 | 0.5-100 | |

TABLE 3. Some physical properties of asbestos fibres

| | surface area† range m²/g | | density g/cm³ |
|-------------|--------------------------------|---------------|------------------|
| chrysotile | 13-18 | 25–4 0 | 2.55 |
| crocidolite | 2-8 | 25 - 48 | 2.55 |
| amosite | 1-5 | 20 - 25 | 3.45 |

[†] By nitrogen adsorption, outgassing temp. 100° C (Hodgson & White 1967).

Other physical properties of asbestos fibre are given in table 3. The surface areas shown cover a range from raw grades to processed varieties. The measured surface areas of asbestos fibres are of the same order as those calculated from observed mean diameters, but the upper limit of surface area calculated from the smallest observed diameters (0.01 µm for chrysotile and crocidolite, and 0.07 µm for amosite) is 5-10 times greater than the measured figures. This might point to some deficiency in the application of the nitrogen adsorption method to as bestos fibres, but it is then likely that the outgassing of fibre samples at 100 or even 200 °C before nitrogen adsorption fails to remove other tenaciously adsorbed gases or molecules from their surfaces.

Tensile strength is included here to show that amosite is the weakest, by a factor of one-half, of the three most important asbestos fibres. Amosite is the most brittle, presumably because there are more flaws in the discrete crystal structure. Consequently, when it is milled either in refining or in product processes, it will break to form a higher proportion of shorter fibres than would chrysotile or crocidolite under exactly the same conditions of work.

The densities of the two amphibole fibres are some 40 % higher than that of chrysotile, perhaps a disadvantage to amphibole producers who must sell their product by mass rather than volume. In terms of fibre physics a chrysotile aerosol will survive longer than aerosols of crocidolite or amosite (being the heavier fibres) assuming equal numbers of fibre of identical dimensions.

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One physical property of asbestos which cannot be expressed quantitatively is that of texture. In descriptive terms amosite and crocidolite are straight needle-like fibres, displaying flexibility and springiness only in macro-length forms. Chrysotile is soft and lacks springiness, because of its considerable flexibility at all lengths. Airborne chrysotile fibres within the 5 to 20 µm length range often have a randomly curved habit.

In recent years some interest has been given to the magnetic properties of asbestos fibres. Timbrell (1972) used a powerful magnetic field to align fibres in a preliminary study toward improvements in fibre measurement methods. The most interesting feature of this work is that while crocidolite fibres (Cape Province type) align parallel to the magnetic field, amosite fibres (Transvaal type) align both parallel and normal to the magnetic field. This would imply that there are structural reversals in amosite, perhaps in the form of multiple twinning along the fibre axis, the proportion of which in any one fibre determines its magnetic susceptibility. Such an explanation would be in accordance with tensile strength relationships among these amphibole fibres.

SUMMARY

In the broad context of environmental mineralogy, asbestos is not unique. In common with other industrial minerals its handling at all stages from ore extraction to industrial application releases a proportion of potentially hazardous airborne dust. To protect the working environment, there is an obligation to reduce airborne dust concentrations to a non-hazardous level by means of exhaust equipment and filters, and the dust so collected must be disposed of in a safe manner. As is well known these requirements apply widely in the mineral industry wherever stages of dry processing exist.

However, in a specific sense asbestos is unique in that it is a mineral presented in the form of extremely strong fibres which range down to sub-micrometre diameters. Moreover, the term asbestos includes several type-minerals each of which has its own distinctive physical and chemical properties.

Fibre physics are important in all aspects of dust control in the asbestos industry. The dimensional characteristics of asbestos fibre place special demands on dust exhaust equipment in terms of air flows and filter materials. Physical properties suggest that all types of asbestos fibres are comparable in the generation of respirable dusts, in that subdivision to fine fibres gives lengths, diameters and numbers of similar order. However, on a mass basis, because of density differences, equal masses of the several forms of asbestos if completely subdivided to respirable size will produce different numbers of fine fibres, chrysotile generating some 40 % more fibres than amphiboles. Surface chemistry too plays some part in that because of their high surface area, asbestos fibres will easily adsorb moisture. They are thus susceptible to changes in humidity, which may determine whether they are wholly dispersed or partially agglomerated in aerosols.

Investigations into the biological effects which have been associated with asbestos, in one way or another call upon all the properties of asbestos which have been outlined here. The dimensional characteristics of these fibres in relation to living tissue are obviously important when considering their entrapment in the airways of lungs. Indeed the definition of the dimensions of respirable fibres has been determined from consideration of the dimensions of the minutest airways of lung tissue.

From the biochemical standpoint, fine respirable asbestos fibres of high surface area have considerable capacity to adsorb other substances. They may therefore selectively adsorb the constituents of living cells and thereby upset the delicate balance of cell reproducibility. They may also adsorb pollutants from the atmosphere to be transported to the lung and deposited in the tissue. Alien substances moreover may be present on asbestos fibres due either to a primitive source or through contact with the machinery used in mining and milling operations.

Aside from this issue the basic chemistry of the types of asbestos bears consideration in relation to biological effects. Chrysotile has a totally different chemistry from that of the amphiboles and not only shows alkaline reactivity, but is susceptible to surface leaching under mild conditions which may change this reactivity. Amphibole asbestos has considerable resistance to degradation, although a little cationic leaching from the amphiboles can take place over long periods of time. The most interesting aspect of the chemistry of the amphiboles is their proton mobility, which under long-term ambient conditions may promote reductive reactions in a biochemical system.

From the view of the mineralogist and the geologist, the major forms of asbestos possess notable differences which are determined by their genetic origins. All chrysotiles are fairly high-grade metamorphic minerals, having an ultrabasic igneous origin, with the exception of the few occurrences associated with metamorphosed dolomites. There are grades of metamorphism among the chrysotiles which have given rise to marginal differences in their physical and chemical properties and thus to softer or harsher varieties of the fibre. The major forms of amphibole asbestos, the amosite and crocidolite of South Africa have a distinctly sedimentary origin. Crocidolite, both from Cape Province and Western Australia, is a product of relatively low grade dynamic metamorphism. The crocidolite and amosite of the Transvaal are metamorphic minerals of a higher grade and their development as fibrous materials appears to be closely linked with the Bushveld Igneous Complex. Anthophyllite which has been mentioned only briefly here is a product of high grade thermal metamorphism in both acidic and ultrabasic igneous rocks.

The origins of the different types of asbestos are closely linked with their differing physical, chemical and structural features and an appreciation of all these many factors is essential to an understanding of the associated biological problems.

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Discussion

- I. V. SMITH (Dept. of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.). Dr Gilson in his fascinating account of cohort studies of persons exposed to asbestos pointed out that cigarette smokers suffered about 50 times more excess mortality than non-smokers. You mentioned that amphibole could liberate hydrogen upon heating (presumably by the simultaneous oxidation of iron), and, if I understood you correctly, suggested that this might be related to the cancer problem. Would you please clarify this suggestion, and comment on the possibility of a chemical reaction between the products of inhaled cigarette smoke and amphibole in ingested asbestos. It should be noted that the oxyhornblende reaction proceeds only at elevated temperature in experimental systems (e.g. over 500 °C for a measurable reaction velocity).
- E. J. W. WHITTAKER (Dept. of Geology & Mineralogy, Parks Road, Oxford OX1 3PR). The natural assumption that amphibole fibres are likely to be bounded by (110) cleavage faces receives no support from transmission electron microscopy. Fibres thin enough to give diffraction patterns suitable for the determination of orientation commonly lie on the grid in such a way that either (100) or (010) is roughly parallel to the plane of the grid. The (010) orientation, which is common for amosite and crocidolite though not observed for tremolite, is especially irreconcilable with the presence of dominant (110) cleavage faces, since these would then make an angle of about 62° with the plane of the grid.
- Professor R. G. Burns (Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.). Dr Hodgson referred to dehydroxylation and hydrogenation reactions of amphiboles as a possible catalyst for the carcinogenic properties of blue asbestos. There is another mechanism which may be responsible for the cancerous activity of this sodic amphibole. Chemical analyses show that crocidolites (blue asbestos) are

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frequently deficient in sodium. The Na⁺ ions lie in M_4 positions of the structure, and the M_4 positions are also points of intersection of the I-beam prismatic cleavage planes of amphibole. The fibrosity of crocidolite, and hence the large surface areas, would make the sodium ions highly vulnerable to cation exchange and other chemical reactions. I wonder whether activity associated with the sodium ions holds the key to the carcinogenic properties of crocidolites and other asbestiform minerals, rather than the hydroxyl ions which are shielded within the I-beams