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CHRYSOTILE: ITS OCCURRENCE AND PROPERTIES AS VARIABLES CONTROLLING BIOLOGICAL EFFECTS

A. M. LANGER and R. P. NOLAN

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Abstract—see p. 407.

THE SERPENTINE MINERALS

CHRYSOTILE is but one of three principal serpentine minerals among the seven common varieties recognized (Table 1). Chrysotile, lizardite and antigorite, have been referred to, in the past, as polymorphs (i.e. as having the same chemistry, but different crystalline structures and, as a result, displaying different properties), but antigorite has measureable and systematic differences in chemistry from lizardite and chrysotile, and should be classified as a separate mineral. Antigorite has a unique periodic undulating wave structure, associated with a reduction of the magnesium content of the serpentine unit cell from 3.0 to ~2.8 as the structural water is reduced from 4.0 to ~3.8: alumina is also invariably found. Lizardite and chrysotile are however, virtually identical chemically, with the magnesium silicate hydrate unit cell. In accordance with the mineralogical phase rule they must be regarded as forms of serpentine different from antigorite and thus as different minerals (FAUST and FAHEY, 1962); only chrysotile and lizardite may be considered as polymorphs.

The serpentine minerals are made of a silicate sheet, $(Si_2O_5)_n^{-2n}$, which is overlain by a brucite sheet, $[Mg_3O_2(OH)_4]_n^{+2n}$ (Fig. 1) (SKINNER *et al.*, 1988). The silicate sheet's apical oxygens are structurally assigned to the overlying brucite octahedra. Occasionally, the stacking arrangements between units of the serpentine minerals differ which produces structural variations referred to as the polytypes (Table 1).

Chrysotile represents the highly fibrous (asbestiform) serpentine variety (Fig. 2). Conferences on the serpentine minerals provide excellent overview summaries (see for example WICKS, 1979). Only chrysolite has been shown to be biologically active (e.g. SCHEPERS, 1974).

Crystal structure of chrysotile

Powder and single crystal X-ray studies, and high resolution transmission electron microscopy (with selected area electron diffraction) have shown chrysotile to form either as a curled sheet silicate spiralled as a helix about a central capillary, or as concentric complete cylinders formed about a central capillary (FANKUCHEN and SCHNEIDER, 1944; TURKEVITCH and HILLER, 1949; WHITTAKER and ZUSSMAN, 1956; KALOUSEC and MUTTART, 1957; ZUSSMAN *et al.*, 1957; CLIFTON *et al.*, 1966; YADA,

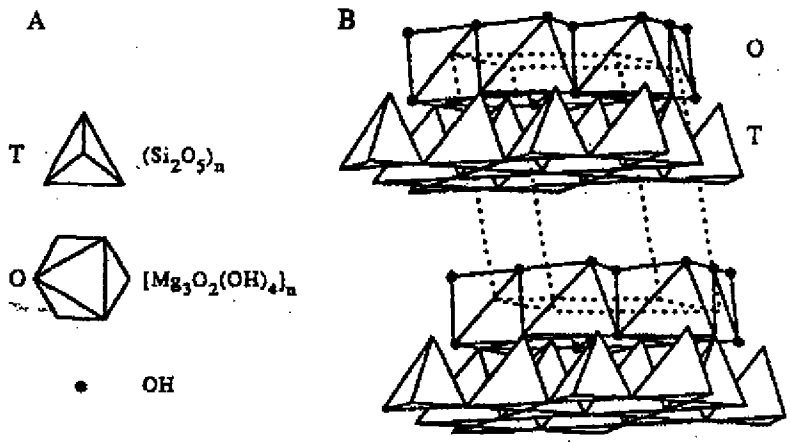

FIG. 1. The building blocks of the serpentine minerals are shown in (A). The notations shown are: T = tetrahedral 'silica' component; O = octahedral 'brucite' component. The hydroxyl group is shown by the heavy 'dot'. One of the stacking orientations of the tetrahedral and octahedral layers is shown in (B). The apical oxygens of the silica sheet substitute within the brucite layer. This figure is modified from SKINNER *et al.* (1988, Fig. 2.3).

TABLE 1. THE SERPENTINE MINERALS

Mineral name	Chemical composition	Crystal system	Polytypic forms*
Chrysotile	$Mg_3Si_2O_5(OH)_4$	Monoclinic	2M
(orthochrysotile)		Orthorhombic	2O
(parachrysotile)†		Monoclinic	2M
Lizardite‡	$Mg_3Si_2O_5(OH)_4$	Monoclinic	1M
Antigorite	$(Mg, Fe^{2+})_3Si_2O_5(OH)_4$	Monoclinic	1M
(Orthoantigorite)		Orthorhombic	2O
(Jenkinsite)	Fe-rich	—	—
(Garniernite)§	Ni-rich	—	—
Amesite	$Mg_2Al(Si, Al)O_5(OH)_4$	Hexagonal	2H, 6H
Greenalite	$(Fe^{2+}, Fe^{3+})_{2-3}Si_2O_5(OH)_4$	Monoclinic	1M
Cronstedtite	$(Fe^{2+}, Fe^{3+})_{2-3}(Si, Fe^{3+})O_5(OH)_4$	Hexagonal	1H, 2H, 3H
Berthierine	$(Fe^{2+}, Fe^{3+}, Mg)_{2-3}(Si, Al)_2O_5(OH)_4$	Monoclinic	1M
		Orthorhombic	1O

*Polytypes are different crystallographic forms of the same mineral resulting from different methods of fitting together (stacking) layers of adjacent structural units.

†Parachrysotile is the form of chrysotile in which the **b**-axis is the fibre axis rather than the **a**. (For details of the structure see MIDDLETON and WHITTAKER, 1979.)

‡Lizardite is a true polymorph of chrysotile. Both have identical chemistries but very different forms: lizardite is a plate, chrysotile is a fibre.

§Garnierite (from New Caledonia) contains substantial amounts of chrysotile, nickeliferous montmorillonite and the platy serpentine, lizardite (LANGER *et al.*, 1980).

1967, 1971, 1979; WICKS and WHITTAKER, 1975; ZUSSMAN, 1979; SKINNER *et al.*, 1988). Chrysotile has a rolled trioctahedral clay structure, and is considered the magnesium analogue of kaolinite (see DEER *et al.*, 1962). The complete chrysotile structure consists of a 1:1 mixed sheet of silica and brucite ($MgO . H_2O$). The distance between identical symmetry elements of adjacent unit cells is of the order of 0.73 nm (WHITTAKER, 1956).

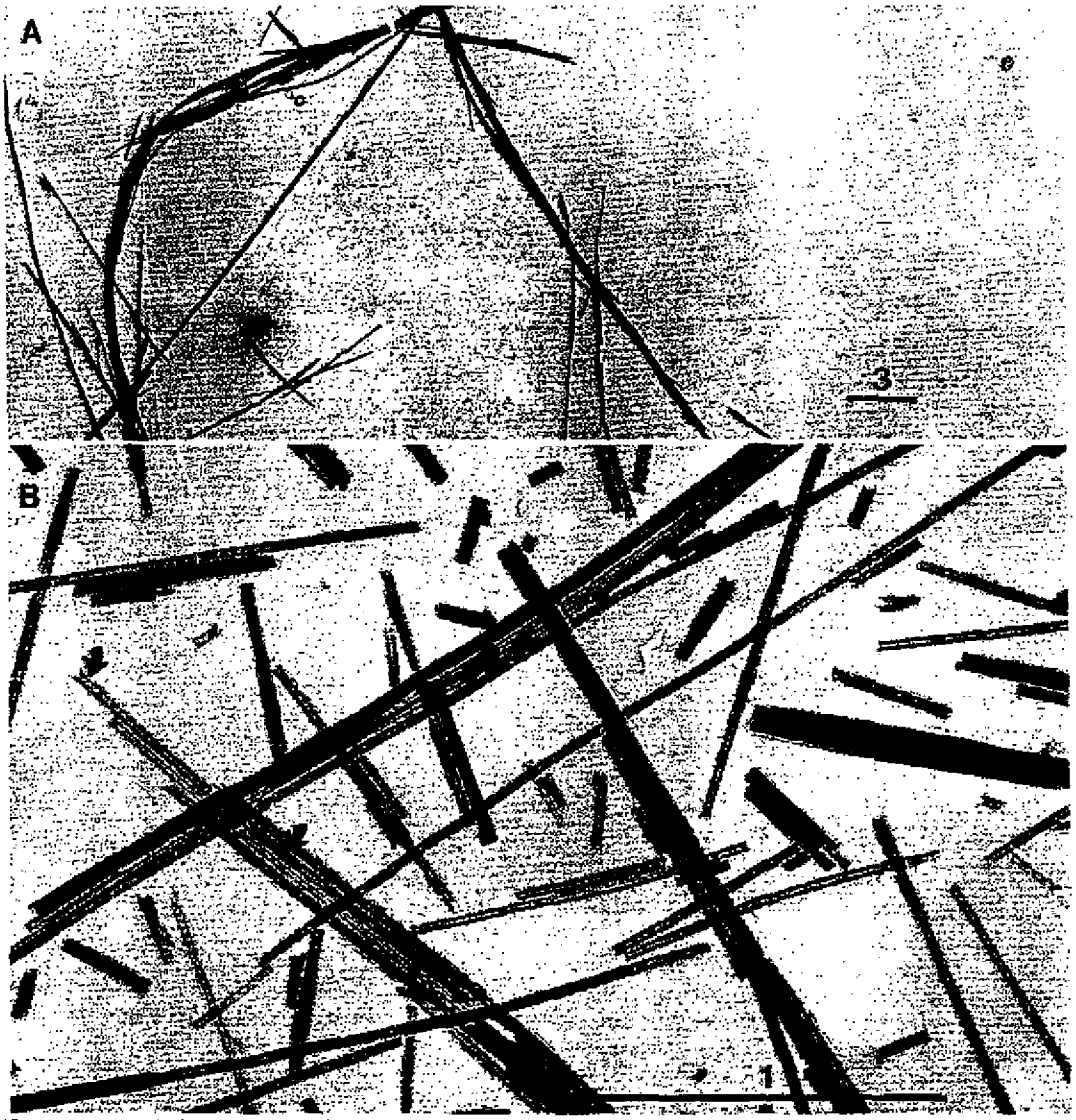

FIG. 2. Transmission electron micrographs of chrysotile: (A) is a relatively low magnification micrograph of chrysotile fibre bundles. The polyfilamentous character of chrysotile is evident. A 3 μm bar is shown for scale in (A). A high magnification micrograph showing the internal capillaries of chrysotile is shown in (B). The arrows indicate a fibril in which the capillary character changes from one of a clear central capillary to one which shows 'beading'. Capillary dimension ranges considerably among the fibrils. A 1 μm bar is shown for scale in (B).

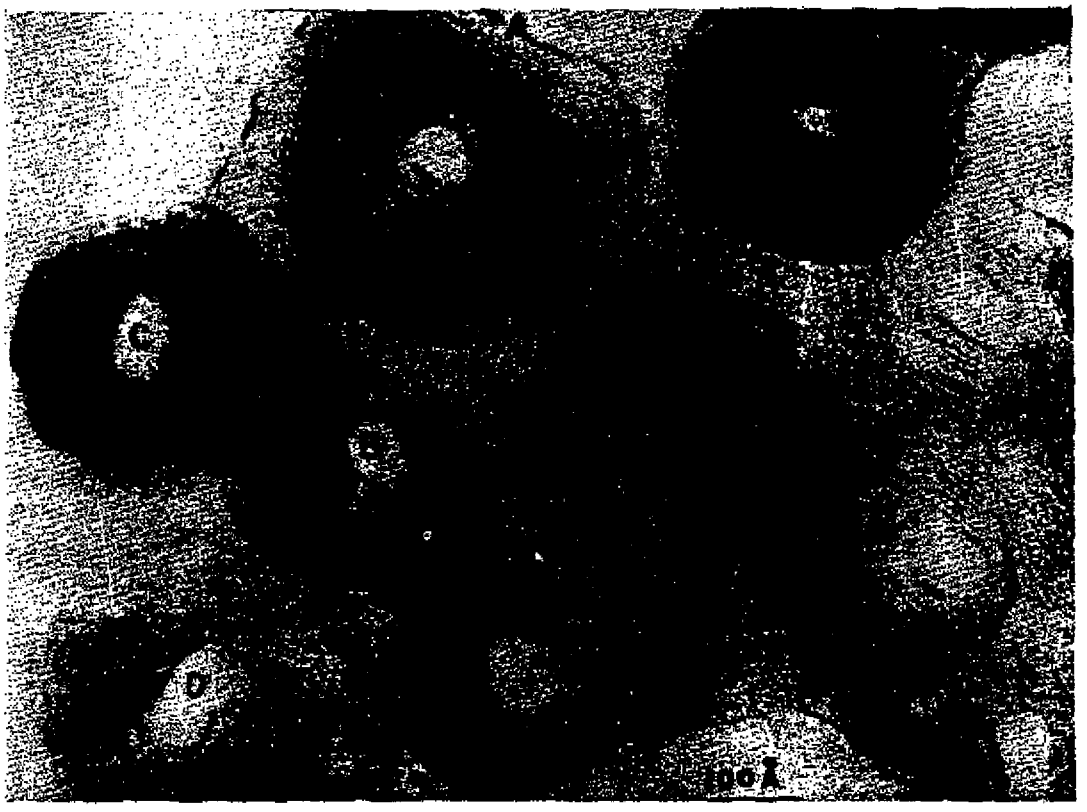

FIG. 3. High resolution transmission electron micrograph of chrysotile fibrils showing its rolled, spiral, structure. The axis of the fibre bundle is perpendicular to the section plane. Fibrils marked as A, B, display round capillaries compared to fibrils C, D, which show oblong capillaries. Fibril F displays a virtually closed capillary. Fibrils range in diameter from ~250 Å (C) to ~375 Å (A). Note some non-crystalline material in the interfibril area (noted as NC). Fibril packing is not hexagonal as indicated by B fibril which is surrounded by five other fibrils; F fibril which is surrounded by seven other fibrils. Scale marked at the bottom of the plate is 100 Å. Micrograph is from YADA (1967).

The brucite sheet (0.54×0.93 nm) is a little larger than the silicate sheet (0.50×0.87 nm) so that there is a slight structural mismatch. Several mechanisms have been suggested to explain how these two layers accommodate each other: unit rotation and/or translation in space (both rotation and tilting of unit tetrahedra and octahedra), or some limited chemical (cation) substitution.

The curvature of chrysotile's structure produces low chemical and mechanical stability. A comparison study of chrysotile's chemical stability with lizardite and with antigorite supports this (NAGY and BATES, 1952). Chrysotile is readily attacked and degraded in organic acids and is therefore one of the few silicate minerals which can change elemental composition *in vivo*. Degradation *in vivo* has been observed utilizing electron probe assays of recovered fibres (LANGER *et al.*, 1972a,b) and by whole-body assays utilizing implanted neutron-activated chrysotile in animals (MORGAN and HOLMES, 1969; MORGAN *et al.*, 1975).

The structure of chrysotile may be complicated by different stacking arrangements of its unit cells giving rise to polytypes (Table 1). Adjacent layers may be ordered parallel to the **a** fibre axis yet need not be ordered in the **ab** plane, in the translational **b** direction (in clino-chrysotile): in this case the atoms are not precisely located in the theoretical depressional sites of adjoining layers (ZUSSMAN *et al.*, 1957). These structural imperfections further impart low mechanical stability to the mineral. Milling causes the mineral to lose its crystalline character (LANGER *et al.*, 1978).

THE CHRYSOTILE UNIT FIBRIL

Electron micrographs show that single chrysotile fibrils tend to morphologically resemble hollow cylindrical tubes (BATES *et al.*, 1950; BATES and COMER, 1959; MASER *et al.*, 1960; Pundsack, 1961; WHITTAKER, 1963; CLIFTON *et al.*, 1966; LANGER and POOLEY, 1973; LANGER *et al.*, 1974). Several studies, by high resolution transmission electron microscopy, have shown the dimensions and form of the central capillaries (YADA, 1967, 1971, 1979) (see Fig. 3). Dimensionally capillaries have been found to range from approximately 2 to 13 nm (BADOLLET, 1948; PUNDSACK, 1956, 1961; BATES and COMER, 1959; MASER *et al.*, 1960; WHITTAKER, 1963; YADA, 1967, 1971; LANGER *et al.*, 1974) although dimensions of 2–4 nm are more commonly found (POOLEY, 1987). Individual fibrils have been reported up to 80 nm in width (WHITTAKER, 1963), while the range is generally 20–40 nm and the mean average is about 28 nm (POOLEY, 1987). Some authors have suggested that chrysotile fibril dimensions may vary among the ores derived from different geological localities, with Canadian fibrils tending to be greater in diameter than fibrils from the South African deposits. Several papers have demonstrated the existence of chrysotile fibrils without a visible central capillary (YADA, 1967, 1971), see Figs 2 and 3.

The organization of the fibrils into fibres may control the relative dustiness of different work environments where chrysotile ores from different geological locales and of different grades are fiberized. The ease with which this fibre disaggregates to form respirable aerosols is related to the inherent properties of the fibre grade and the amount of mechanical manipulation required for its industrial application.

THE CHRYSOTILE FIBRE BUNDLE

The chrysotile fibre is a polyfilamentous bundle of unit fibrils (Fig. 2). The unit fibrils are oriented with their fibre axis (**a**) in common alignment (for clinochrysotile). In addition to the common central capillary in each fibril, the spaces between adjacent fibrils may be either voids (channels) or partially filled channels. The filling material is a non-crystalline hydrated magnesium silicate, possibly alpha sepiolite, as proposed by BATES and COMER (1959). PUNDSACK (1961) described and HEALEY and YOUNG (1954) postulated that each of these pore structures adsorbed polar molecules differently. An amorphous-looking channel filling is evident in the micrographs produced by YADA (1967) (see Fig. 3); the interstitial channel and central capillary are pore types A and B, respectively. But Pundsack noted that his gas adsorption measurements indicated more open type A pore spaces than closed ones. These features vary among fibres derived from different ore deposits.

The chrysotile bundle possesses parallel extinction when viewed between crossed nicols by polarized light microscopy. This parallel extinction, and the complete random orientation of the fibrils constituting the chrysotile fibre bundle, produces only two measurable indices of refraction (a pseudotetragonal indicatrix) rather than the three characteristic of the monoclinic symmetry of the unit cell. Indices of refraction measured on fibres derived from ultramafic ore deposits are greater than those measured on fibres derived from silicified dolomites (LANGER and NOLAN, 1986). (Ultramafic deposits are deposits of igneous rocks, composed mainly of *mafic* minerals, i.e. minerals high in MgO, $FeO \pm CaO$ and Al_2O_3.)

Chrysotile fibres are frequently intergrown with other minerals, such as magnetite and nemalite, a fibrous form of brucite (LIEBLING and LANGER, 1972; WHITTAKER and MIDDLETON, 1979). Other minerals frequently associated in the fibre bundle include chromite and the other serpentine minerals.

MINERALOGICALLY DISCREDITED SERPENTINE MINERALS

Throughout the geological literature citations appear regarding the occurrence of hydrated magnesium silicate minerals in serpentine rocks which, because of their association, have been called serpentine minerals. Many of these minerals are so fine-grained that the individual components are not resolvable by polarized light microscopy, so that the optical properties cannot be determined. Historically only bulk properties, such as chemistry, guided classification. Bulk chemistry must necessarily reflect the composition of all minerals present, including the associated admixed ones. With the application of new instruments and methods of analysis (especially X-ray diffraction, thermal methods, transmission electron microscopy) many original serpentine minerals were found to be mixtures of the other, more common, forms of serpentine. For example, antillite, marmolite and steatoid, have been found to be complex mixtures of submicroscopic chrysotile and lizardite, and baltimorite, picrolite and williamsite to be mixtures of chrysotile and antigorite. Many of the serpentine minerals originally described have been mineralogically discredited. A detailed discussion and characterization of these mineral admixtures is found in FAUST and FAHEY (1962).

TABLE 2. ROCK TYPES WHICH GIVE RISE TO CHRYSOTILE ORE (AFTER LANGER and NOLAN, 1986)

Rock types*	Major minerals†	Associated minerals‡ (ores)		Associated minerals§ (residual [r] + reaction products [R])
Gabbro	Pxn‖, Oliv¶, Plag**	Magnetite	Fe_3O_4	Nemalite (brucite) (R)
		Chromite	$FeCr_2O_4$	Talc (R)
Norite	Pxn, Plag	Pyrite	FeS_2	Amphiboles* (R)
		Pyrrohtite	FeS	Chlorite (R)
Pyroxenite	Pxn, Oliv	Niccolite	NiAs	Plagioclase (r)
		Arsenopyrite	FeAsS	Magnetite (R)
Peridotite	Oliv, Pxn	Cobaltite	CoAsS	Lizardite (R)
		Platinum	Pt	Antigorite (R)
Dunite	Oliv, Pxn			
Picrite	Pxn, Oliv, Plag			
Dolomite	Dolo††, Calc‡‡	Copper minerals		Amphiboles‖‖
	Qtz§§	Manganese minerals		Talc (R)
				Carbonates (r)

*These rocks, high in MgO, $FeO \pm CaO$, Al_2O_3. Referred to in the geological literature as ultramafics. Dolomite originated as sedimentary rock.

†Mineral content is generally more complex. Most minerals are solid–solution mixtures of end-members.

‡Spinels, sulphides, arsenides and element minerals are common to the ultramafic rocks. Both copper and manganese minerals are common to dolomites.

§(R): minerals produced by reaction of pre-existing minerals and water during serpentinization process; (r): minerals as residuals which have survived the metamorphic process.

‖Pyroxene: expressed in serpentine reactions as enstatite, $MgSiO_3$.

¶Olivine: expressed in serpentine reactions as forsterite, Mg_2SiO_4.

**Plagioclase: $NaAlSi_3O_8$–$CaAl_2Si_2O_8$. Generally CaO- and Al_2O_3-rich.

††Dolomite: expressed in serpentine reactions as $CaMg(CO_3)_2$.

‡‡Calcite: expressed in serpentine reactions as $CaCO_3$.

§§Quartz: expressed in serpentine reactions as SiO_2.

‖‖Amphibole: generally formed as products of reaction, especially tremolite. $Ca_2Mg_5Si_8O_{22}[OH]_2$.

THE ORIGIN OF SERPENTINE ROCK

Serpentine rock (serpentinite) is derived through chemical reorganization of minerals constituting either an ultramafic or a silicified dolomite rock. Under the appropriate conditions of temperature and pressure, and with the availability and activity of water, precursor rocks give rise to serpentines (see DEER *et al.*, 1962). The original rock types, mineral components and associated minor mineral components, which give rise to chrysotile ore specifically, are given in Table 2.

Ultramafic rocks may contain variable quantities of olivine and pyroxene, especially forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$). These participate in a number of reactions leading to the formation of serpentine (Table 3, reactions I–IV and VI), and control to large degree the appearance of the admixed associated mineral brucite. Forsterite alone (the olivine mineral which forms the ultramafic rock-type dunite) alters to serpentine and brucite. In the presence of enstatite (a magnesium pyroxene mineral) the reaction produces a silica-saturated serpentine only. Hence, when the rock type changes from dunite to periodotite, the likelihood of brucite being present decreases (see reactions I and II, Table 3). Rock type controls associated trace minerals. The other minerals which constitute ultramafic rocks may survive these reactions to form either trace or minor minerals in serpentinites.

In the serpentinization of dolomitic sedimentary rock silica (SiO_2) must be introduced into the $CaMg(CO_3)_2$ precursor rock type. This leads to the formation of

TABLE 3. PRINCIPAL REACTIONS LEADING TO THE FORMATION OF CHRYSOTILE (SERPENTINE)

(I)	Forsterite + enstatite + water	→ Serpentine (chrysotile)
	$Mg_2SiO_4 + MgSiO_3 + 2H_2O$	$\rightarrow Mg_3Si_2O_5(OH)_4$
(II)	Forsterite + water	→ Serpentine (chrysotile) + brucite
	$2Mg_2SiO_4 + 3H_2O$	$\rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$
(III)	Forsterite + quartz + water	→ Serpentine (chrysotile)
	$3Mg_2SiO_4 + SiO_2 + 2H_2O$	$\rightarrow 2Mg_3Si_2O_5(OH)_4$
(IV)	Enstatite + water	→ Serpentine (chrysotile) + talc
	$6MgSiO_3 + 3H_2O$	$\rightarrow Mg_3Si_2O_5(OH)_4 + Mg_3Si_4O_{10}(OH)_2$
(V)	Dolomite + quartz	→ Calcite + forsterite + carbon dioxide gas
	$2CaMg(CO_3)_2 + 2SiO_2$	$\rightarrow 2CaCO_3 + Mg_2SiO_4 + 2CO_2$
(VI)	Enstatite + quartz + diopside + water	→ Tremolite
	$3MgSiO_3 + SiO_2 + 2CaMg(SiO_3)_2 + H_2O$	$\rightarrow Ca_2Mg_5Si_8O_{22}(OH)_2$
(VII)	Dolomite + quartz + water	→ Tremolite + calcite + CO_2
	$5CaMg(CO_3)_2 + 7SiO_2 + H_2O$	$\rightarrow Ca_2Mg_5Si_8O_{22}(OH)_2 + CaCO_3 + CO_2$
(VIII)	Serpentine + calcite + carbon dioxide	→ Tremolite + dolomite + water
	$Mg_3Si_2O_5(OH)_4 + 9CaCO_3 + 5CO_2$	$\rightarrow Ca_2Mg_5Si_8O_{22}(OH)_2 + 7CaMg(CO_3)_2 + 7H_2O$

forsterite (Table 3, reaction V) which is then converted to serpentine as shown in reactions I–III in Table 3. Therefore, both ultramafic and carbonate precursor rock types may form serpentine minerals under appropriate conditions.

CHEMISTRY OF CHRYSOTILE

Major oxides

The crystal chemical formula representing the unit cell for chrysotile is $X_6[Z_4O_{10}][OH]_8$. X represents octahedrally co-ordinated cations of the brucite layer. Magnesium most commonly occupies this position up to the available 6.00 sites, although other cations (e.g. iron, nickel and manganese) may take its place. Z represents the tetrahedrally co-ordinated cation within the silica layer and is almost entirely filled by silicon to the hypothetical 4.00 sites available. In rare cases, aluminium may substitute for silicon. The hydroxyl group may be replaced by oxygen, fluorine or chlorine, but again, this rarely occurs. All substitutions are controlled by the original rock types and their minerals and conditions of growth.

The bulk chemistry of some representative fibres derived from ultramafic precursor rocks is given in Table 4. The magnesium oxide content is invariably present in greater concentration, than can be assigned to silica, in the theoretical formulation of chrysotile (the serpentine cell). The excess MgO most frequently represents admixed fibrous brucite. Iron oxides are also high, reflecting the presence of magnetite. The alumina and alkali metals usually reflect the presence of both feldspar and chlorite.

The bulk chemistry of some representative fibres derived from silicified dolomites is given in Table 5. Unlike the ultramafic-derived fibres, the silica content tends to be greater in concentration than the magnesia. This excess reflects free silica (usually in the form of quartz) associated with the fibre. The calcium oxide may reflect admixed carbonate minerals, which is supported by the presence of CO_2 in some analyses. The manganese oxide commonly present is associated with marine-derived sedimentary rocks.

TABLE 4. BULK CHEMISTRY OF REPRESENTATIVE CHRYSOTILE FIBRES DERIVED FROM SERPENTINE ULTRAMAFICS

Oxide	(1)	(2)	(3)	(4)	(5)	(6)
SiO_2	43.35	41.80	41.97	37.63	40.49	38.27
TiO_2	—	0.05	—	—	—	Tr
Al_2O_3	—	0.11	0.10	1.79	1.27	0.73
Fe_2O_3	—	0.68	0.38	3.16	2.53	5.10
FeO	—	0.05	1.57			
MgO	43.66	42.82	42.50	42.43	41.41	40.81
CaO	—	0.10	—	—	—	0.10
Na_2O	—	0.03	—	—	—	Tr
K_2O	—	0.01	0.08	—	—	Tr
H_2O^+	12.99	14.04	13.56	14.50	14.03	14.88
H_2O^-	—	0.28	—			
MnO	—	—	—	—	—	Tr
Other*	—	0.01	—	—	—	—
Total %	100.00	100.11	100.26	99.51	99.76	99.89

(1) Ideal formula: $Mg_6Si_4O_{10}(OH)_8$. Double cell.
(2) Aboutville, New York: Analysis in DEER *et al.* (1962).
(3) Danville, Quebec: Analysis in DEER *et al.* (1962).
(4) Thetford, Quebec: Analyses-average five fibres in FAUST and FAHEY (1962).
(5) Quebec: Analyses average 11 fibres in FAUST and FAHEY (1962).
(6) Quebec: Analysis average eight fibres in FAUST and FAHEY (1962).
*'Other'—CO_2; SO_3.
H_2O^+: water stable until 105°C—considered bound ($E \geq 15$ kcal mol^{-1} to drive off).
H_2O^-: water driven off <105°C—considered sorbed ($E \leq 5$ kcal mol^{-1} to drive off).
Tr: trace.

TABLE 5. BULK CHEMISTRY OF REPRESENTATIVE CHRYSOTILE FIBRES DERIVED FROM SILICIFIED DOLOMITES

Oxide	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
SiO_2	43.35	41.83	42.02	40.75	43.00	42.02	41.56	42.53
TiO_2	—	0.02	—	—	0.02	—	—	—
Al_2O_3	—	0.30	0.52	1.82	0.27	0.52	1.27	0.29
Fe_2O_3	—	1.29	0.19	0.74	1.08	0.19	0.64	0.35
FeO	—	0.08	0.11		0.17	0.11		0.05
MgO	43.66	41.39	41.44	40.69	40.00	41.44	42.05	41.55
CaO	—	Tr	—	—	1.43	—	—	0.03
Na_2O	—	—	—	—	0.03	—	—	0.04
K_2O	—	—	—	—	0.02	—	—	0.03
H_2O^+	12.99	13.66	14.04	12.65	13.17	14.04	12.92	13.69
H_2O^-	—	1.57	1.67	1.86	0.53	1.64	1.39	1.27
MnO	—	0.04	0.03	—	0.16	0.03	—	0.06
Other	—	—	—	—	0.78*	—	—	—
Total %	100.00	100.18	99.99	98.51	100.71	99.49	99.83	98.89

(1) Ideal formula.
(2) Transvaal, South Africa, Limestone, in DEER *et al.* (1962).
(3) Arizona, Gila County, in DEER *et al.* (1962).
(4) Arizona, Coon Butte, in DILLER (1919).
(5) Arizona, Globe, in FAUST and FAHEY (1962). Other = CO_2; ZnO; Cr_2O_3.
(6) Arizona, Globe, in FAUST and FAHEY (1962).
(7) Arizona, Ash Creek, in DILLER (1919).
(8) Chrysotile from carbonate rock, in FAUST and FAHEY (1962), average eight fibres.

Trace elements

Nickel, chromium and cobalt have been identified as trace elements in chrysotile ores derived from ultramafic bodies. Iron is ubiquitous. These elements may occur as substitutional cations within chrysotile (for magnesium) or as major elemental components of associated trace mineral phases, such as chromite.

NATURE OF CHRYSOTILE ORE

Continuous scan X-ray diffraction analysis of bulk specimens of fibre derived from ultramafic and carbonate sources produces the standard pattern of chrysotile with little variation. These are line-broadened, characteristic of particles on the order of 100 nm and less in diameter. Clino-chrysotile is the prevalent polytype in the specimens examined (tabulated X-ray data appear in LANGER and NOLAN, 1986).

Canadian fibres show gross contamination both with magnetite and with brucite. Slip fibre from the Jeffrey pit is predominantly brucite and suggests that the harshness of some Canadian fibre is, in part, related to the amounts and scale of intercalcated intergrowth mineral. The mineral purity of chrysotile ore will vary as a function of the rock type giving rise to it, of local geologic conditions and of the nature of the individual ore seam.

THE FORM OF FIBRE IN THE ORE

Chrysotile fibres can occur in ore bodies in three recognized forms, given as follows.

(1) *Cross-fibre*

Cross-fibre occurs with fibre axis (a) at right-angles to the seam or vein in which it occurs. These fibre seams tend to form as thin lenses which follow both cracks and crevices in the serpentine mass itself. Cross-fibre seams are usually discontinuous so that they may appear, disappear and reappear within a distance of several metres. They may have widths from millimetres to ~10 cm but in general are 2–3 cm.

(2) *Slip-fibre*

In serpentine masses which are faulted or sheared, the fibre may develop an orientation with the fibre axis parallel to the translated rock faces. The fibre therefore develops with its long axis (a) parallel to the seam. Slip-fibre tends to be longer, more admixed with non-chrysotile minerals (WHITTAKER and MIDDLETON, 1979) and to possess fibre bundles with greatly reduced tensile strength compared to cross-fibre. Occasionally, slip-fibre may compare favourably in properties with cross-fibre, as with chrysotile mined in southern Rhodesia (Zimbabwe). In folded chrysotile deposits slip-fibre may be intermixed with cross-fibre (see SINCLAIR, 1959).

(3) *Massive-fibre deposits*

Massive chrysotile occurs within serpentines in the absence of any apparent structural control of fibre growth. These deposits occur principally in altered ultramafic bodies where the entire serpentine has undergone mineralization to chrysotile. Such deposits occur in the New Idria area of California and in Stragad, in the former Yugoslavia. Here, the collision of large structural plates (as in plate

tectonics) has thrust ultramafic bodies, derived from the upper mantle, through the crust where they have undergone extreme fracturing and alteration to serpentine. The chrysotile ore has been recovered through surface open-pit operations at New Idria. The serpentinized ultramafic comprises approximately 60% chrysotile fibre.

MINERALS ADMIXTURED WITH CHRYSOTILE ORE

Alteration of precursor rocks to serpentine may, depending on local geological conditions, include the survival of pre-existing minerals (Table 3). Additionally, especially for the ultramafic-derived chrysotile, the serpentinization reaction may result in the formation of nemalite (fibrous brucite), magnetite, tremolite, anthophyllite and a number of other minerals (BADOLLET, 1952; HUGGINS and SHELL, 1965; BOWLES, 1955). The quantities and sizes of associated minerals may range considerably.

There have been reports concerning the frequency of tremolite fibre in pulmonary tissues of miners, millers and factory workers (see this Workshop). These suggest that the associated amphibole in chrysotile ore plays a role in the etiology of some diseases which follow chrysotile exposure. However, of 42 analyses of chrysotile fibre by FAUST and FAHEY (1962) only 14 contained detectable quantities of CaO, and of these 14 more than half also contained Al_2O_3 and/or CO_3, suggesting the presence of a feldspar and/or of a carbonate mineral. Tremolite is not ubiquitous nor homogenous in all chrysotile ores. A study of 81 chrysotile samples by ADDISON and DAVIES (1990) showed the presence of tremolite in only 28 ($\sim$34%) at an average concentration of 0.09%, the analytical sensitivity of the techniques employed being 0.01% (100 ppm) by mass. More than trace amounts of tremolite fibre may be present in some ores, and in some specimens, and only in these instances may be detectable (ADDISON and DAVIES, 1990).

Our laboratory has examined chrysotile ore from Bell mine, Thetford, Quebec. Tremolite was detected, at very low concentrations, by transmission electron microscopy. The morphology of the particles found, and selected area electron diffraction characterization, showed that they were cleavage fragments, not asbestos fibres (Fig. 4). This held for fibres of high aspect ratio ($\sim$10:1) as well as for fragments not classed as fibres. If tremolite asbestos is present in the ore, its concentration must be below the detection level ($\sim$0.01%).

PROPERTIES OF CHRYSOTILE

Harsh and soft chrysotile

There appear to be differences in the general physical condition, for example in the relative flexibility, of chrysotile fibres from different geological locales and even within the same deposit. These have been termed harsh fibre and soft fibre. Chrysotile naturally occurs with a range of industrial properties depending on its geological origin and its grade (COSSETTE and DELVAUX, 1979). The relative flexibility and feel of the fibre bundle has been used to distinguish among these (BADOLLET and GANTT, 1965). Although the terms harsh and soft have been applied to suggest extreme characteristics, fibres occur with a range of properties between these extremes (BADOLLET, 1948).

Occasionally, fibre bundles are found that do not flex to angles greater than 90° and that possess all the physical attributes of harsh fibre, yet are not harsh. These tend to be fibre bundles intergrown with mineral impurities, such as magnetite and nemalite. The

removal of these 'contaminant' minerals from the fibre, where possible, restores its soft, flexible character. Slip fibre tends to be harsh and nemalite-rich.

Owing to their straight splinter form harsh fibres tend to behave more like amphibole asbestos fibres when aerosolized. Inhalation of respirable straight fibres is associated with greater penetration to the terminal bronchioles as compared to curly fibres (TIMBRELL, 1965).

In our laboratory soft chrysotile which had been heated (temperatures between 200 and 400°C) behaves like harsh fibre in water, i.e. it settles rapidly, does not form a gel and sheds water easily from its surface. Fibres were heated in order to speed up filtration time of water through chrysotile filter pads. This change in behaviour has enabled the experimental pathologist to use chrysotile which had been heated for intracavitary (injection) animal studies.

Chemical stability of chrysotile

The chemical stability of chrysotile depends on its environment. When in contact with dilute acids, or even aqueous medium at pH < 10, magnesium readily disassociates from the fibre surface (HARGREAVES and TAYLOR, 1946; NAGY and BATES, 1952; ATKINSON, 1973). On a comparative basis, chrysotile is much less stable than the other serpentine minerals. Parachrysotile, with its **b** axis as the fibre axis, is the least stable polymorphic form (HARGREAVES and TAYLOR, 1946) and readily disassociates in water.

Magnesium loss *in vivo* has been demonstrated both by electron microprobe analysis of fibres recovered from tissues and by studies of neutron-activated fibres implanted into laboratory animals (see review in MORGAN *et al.*, 1977; JAURAND *et al.*, 1977; LANGER and NOLAN, 1986). Chrysotile is degraded rapidly in acids and slowly in bases. Kinetic studies of aqueous dissolution has shown activation enthalpies as low as 5.5–6.5 kcal mol^{-1} (CHOI and SMITH, 1972).

The biodegradation process is diffusion-dependent, a function of the ability of magnesium in some form to migrate through the silica skeleton outwards from inside the fibre. The liberation of magnesium from the structure leaves a leached fibre, whose surface area is greatly increased, reaching values of 350 $m^2\ g^{-1}$. Although the fibre shape may be retained in some instances, its physico-chemical properties are altered (ATKINSON, 1973).

Physical stability of chrysotile

Chrysotile loses its crystalline character when it is comminuted by impaction milling (LANGER *et al.*, 1978). In LANGER *et al.*'s (1978) study structural changes were followed by X-ray diffraction, by electron spin resonance and by i.r. spectroscopy. Grinding reduced the intensity of selected X-ray reflections, which indicated disordering along the b-axis, and extensive ball milling can produce a material which is X-ray amorphous. The loss of crystallinity is paralleled by changes in its surface character, that is, of the ability to reduce free radicals, bind organic molecules and a loss of membranolytic activity.

Milling has been used further to reduce the UICC chrysotile fibres prior to administering them to animals. The loss of the ability to form a gel may have resulted from the alteration of the mineral surface, as well as from the reduction of fibre length.

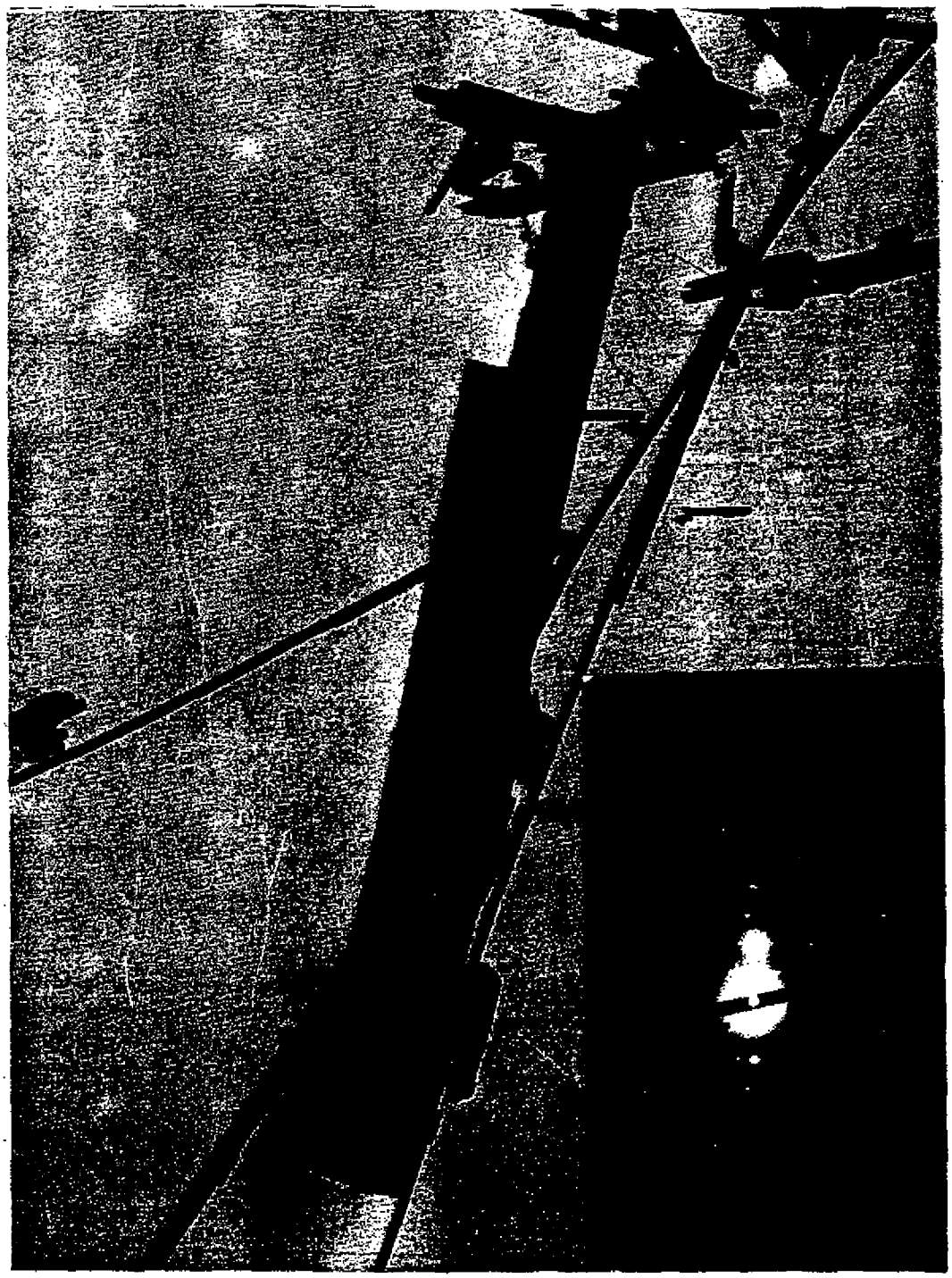

FIG. 4. Tremolite found in Bell mine chrysotile ore at Thetford, Quebec. Tremolite 'fibre' is 4.2 μm in length, ~0.45 μm in width with a resulting aspect ratio of ~9.3:1. Nearby chrysotile fibrils show diameter up to 0.041 μm (~410 Å). The insert is a selected area electron diffraction pattern obtained on the tremolite particle edge. The pattern shows reciprocal lattice vectors h, k, l. Circles form strong diffraction nets containing b^*. Calculation of d-spacing for b^* is about 9.1 Å. The tremolite orientation is that commonly observed for cleavage fragments rather than asbestiform fibres.

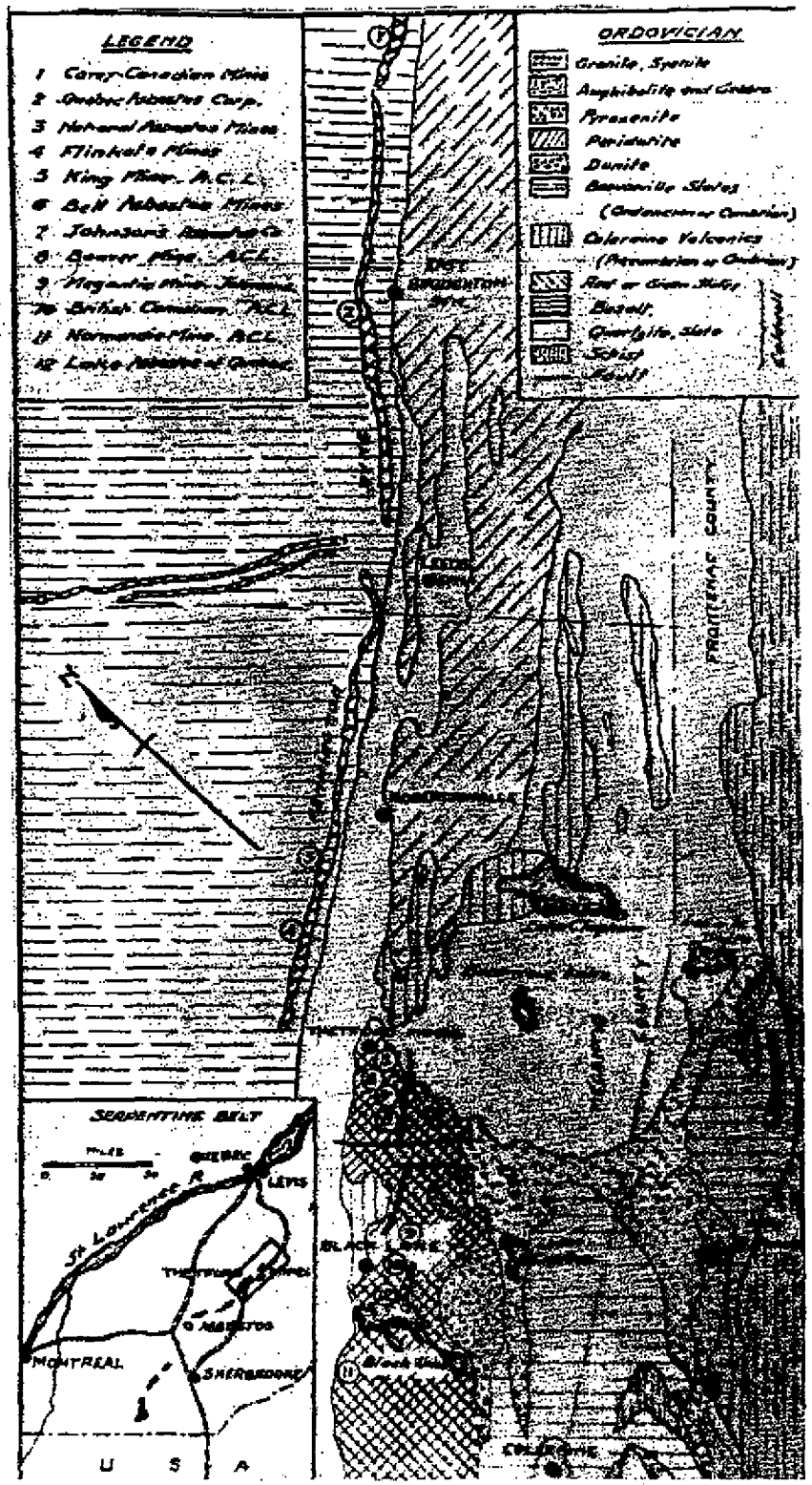

FIG. 5. General geological map and location of principal chrysotile mines in the Quebec Eastern Townships. The town of Asbestos, with its nearby Jeffrey pit, lies to the southwest (see insert map). The geological map indicates an abundance of ultramafic rock types (pyroxenite, dunite, periodolite). The UICC Chrysotile 'B' is constituted of ores from the Jeffrey pit and from seven mines in the Thetford–Black Lake area. Figure from SINCLAIR (1959).

Impurities incorporated during mining, milling, processing and fabrication

Occasionally, during the processing of chrysotile asbestos, small amounts of adventitious substances are inadvertently admixed with, or adsorbed onto, the fibre (BADOLLET, 1952; HARINGTON, 1962, 1965; WAGNER *et al.*, 1973; BARBEAU *et al.*, 1985). The biological importance of these additional abraded metal chips and organic compounds has been the subject of much speculation and study.

Adsorption of exogenous hydrocarbons onto the chrysotile surface also occurs naturally (HARINGTON and ROE, 1965; HARINGTON, 1965), though this is less common than the contamination which results from industrial manipulation.

Density of chrysotile

Natural chrysotile fibres display a range of densities: Arizona chrysotile (serpentinized dolomites) values reported between 2.19 and 2.25 g cm^{-3} (PUNDSACK, 1956; HUGGINS and SHELL, 1965), and that from Canada is approximately 2.56 g cm^{-3} (BATES and COMER, 1959; PUNDSACK, 1956). These reported ranges in the density of chrysotile have been attributed both to mineral impurities intercalated within the fibre bundles and to the presence of interfibril and intrafibril alpha sepiolite. High-density chrysotiles are probably intergrown with other minerals, especially magnetite and chromite, in ultramafics, and carbonate minerals in dolomite-derived ores.

Surface character

Chrysotile possesses a complex surface and behaves like an amphoteric compound depending on the local pH conditions. This behaviour befits the outermost brucite layer, $Mg(OH)_2$ (LANGER and WOLFF, 1978).

Surface hydroxyl groups may interact with organic compounds either to reduce or to oxidize them. The proton-donor character of the surface has been described previously (LANGER *et al.*, 1978). Reduction of organic compounds on chrysotile's surface was recognized and followed by ROBOCK and KLOSTERKOTTER (1971). Chemisorption, free-radical generation and acid–base interaction are functions of surface manipulation (LANGER *et al.*, 1978). SCHNITZER and BUNESCU (1970) noted that proton-accepting compounds bound to chrysotile, but not as well as to quartz.

Chrysotile is isoelectric (zero charge), over the pH range ~10.0–12.0, and tends to have a positive charge at physiological pH. The surface charge of chrysotile has been found to be positive, with a value which may range between 40 and 100 mV, as determined by PUNDSACK (1956, 1961). The positive charge of chrysotile tends to increase as pH decreases (NAUMANN and DRESHER, 1966). As the surface continues to react in acids, the magnesium depletion will eventually drive the zeta potential from positive charge, to zero charge, and then to negative charge, as is commonly observed for silicate surfaces.

Because of its strong positive charge, polyanions bind strongly to chrysotile, and for example carboxymethylcellulose does so to the extent of blunting its cytotoxicity (MACNAB *et al.*, 1967; SCHNITZER and BUNESCU, 1970; SCHNITZER and PUNDSACK, 1970; HARINGTON *et al.*, 1971).

The surface properties of chrysotile may be altered in an aggressive chemical environment or by aggressive mechanical treatment (impact grinding).

TABLE 6. LOCALES OF COMMERCIALLY IMPORTANT CHRYSOTILE EXPLOITATION—BY COUNTRY (*ca* 1955)

Australia
Brazil
Canada
China
Cyprus
Czechoslovakia
India
Italy
Kazakhstan
Kenya
Nyasaland
Republic of South Africa
Russia
Tanganyika
Uganda
United States of America
Uruguay
Venezuala
Zimbabwe (formerly Rhodesia)

Note: In 1955, more than half the chrysotile produced in the world came from two countries: Canada and the Soviet Union. Twenty-five nations are currently producing it (see PIGG, 1994). Only seven produce the bulk of the world's fibre: Brazil, Canada, China, Russia, South Africa, Zimbabwe and Kazakhstan.

DISTRIBUTION OF CHRYSOTILE DEPOSITS IN THE WORLD

Both serpentinite masses and silicified dolomites are found virtually everywhere. Chrysotile asbestos is ubiquitous. Nevertheless, the principal producers of the fibre are limited in number and each has multiple locales of exploitation (see Table 6) (PIGG, 1994). Some of the important producing countries require detailed description.

Canada

The Eastern Townships of Quebec is a major world producer (Fig. 5). For a distance of approximately 50 miles, from the Jeffrey pit, extending northeast to the operation for Carey Canadian, a number of mines produce the bulk of Canadian fibre (Fig. 5). The principal producers lie near the towns of Asbestos, Black Lake, Thetford and East Broughton. The asbestos operation on the west coast of Canada, in British Columbia, was a major producing area, but has been closed (Cassiar). The mine located at Baie Verte, Newfoundland, has also been shut down (the Advocate Mine).

Zimbabwe (formerly southern Rhodesia)

All of the important chrysotile workings in Zimbabwe lie in its southern regions between the Limpopo River on the south and the Zambesi River to the north, along the strike of the geological feature called the Great Dyke. The dyke runs a distance of approximately 335 miles in a north–south direction. Many important chrysotile deposits lie along the dyke (Fig. 6). Of these mines, the Shabani and the Mashaba are the main workings. These ores are low in iron and represent both high quality cross-

fibre and some slip-fibre. The UICC A chrysotile specimen is a mixture of ores from Shabani and Mashaba.

Republic of South Africa

Just south of the Limpopo River, in the Transvaal, a number of chrysotile deposits are commercially exploited. The deposits are both serpentine- and carbonate-derived: they include those at Barberton (which includes areas in Swaziland), at Havelock (in Swaziland), at Kaapsche Hoop, and those of carbonate origin in the Carolina area, at Kalkkloof and at Krugersdorp.

United States

The United States has exploited chrysotile in the state of Vermont, the southern extension of the Quebec deposits. There has also been major fibre production in Globe, Arizona, principally an iron-free carbonate deposit. In California, at New Idria, the deposit consists entirely of mass-fibre, which constitutes the bulk of the serpentine. The New Idria deposit was worked by a number of important asbestos producers and the fibre was considered short according to commercial-grade classification (the Quebec Screening System for the deposit yields a value of 0–0–0–16). Of the U.S. deposits only California produces fibre today, and only for export.

THE UICC STANDARD REFERENCE SAMPLES OF CHRYSOTILE ASBESTOS

At the conclusion of the New York Academy of Sciences Asbestos Conference, in October 1964, a number of participants remained in New York to form working groups to discuss important issues in asbestos research. [The groups met under the auspices of the International Union Against Cancer (UICC) which included the Geographical Pathology Section of the Working Group on Asbestos and Cancer.] They met for several days, and made recommendations which were included as an appendix in the conference proceedings (SELIKOFF and CHURG, 1965).

Two principal sets of recommendations were put forward by the physics and chemistry sub-group: (1) that an analytical protocol suggested for the identification and quantification of asbestos in human tissues be adopted; and (2) that a set of well-characterized asbestos specimens be prepared for use in experimental work. Among the fibres recommended for collection, preparation and characterization, were chrysotiles from Arizona, Havelock (Swaziland), Quebec and Shabani (Zimbabwe).

The UICC developed a standard reference set of five asbestos samples for the main types of asbestos which accounted for 98% of all asbestos used commercially (TIMBRELL *et al.*, 1968a). These included two chrysotile specimens: UICC Chrysotile 'A' (Zimbabwe) and UICC Chrysotile 'B' ("Canadian Chrysotile, from eight mines roughly in proportion to their annual production, and pooled . . .").

About 3000 lbs (1360 kg) of each asbestos specimen was used for this purpose. All of the asbestos specimens were 'Grade IV' on the Canadian Quebec Screening Scale (QSS), or the nearest equivalent (for ores received from countries which did not grade according to this method). It is noteworthy that the original description of the materials as Grade IV is actually the standard Canadian class Group 4, also commercially referred to as shingle fibres. This particular group in the QSS classification includes seven *grades* of fibre (4D–4Z, each grade with its own QSS

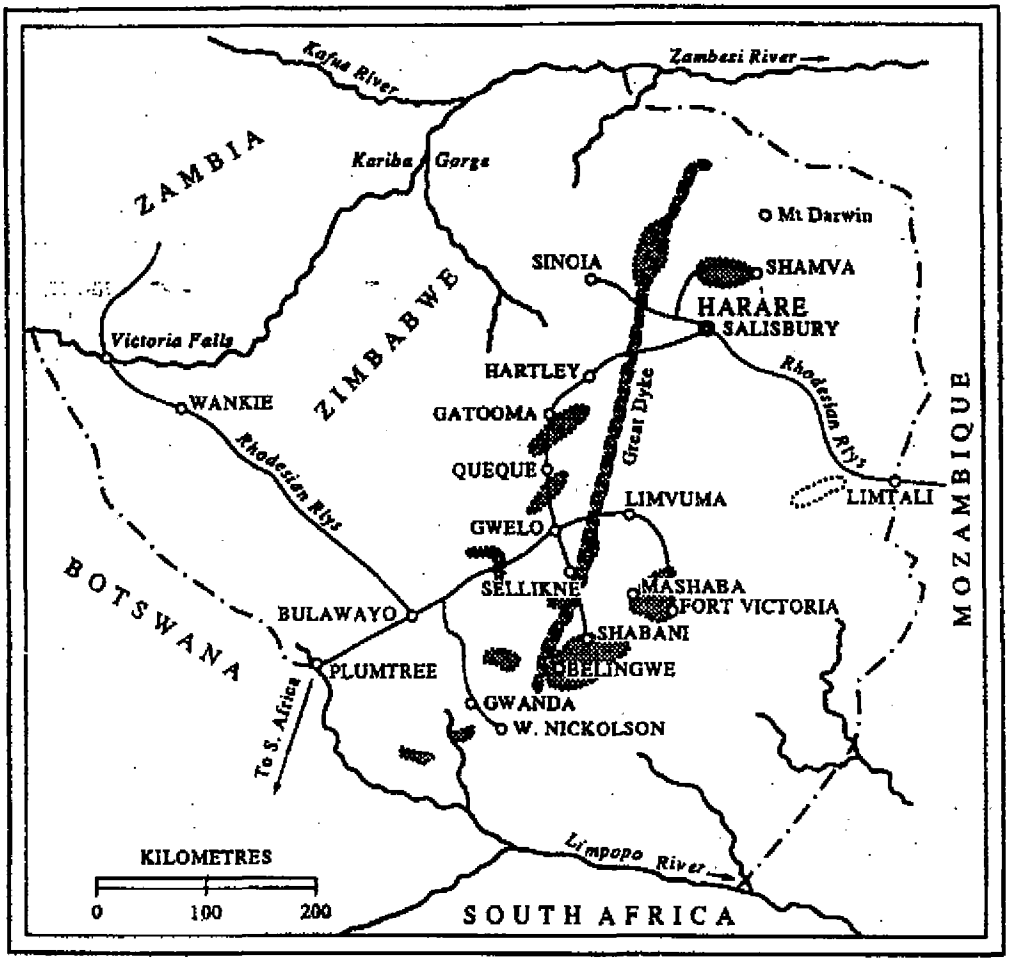

FIG. 6. The location of chrysotile producing areas in southern Rhodesia (Zimbabwe) along the Great Dyke. The UICC Chrysotile A specimen is a mixture of ores from principally the Shabani and from the Mashaba deposits. Figure from SINCLAIR (1959). This map also includes historical names and shows locations of important chrysotile workings (shaded areas) in the country formerly called southern Rhodesia. It is shown in this manner because documents published prior to 1980 contain these names and locations. The following are the modern names.

Old map name	New map name
Rhodesia	Zimbabwe (shown on map)
Rhodesian rails	Zimbabwe rails
Northern Rhodesia	Zambia (shown on map)
Bechuanaland	Botswana (shown on map)
Portuguese East Africa	Mozambique (shown on map)
Salisbury	Harare (shown on map)
Hartley	Kadoma
Gatooma	Umniati
Wankie	Hwange
Queque	Kwekwe
Gwelo	Gweru
Umvuma	Mvuma
Selukoe	Somabula
Fort Victoria	Chibi
Shabani	Zvishavane
Belingwe	Mberengwe
Gwanda	Colleen Bawn

Note: area in Republic of South Africa south of the Limpopo River is the Transvaal.

value). Canada provides approximately 37 grades of milled asbestos fibre among the various groups.

The aim of the UICC Working Group was to obtain material of relatively short fibre length, with a minimum of rock fragments. Approximately 1200 lbs (545 kg) of the 3000 lb bank of material was milled and homogenized: the remainder was stored for future use. The details of the preparation and blending processes are described by TIMBRELL and RENDALL (1971).

The Canadian sample, UICC Chrysotile 'B', resulted from blending approximately 1400 lbs (636 kg) of fibre from the Jeffrey Pit, and another 1400 lbs total from seven other smaller operations in the Thetford–Black Lake area of Quebec (see Fig. 5). The details of the method of selection and of the accompanying quality control are given by TIMBRELL and RENDALL (1971). The blending of these fibres was thought to be representative of chrysotile production from the Eastern Townships of Canada.

Special care was exercised to avoid loss of crystalline structure by excessive grinding and to avoid the introduction of unwanted adventitious substances (metals, organics). The end product was to have been so homogenized that a 10 mg aliquot would be representative of the entire half-ton blend.

The Pneumoconiosis research units both in Wales and in Johannesburg, noted that the Rhodesian chrysotile was 'more coarse and more difficult to blend' than the Canadian fibres (TIMBRELL and RENDALL, 1971). The Canadian fibres were derived from operations owned by the Johns-Manville Corporation and the member producers of the Quebec Asbestos Mining Association (QAMA).

The UICC specimens were characterized by: continuous scan X-ray diffraction; optical microscopy which included dispersion staining and measurement of indices of refraction; a size distribution determination both by optical and by transmission electron microscopy; bulk chemistry, and trace metal contents, of bulk specimens and individual size splits; determination of extractable organic compounds; surface area determination both for specific total surface and for exposed surface, measured by adsorption and permeability determinations; and relative stability in aggressive chemical environments. Work at the same time included the design of an appropriate aerosol generator to be used specifically with the UICC standard samples (TIMBRELL *et al.*, 1968b, 1970). Additional work on the UICC Standard Reference Asbestos Samples included characterization of individual fibres by selected area electron diffraction (SKIKNE *et al.*, 1971). (See available data, Tables 7 and 8.)

THE PROPERTIES OF CHRYSOTILE AND THEIR RELEVANCE TO BIOLOGICAL BEHAVIOUR

Among the physico-chemical properties of chrysotile which determine its biological potential are the degree of fiberization of the ore, which ultimately determines the character and size distribution of any liberated fibre; the nature of associated minerals admixed in the ore itself, especially any of the amphiboles and possibly brucite; and the chemical characteristics of the mineral surface, which control its interactive properties. The relative importance of these and other natural and superimposed properties, are discussed in detail in LANGER and NOLAN (1986).

The study of the nature of chrysotile and its ores provides insight into some factors which may contribute to its biological effects. For example, the geological provenance

TABLE 7. PHYSICAL–CHEMICAL PROPERTIES OF UICC CHRYSOTILE STANDARD REFERENCE ASBESTOS SAMPLES

(1) Per cent fibres with lengths greater than 3.0 μm* Length:	3–5	5–10	10–25	25–50	50–100	100–200 μm
Chrysotile 'A' Rhodesian	45.93	25.06	22.07	5.62	1.32	0.00
Chrysotile 'B' Canadian	57.27	25.05	13.24	3.44	11.00	0.00

(2) Per cent fibres with lengths less than 3.0 μm† Length:	0.2–0.5	0.5–1.0	1.0–2.0	2.0–5.0	5.0–10.0	>10.0 μm
Chrysotile 'A'	20.7	34.9	23.1	15.2	4.5	1.6
Chrysotile 'B'	30.6	33.4	19.8	13.2	1.9	1.1

(3) Combined length distributions (from RENDALL, 1970, Table I)

Length:	0.2–0.5	0.5–1.0	1–2	2–5	5–10	10–25	25–50	50–100	100–200 μm	Total
'A'	20.7	34.9	23.1	15.2	2.83	2.49	0.62	0.15	0.00	99.99
'B'	30.6	33.4	19.8	13.2	1.76	0.93	0.24	0.07	0.00	100.00

*Suspension in alcohol; Projection Microscope. Difficulties with sizing noted. Use of optical micrographs cited in RENDALL (1970). Data combined from RENDALL (1970), PRU Johannesburg UICC data sheets, and TIMBRELL (1970).

†Sizing from electron micrographs.

TABLE 8. PHYSICAL CHEMICAL PROPERTIES OF UICC CHRYSOTILE STANDARD REFERENCE SAMPLES OF CHRYSOTILE

Property		UICC Chrysotile A		UICC Chrysotile B	
Specific surface in $m^2 g^{-1}$*		20.9±1.3	$N=5$	26.6±0.8	$N=5$
Permeability in $m^2 g^{-1}$†		5.4±2.1	$N=2$	4.4±0.3	$N=2$
Respirable per cent (by weight)‡		80.6±3.5	$N=5$	86.5±7.9	$N=4$
Respirable length >5 μm (%)		7.3		9.4	
Bulk chemistry§	SiO_2	39.23		38.33	
Average $N=8$	MgO‖	36.13		42.02	
	FeO	0.39		0.76	
	Fe_2O_3	0.93		1.49	
	CaO	0.12		0.09	
		76.80		82.69	
Trace metals¶ (in ppm)	Ni unground bulk;	−10 μm	1284; 1844		875; 1508
	Cr unground bulk;	−10 μm	1175; 1488		317; 999
	Co unground bulk;	−10 μm	43; 53		46; 60
Extractable oils (benzene)**		0.096%		0.084%	

*Nitrogen adsorption by Strohlein Areameter; Sorptometer. Both static and continous flow methods employed. Measurement includes *all* surfaces, including internal pores, cracks, channels. Values published by RENDALL (1970) are slightly higher than mean, but well within 1σ.

†Permeability measurement is of external surface only.

‡Measurement of static cloud utilizing Unico Cyclone 18 sampler. Total dust. Other determinations made by Gravimetric sampler yields lower values, but B respirable fraction exceeds A.

§Original PRU data sheet indicates method of determination as 'chemistry'. Details given in TIMBRELL (1970).

‖Re-converted to oxide. Given as magnesium %.

¶Metals by neutron activation; emission spectroscopy; X-ray fluorescence. The presence of many other trace metals was noted.

**Extraction of oils by Dr B. Commins, APRU, St. Bartholomews, London. Subsequently published as COMMINS and GIBBS (1969) in *Br. J. Cancer*. The principal compound is tetratertiary butyl diphenoquinone.

of the ore, principally the precursor rock type, dictates in large degree the nature of the associated minerals. Dunite rock (principally olivine, but also containing pyroxene) is undersaturated with respect to silica. The addition of water results in the formation both of serpentine (chrysotile) and of brucite. If fibrous brucite (nemalite) contributes to the biological potential of inhaled ore dust the dunite-derived ores add to the hazard. The increase in pyroxene content of precursor rocks (peridotites, pyroxenites) tends to favour the formation of serpentine only, rather than brucite. These ores, by mineral composition, would be less hazardous.

All precursor ore-forming rocks with iron favour the formation of platy serpentine minerals and associated spinel minerals, including magnetite. It is thought that nemalite, the fibrous form of brucite, is formed only when iron (substituting for magnesium) is present (LIEBLING and LANGER, 1972). Iron in fibres has been given much attention in studies which focus on free-radical-induced lung injury. If so, ores derived from carbonate sources would be inherently less toxic than counterpart ores derived from ultramafics.

The unit fibril of chrysotile varies in diameter among the various ore deposits, and if fiberized to produce fibrils the character of the respirable dust will vary accordingly. Fibril number and surface area could vary among deposits, the variation depending on several factors.

The role of trace metals in asbestos carcinogenesis has been discussed for many years (DIXON *et al.*, 1970; CRALLEY, 1971). In ultramafic-derived chrysotile ores nickel and iron often replace magnesium. The instability of chrysotile in the biological environment has been demonstrated, with magnesium and all other octahedral cations being leached *in vivo* (MORGAN and HOLMES, 1970; LANGER *et al.*, 1972a,b). The release of nickel and iron into the biological environment, on a cellular level, was thought to produce pathological effects, though no toxic effect brought about by this process has as yet been demonstrated in any experimental model. If such an effect were important, exposure to dusts from carbonate-derived ores would be less toxic to humans.

Adsorption and binding of components of cigarette smoke onto the chrysotile surface, either directly or indirectly in adsorbed lipids, is considered by some investigators (e.g. GERDE and SCHOLANDER, 1989) to be one of several mechanisms involved in the etiology of lung cancer in cigarette smoking workers exposed to chrysotile fibres. The fibre in this instance first acts as a direct or indirect vehicle which transports polycyclic aromatic hydrocarbons (PAHs) to the target cells. After transporting the proximate carcinogen across the cell membrane, the organic component is released from the mineral surface into the cell where microsomal processes participate in metabolizing the compound to its ultimate carcinogenic form. After PAH elution, the natural fibre surface is freed to act as a promoting compound, stimulating inflammatory processes through its action as a cytotoxic agent.

This scenario is attractive from a number of standpoints: chrysotile is a good adsorber of lipid molecules and is a powerful cytotoxic mineral agent (ALLISON, 1971; BECK *et al.*, 1972; DAVIS *et al.*, 1978). Some experimental data support the promotion hypothesis for lung cancer.

Chrysotile ore occurs with a range of physical qualities which connote the mineral's flexibility, brittleness (or lack of it) and surface properties. Fibres which are described as harsh cannot be woven, are brittle, shed water quickly and in an aqueous medium behave like amphiboles. Not important for the textile industry, harsh fibre is useful for

filtration. It has been shown to produce a more rapid onset of malignant tumours in laboratory animals as compared to identical aliquots of 'soft' fibre administered in the same way (SMITH, 1974). Harsh fibres are more straight and splintery and as a result are thought to be more respirable. Chrysotile fibres mixed with nemalite (fibrous brucite) appear harsh but removal of nemalite restores the fibre's flexibility. Exposure to harsh fibre is presumably more dangerous than equivalent exposure to soft fibre.

The minerals associated with, and admixed into, chrysotile ore vary according to geological provenance. Tremolite, an amphibole mineral, is important in this regard, since tremolite asbestos, in appropriate concentration, is considered to be the agent responsible for pleural mesothelioma found amongst chrysotile-exposed workers.

The UICC Chrysotile 'A' and 'B' satisfied many of the purposes originally intended. They were used as standard fibres in experiments involving intact animals of different species, exposed to chrysotile by a variety of routes of administration. Differences in patterns of biological outcome were then explained on the basis of host response rather than of differences in fibre character and preparation. This contributed significantly to the understanding of asbestos carcinogenicity and aided in the development of animal models specific for the different asbestos diseases.

However, as work progressed, the experimental community began to re-manipulate the standard specimens, alter some of its properties, and thereby reduce its value as a reference material. The most common form of manipulation was milling, undertaken to reduce particle size. Further, as experiments were designed to test some specific feature of the dust thought to be crucial to outcome, such as fibre length, the mineral mixtures proved to be unsatisfactory. This became very clear as *in vitro* testing expanded both in design complexity and in biological endpoints.

Epidemiological studies indicated that for the same fibre type derived from different geological sources human experience varied. For example, mesothelioma incidence among the Jeffrey miners and millers in Quebec was lower than it was among the Thetford workers in the same province: the different character of the ores, possibly the associated amphibole minerals, were thought to be the cause of this. The UICC standards were of no use in resolving this problem.

Ironically, the most severe shortcoming of the samples had virtually nothing to do with the standards themselves. It was not made clear that each of the standards should have been recharacterized as a bulk material, as a dust cloud (if inhalation was the route of administration) and as a residue in the host animal. As the questions become more focused and narrow, the requirements for characterization increased. The UICC data sheets left the experimentalist with the impression that all the important characterizations had been done: this was simply not the case.

In addition to the inherent mineral properties of chrysotile, thermal, mechanical and chemical events in and after the industrial processing further affect the fibre. Some of these may enhance, and some may reduce, the mineral's biological potential. For example, the heating of a chrysotile insulation product over a period of many years of service increases the 'dustiness' of the fibre in the product. The hazardous nature of the product increases with time. On the other hand, the thermal shock at the interface between a brake pad and a wheel assembly completely dehydroxylates the fibre causing it to lose its crystalline structure, so that the hazardous quality of the fibre is greatly reduced: at higher temperatures it recrystallizes as forsterite. The mechanical carding of fibre bundles in a breaker causes the dust in a textile mill to become very toxic, whereas

mechanical shear on a brake pad greatly reduces its toxicity. Such superimposed events greatly alter chrysotile's biological behaviour.

The mineral nature of chrysotile controls its biological behaviour. These factors must be considered in developing any health criteria document, and resolving health effects following exposure to dust.

[For the discussion of the issues raised in this and the other allied papers see pp. 408–409.]

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