FIBROUS CHLORITES IN THE VOLCANIC ROCKS OF DERBYSHIRE

by

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Summary

Records of chlorites and of presumed asbestos minerals from Derbyshire are reviewed. It is shown that fibrous minerals from three Derbyshire localities (Calton Hill, Tideswell Dale and Waterswallows) are chlorites, variously weathered to montmorillonoids or amesite, and that the dominant fibrous mineral at a fourth locality (Ible) is calcite. There is found to be no evidence of any asbestiform mineral from Derbyshire.

Introduction

The chlorites are a group of hydrous silicates of magnesium and aluminium, containing variable quantities of ferrous or ferric iron, chromium or manganese. They are typically green in colour, but this varies, according to composition and the presence of impurities, to brown or even black.

The chlorite molecules form two-dimensional sheet-like structures of SiO_4 tetrahedra, linked by three of their corners. Crystallisation is in the monoclinic system, crystals being sometimes pseudo-hexagonal; a perfect basal cleavage (parallel to the SiO_4 sheets) causes splitting into flakes. The chlorites are very soft, hardness averaging about 2 on Moh's Scale, and can thus be scratched with the finger-nail. In all these properties, they resemble the micas: they differ, however, in composition, in the fact that the flakes are flexible but not elastic, and in certain optical properties. (The micas are also somewhat harder, averaging 2.5).

Many different varieties of chlorite have been named, primarily on the basis of chemical analysis, supported by optical measurements. The variation in composition results from isomorphous replacement of the electropositive atoms within the same general structural framework; under X-ray examination, it is found therefore that there is very little difference in molecular structure between the chemically different varieties, only the secondary characteristics of the X-ray diffraction pattern being altered (see Brindley and Robinson, 1951).

The chemical composition is extremely variable in detail; there is complete gradation between the different named types of chlorite, the names being merely employed to indicate that a specimen lies within certain compositional limits. The first classification put forward was by G. Tschermak (1890, 1891), who recognised two basic groups: the ortho-chlorites, with compositions between $(Mg,Fe'')_2\ Al_2\ SiO_5\ (OH)_4$ and $(Mg, Fe'')_3\ Si_2\ O_5\ (OH)_4$, and the leptochlorites, with compositions not considered explicable on this basis and generally richer in trivalent ions (especially Fe''') relative to silicon and divalent ions. The two presumed end-members of the orthochlorite series were amesite and serpentine; but it is now known that neither of these minerals has a true chlorite structure.

Later work by A. N. Winchell (1926, 1936) and others showed the leptochlorites to contain considerable amounts of ferric iron: a recomputation of their analyses with this iron in the ferrous state brings them into line, structurally speaking, with the orthochlorites. The leptochlorites are therefore simply oxidised chlorites.

The classification now generally adopted was proposed by M.H. Hey (1954). A basic division is made between the normal, or orthochlorite, series, and the oxidised chlorites (the "leptochlorites" of Tschermak), an arbitrary figure of 4% Fe_2O_3 being taken as the dividing line. The two series are further subdivided into mineral species on the basis of proportions of iron and magnesium. Eleven species of orthochlorite are thus recognised (corundophilite, pseudothuringite, sheridanite, ripidolite, daphnite, clinochlore, pycnochlorite, brunsvigite, penninite, talc-chlorite and diabantite) and three species of oxidised chlorites (thuringite, chamosite and delessite). (See Hey, 1954, Text-fig. 1; Deer, Howie and Zussman, 1962, Text-fig. 35). Chlorites also exist in which the magnesium has been partially, or wholly, replaced by manganese:- manganese-penninite and grängesite (manganiferous brunsvigite) contain small percentages of MnO; pennantite is a thuringite in which almost all the magnesium has been replaced by manganese; and gonyerite approximates to serpentine in composition, whilst retaining a chlorite structure. There are, in addition, chlorites containing chromium:kämmererite (a variety of penninite) and two varieties of clinochlore - chrome - clinochlore (less than 4% Cr_2O_3) and kochubeite (more than 4% Cr_2O_3).

Chlorites may be formed in a variety of different ways. In igneous rocks, they occur principally as products of the hydrothermal alteration of pyroxenes, amphiboles, and biotite mica, their composition being dependent on the composition of the mineral they are replacing. Frequently the chlorite pseudomorphs the mineral it is replacing. They are commonly found in amygdales in lavas or as lamellar coatings, often slickensided, in joint planes and fissures. Chlorites are widespread as products of the low-grade metamorphism of igneous and sedimentary rocks, being the most characteristic minerals of the green-schist facies; they disappear in higher grades of metamorphism. In sediments, they occur both as detrital and as authigenic minerals in argillaceous rocks; and chamosites, in the form of ooliths, are important constituents of sedimentary iron formations, such as the Northampton Ironstone.

Previous Records of Chlorites from Derbyshire

The first mention of a chlorite from Derbyshire was by Woodward and Mello (1881, p. 185), who record "viridite", here used as a synonym of chlorite, from dolerites at Matlock, Millers Dale and Castleton.

Green, Strahan et al. (1887, p. 136) recorded delessite, coating calcite in toadstone vesicles at Mill Dam Mine, Great Hucklow (National Grid Reference SK 177780).

Sargent, in a discussion of spilitic lavas from various localities in Derbyshire, noted "chloritic minerals" in the lavas at Tideswell Dale (1917, p. 12); chlorites in lavas at Salters Lane, Matlock (SK 276593) and in the waste-heaps of Seven Rakes Mine, Masson Hill, Matlock (p. 14: SK 285590); and a "fibrous green chloritic substance" lining the margins (the fibres "standing out well from the walls of the cavity") and occupying the centres of vesicles in the lava of Worm Wood, near Bakewell (p. 16: SK 211694). The most abundant of these latter chlorites was stated to be "helminth", an old name for ripidolite; and a yellowish-brown chlorite, near delessite, was noted as also present.

Garnett (1920, 1923b) recorded diabantite from Millclose Mine, Darley Dale (SK 259625), as dark green, radiated spherical aggregates, up to 2 cm. in diameter, in amygdales in weathered dolerite: a yellowish-green chlorite (unspecified) was noted as present in the groundmass. Subsequently (1923a) he recorded a chlorite occurring in a well defined stratum and as fibrous veins in the Ible Sill; this occurrence will be discussed more fully in a later section.

Tomkeieff (1926) described the presence of green chlorite (determined on analysis to be near delessite) in vesicles in decomposed basalt at Calton Hill, near Buxton. He also records chlorite in the groundmass of, and filling vesicles in, the lavas of Knot Low, Millers Dale (SK 135735) - not analysed, but stated to be near chlorophaeite, a mineral species described originally from similar situations in the Western Isles. [The name "chlorophaeite" seems to have fallen into disuse in Western literature and is not mentioned by either Hey, 1956, or Deer, Howie and Zussman, 1962; it remains current among Russian mineralogists, e.g. Ivanov, 1958. In absence of an analysis by Tomkeieff, no alternative name can be suggested for the Derbyshire chlorite.] Tomkeieff reviewed the earlier work of Garnett and Sargent, and concluded that the Derbyshire chlorites were of three types:-

i) Primary chlorite, present in the glassy material (palagonite) of lavas

ii) Chlorite of a post-volcanic phase, filling vesicles

iii) Secondary chlorite produced by atmospheric weathering, found in the weathering-crust of lavas and in the green clays produced from such weathering

Later (1928, p. 709), in a fuller account of the geology of Calton Hill, Tomkeieff referred again to the chlorite amygdales and assigned them to the delessite-diabantite group.

Cope (1933), in a description of a tholeiite dyke in Great Rocks Dale, near Buxton (SK 103737), records greenish yellow chlorites, forming rounded or six- to eight-sided bodies, as visible in thin section in the tholeiite; he also notes chlorites to be present in xenoliths of sedimentary rock from the dyke margins.

Hamad (1963, p. 485), in a note on olivine nodules in the Calton Hill basalts, mentioned a dark green chlorite as occurring as aggregates of fibrous spherulites in the basalt. He gave analyses of the basalt and commented that the high water content revealed might be attributed to the presence of the chlorite (p. 487).

Finally, Ford and Sarjeant (1964, p. 137) brought together earlier references to chlorites in the "Peak District Mineral Index" and quoted, in addition, the occurrence of delessite in Lathkill Dale (SK 184658).

The Supposed Derbyshire "Asbestos"

A number of minerals occur naturally in the form of very long, fine, flexible crystals, easily separated by the fingers and capable of being spun into a yarn. These are of commercial importance because of their resistance to heat and (to a lesser degree) to acids; they are employed in the manufacture of fire-proof clothing and paints, roofing-tiles, boiler covers, insulating cements, etc. Asbestiform minerals include various amphiboles (actinolite, anthophyllite, amosite, crocidolite) and one form of serpentine (chrysotile).

There is a long-standing tradition among Derbyshire mineralogists that asbestos is to be found in the volcanic rocks of the Peak District. Garnett (1923, p. 62) notes that the fibrous chlorites of the Ible Sill had been supposed to be chrysotile; he does not cite a reference for this supposition, but it is likely that this is the first echo in geological literature of the "Derbyshire asbestos".

A mineral supposed to be asbestos was collected by a Sheffield University party, led by Mr. W.H. Wilcockson, M.A., from the Calton Hill road metal quarry around 1950. The specimens (which were accompanied by a sketch illustrating the form of occurrence) survive in the Sheffield University collections and were examined by the present author in 1956. During a series of visits to Calton Hill Quarry, similar fibres were found forming bands within the weathered basalt. These were described in a short note (Sarjeant, 1957); the asbestiform nature of the mineral was not contradicted by the brief examination made, and it was tentatively suggested that the mineral might be either chrysotile or amthophyllite. Specimens of the Calton Hill mineral were exhibited at the 1956 meeting of the British Association in Sheffield and attracted a fair measure of interest.

Subsequently, after a joint expedition to Calton Hill Quarry with the author, Dr. W. Eric Addison, of the Department of Chemistry, University of Nottingham, prepared X-ray powder photographs of the mineral, suggesting a mixture of calcite + chrysotile. Agreement was not perfect, the weaker chrysotile lines not being observed; Dr. Addison emphasized that the result was "not too convincing" (personal communication).

In the "Peak District Mineral Index", it is noted that "many of the obscure notes of asbestos in Derbyshire may well be Chrysotile" (Ford and Sarjeant 1964, p. 137) and that "an asbestiform mineral occurs in the toadstones of Calton Hill, Tideswell Dale and Ible" (p. 138).

The present author has therefore done much, inadvertently, to bolster the tradition of Derbyshire asbestos. However, studies subsequent to 1964 indicate that the supposed "asbestos" of Calton Hill, Tideswell Dale and Ible is, in fact, simply a very impure, fibrous chlorite, altered in varying measure to clay minerals. The results of these studies are presented in the following section.

Fibrous Chlorites by Locality

CALTON HILL

The Calton Hill roadmetal quarry, operated by Derbyshire Stone Co. Ltd., is situated south of the Buxton-Bakewell road, about 4 miles east of Buxton (SK 117715). Volcanic rocks were first noted from Calton Hill by Arnold-Bemrose (1894, 1910): the opening of the quarry, in the early 1920's, afforded opportunity for a fuller study by Tomkeieff (1928). He noted three principle groups of rocks:-

i) Stratified volcanic agglomerate and tuff

ii) Greatly decomposed vesicular lava ("toadstone")

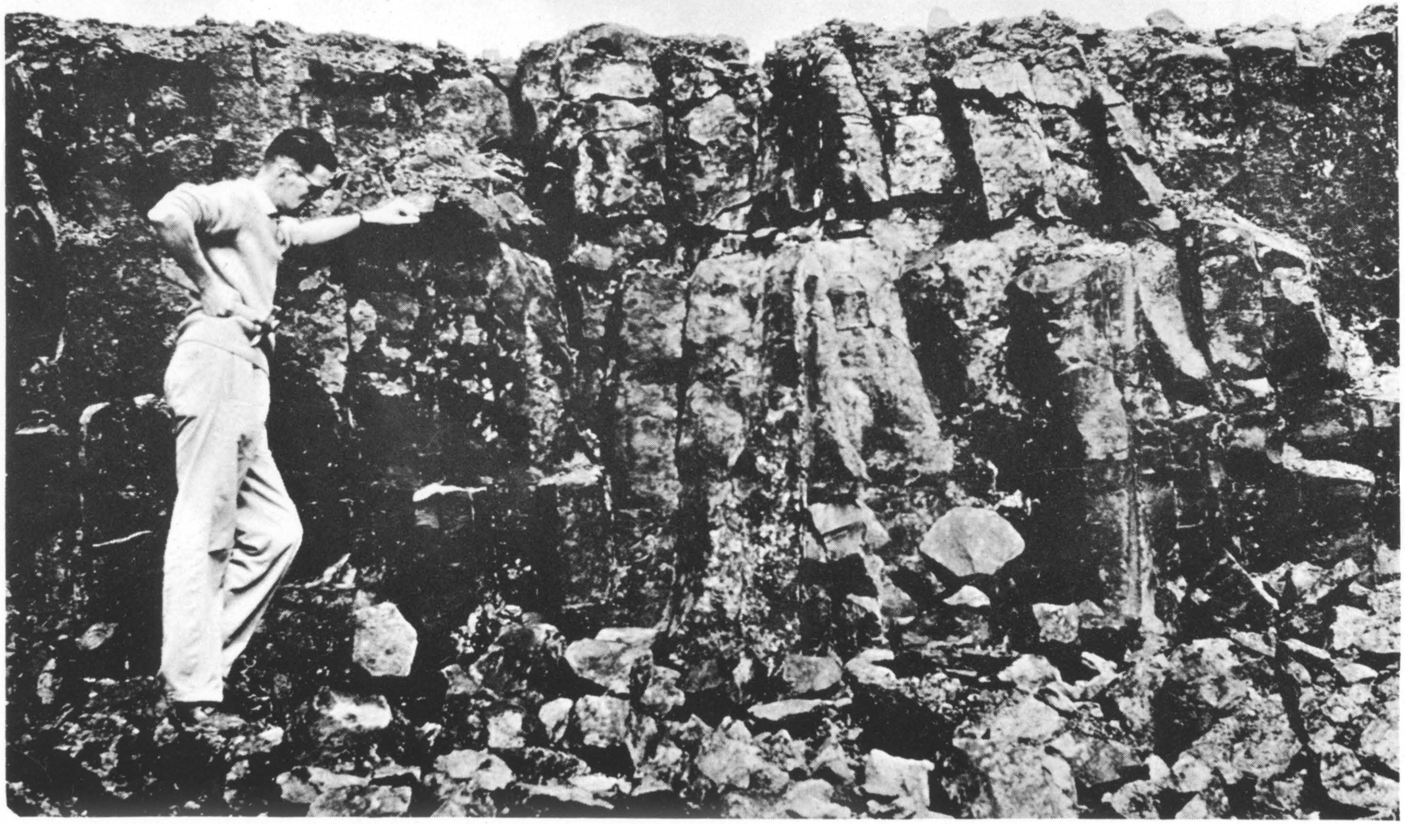
iii) Fresh, compact analcite-basalt with peridotite inclusions

He concluded that the first two groups represented an extrusive phase of eruption, and the latter an instrusive phase. Although the enormous extension of quarrying since 1928 has revealed a greater complexity of structure than Tomkeieff visualised, so that his maps and sections are now difficult to apply, his conclusions remain sound. The lowest levels now exposed, at the southern end of the quarry, show an impressive development of columnar jointing in the basalt intrusion (Plate 2).

The fibrous minerals were located in a deeply-weathered surface of analcite basalt, in deep workings near the centre of the quarry. They were arranged in bands around relatively unweathered cores (see Sarjeant, 1957, Text-figs. 2-3), the fibres being usually perpendicular to the vein margins, but sometimes at an angle when a block had slipped. (This part of the quarry has now been filled in). Subsequently, bands of fibres were found also in a crag of vesicular lava towards the southern end of the quarry.

The length of the fibres ranged from about 6mm to about 45 mm and the colour varied from yellowish-brown through greenish to grey-black, the darker fibres sometimes exhibiting a resinous to silky lustre. The lighter fibres are very brittle, splitting to form flat, columnar aggregates and readily breaking down to a powder; the darker fibres are more flexible but would not be capable of weaving.

Plate 2.



Columnar basalt in the lower levels Calton Hill Roadmetal Quarry, nr. Buxton, being examined by Mr. Leslie O. Ford. The photograph was taken on Sunday 30th July, 1961, when the exposure was still fresh: it is now much decayed.

(Photo: W. A. S. Sarjeant)

A number of X-ray powder photographs have been made at different times from fibres taken from various bands. The earliest of these, prepared by Dr. W. E. Addison, have been already discussed. Subsequent films consistently show the strong 14 Å line typical of chlorites and montmorillonoids; its presence rules out the possibility that the mineral is a serpentine. (The lowest lines were apparently missing from Dr. Addison's film; his higher lines accord well with subsequent observations). The X-ray patterns indicate that the fibres are chlorites, showing a parallel intergrowth with calcite and sometimes with quartz, and weathering to form clay minerals (montmorillonoids).

A chemical analysis of the fibres from veins in the analcite basalt is here presented and compared with Tomkeieff's (1926) analysis of the green chlorite from vesicles in the decomposed lava:-

% Weight	Fibrous chlorites (Howie, in litt., 1964)	Chlorite in vesicles (Tomkeieff, 1926)
SiO_2	35.42	35.92
TiO_2	0.09	0.00
Al_2O_3	7.86	12.20
Fe_2O_3	12.99	7.59
FeO	2.53	4.66
MnO	0.08	-
MgO	18.57	21.82
CaO	0.84	1.82
Na_2O	0.03	-
K_2O	0.01	-
H_2O+	8.01	9.20
H_2O-	13.28	6.50
CO_2	-	0.13
Total	99.71	99.84

Howie's analysis, recalculated on the basis of 28 oxygens, gives the following result:-

$$(Si_{7.609}Al_{0.391})\ (Al_{1.600}Ti_{0.014}\ Fe^{+3}_{2.101}\ Fe^{+2}_{0.454}\ Mn_{0.014}\ Mg_{5.945}\ Ca_{0.193}\ Na_{0.001})\ O_{28}$$

The value of $Fe^{+3} + Fe^{+2}/Fe^{+3} + Fe^{+2} + Mg$ is thus 0.300 and the Si/Al ratio puts it in the delessite group.

A second analysis was made of fibres from the decomposed lava by Mr. D. J. Mather, under the direction of Dr. R. J. Firman. The result was somewhat different. (see Table on following page).

Firman's analysis suggests the presence of free quartz intimately admixed with the chlorite. Assuming SiO_2 percentage to be 35%, recalculation on the basis of 28 oxygen atoms still fails to fit the chlorite formula. This suggests that the chlorite is highly altered to a montmorillonoid, so that the original character of the chlorite can no longer be determined.

% Weight	Fibrous chlorites (Firman, personal communication, 1966)	Fibrous chlorites (Howie, in litt., 1964)
SiO_2	42.58	35.42
TiO_2	0.01	0.09
Al_2O_3	7.69	7.86
Fe_2O_3	9.50	12.99
Fe O	1.95	2.53
MnO	0.01	0.08
MgO	17.52	18.57
CaO	1.74	0.84
Na_2O	0.03	0.03
K_2O	0.01	0.15
H_2O+ } H_2O- } CO_2 }	18.44	21.29
P_2O_5	0.01	-
Total	99.61	99.71

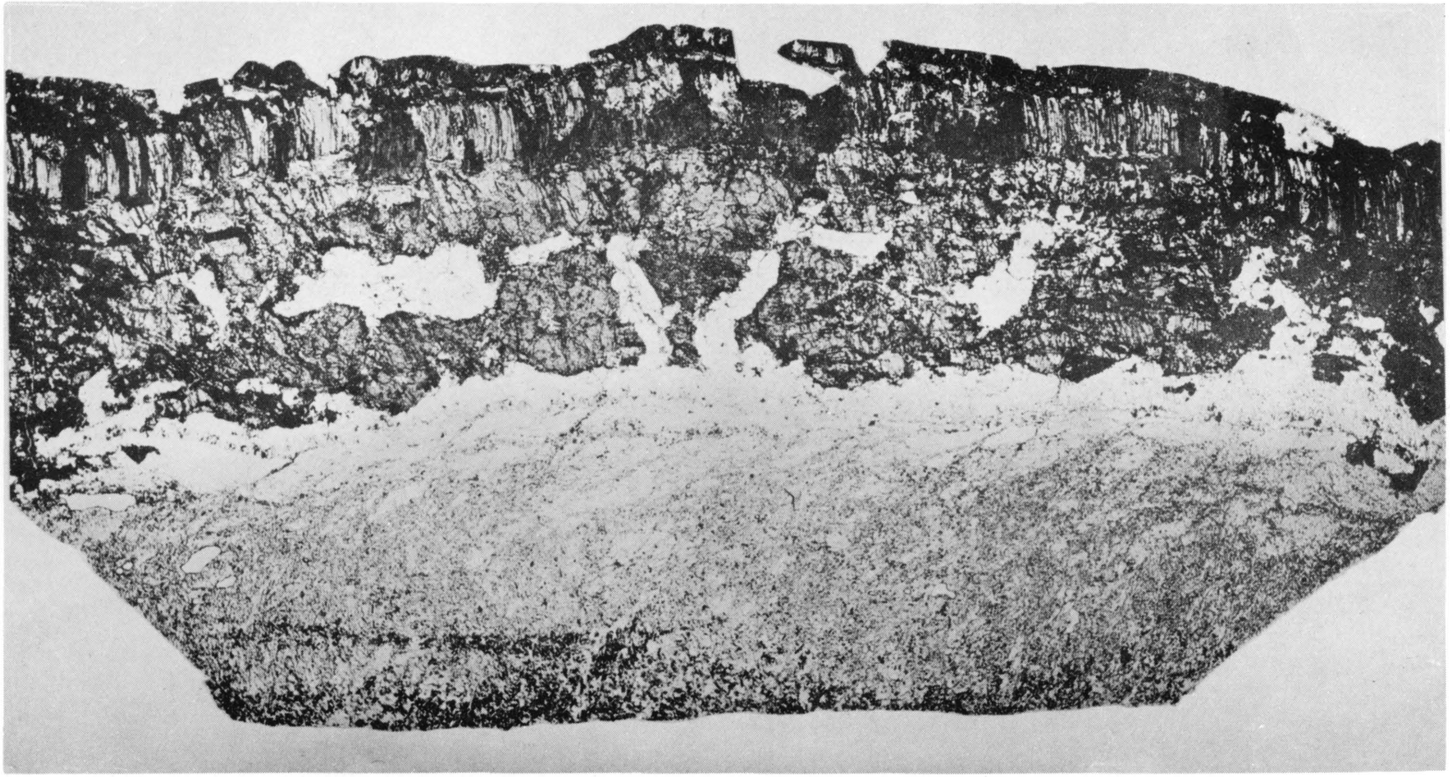
IBLE

The Ible Sill is exposed in a small quarry, abandoned before 1920, which is situated immediately to the south-east of the village of Ible (SK 253568). It was first described by Arnold-Bemrose (1907, p.275) and subsequently by Garnett (1923a). It consists of an ophitic olivine-dolerite, containing (in the quarry - lateral extent unknown) a 4 - foot chlorite-rich horizon, apparently produced by hydrothermal alteration of the dolerite; the chlorite is dark olive-green in colour and is in the form of a confused mass of intergrown lamellar and foliated aggregates.

Traversing both dolerite and chlorite-rock are numerous small veins of fibrous to columnar minerals. The veins are at their largest and most numerous in the upper parts of the metamorphosed horizon and immediately above it; they range in thickness from about 5 mm. to over 100 mm. The vein material consists very largely of fibrous to columnar calcite, white to yellowish in colour; amongst this were patches of yellow-brown to dark olive-green fibres, with a resinous to dull lustre, superficially similar to the material from Calton Hill. The long axes of the fibres are always vertical, regardless ot the attitude of the veins (except at the tips, which meet the vein margins at right-angles). Thus the fibre axes are perpendicular to the margins of horizontal veins and at varying angles to the margins of all other veins - unlike the fibrous minerals of Calton Hill, whose axes were consistently perpendicular to vein margins, regardless of vein attitude (except where a block had slipped). A section, prepared from the darker material, showed that the fibres were uniformly of calcite, the colour being caused by patches of another mineral in among the calcite fibres (Plate 3).

X-ray powder photographs of the darker mineral proved unsatisfactory; in all films prepared, strong calcite or quartz lines were present, masking other lines. A 14 Å line, suggestive of chlorites or montmorillonoids, was, however, consistently present. A chemical analysis of calcite-free vein material was made by Mr. D.J. Mather, under the direction of Dr. R.J. Firman; the result is given below and

Plate 3.



Thin section of a vein in the chlorite rock of Ible, Derbyshire. The ground mass, seen at bottom, is dominantly of calcite and opaline silica where it approaches the vein margins. Opaline silica (white) forms the lower vein margin and irregular patches within the vein. The calcite fibres form two layers: a lower, imperfectly fibrous layer containing much opaline silica, and an upper, more perfectly fibrous layer, containing a little quartz and opaline silica and more numerous darker patches, interpreted as chlorites and/or montmorillonoids. Magnification X 6 approx.

Photo: J. Eyett

compared with analyses made by Garnett (1923a, p. 63):-

% Weight	Vein material (Firman, personal communication 1966)	Fibrous chlorite (Garnett, 1923)	Chlorite from aggregates in the chlorite-rock (Garnett, 1923)
SiO_2	44.90	42.7	37.5
TiO_2	0.01	-	-
Al_2O_3	8.04	8.2	10.4
Fe_2O_3	8.21	13.6	8.8
FeO	1.83	2.8	10.8
MnO	0.01	-	-
MgO	18.40	20.7	20.8
CaO	1.77	0.0	0.0
Na_2O	0.01	-	-
K_2O	0.60		
H_2O+	} 15.93	} 11.7	} 9.6
H_2O-		0.0	0.0
CO_2			
P_2O_5	0.01	-	-
Total	99.71	99.7	100.3

The vein mineral partially dissolved in hydrochloric acid (as do chlorites); the insoluble residue consisted of over 75% SiO_2, suggesting the possible presence of an admixture of free silica in the vein mineral.

Garnett compared his analyses with analyses of epichlorite, given by Zincken and Rammelsberg (1849, quoted in Garnett, 1923, p. 63) in their original description of that mineral from the Harz Mountains, Germany. Epichlorite is described as a fibrous or columnar mineral, occurring in thin veins; the characters are said to be intermediate between chlorite and bastite serpentine. Hey (1954, p. 280) includes epichlorite among a group of mineral species about which he states "... if they are really chlorites and the analyses are trustworthy, they form a third division of true leptochlorites, in which the total cations are less than 10 per 14 oxygen cations (anhydrous basis)".

Comment on Garnett's conclusions is doubly difficult, in view of the doubtful status of epichlorite and the fact that, in the specimens collected by the present author, the darker mineral was never itself fibrous, but merely intergrown with fibrous calcite (Garnett notes also the presence of quartz in the veins as "more or less fibrous aggregates" [1923a, p. 62]). Neither the X-ray powder photographs nor the analyses permit of any firm conclusions. All that can be said is that, at the present, the fibrous mineral occupying the veins is almost wholly calcite; and that within the veins, quartz and another mineral or association of minerals (chlorites or clay minerals belonging to the montmorillonoid group) form a relatively minor component.

TIDESWELL DALE

The Tideswell Dale igneous body is well exposed in an abandoned quarry about ½ mile south of Tideswell (SK 155737). It was originally worked around 1850 for the marble underlying the sill, but quickly abandoned owing to the high cost of removing the toadstone. Subsequently the toadstone itself was worked for road-metal; the rusting crushing-plant, a considerable eyesore, was recently removed through the intervention of the Peak Park Planning Board. Arnold-Bemrose (1899) considered the igneous body to represent lava-flows of olivine-dolerite, into which a sill of the same material had been intruded, the rocks above and below the intrusion being markedly vesicular. He comments:-

> "The rock in the quarry is traversed by numerous small veins of a mineral that is probably chrysotile. It is of a golden yellow and consists of prisms or bundles of parallel fibres arranged perpendicular to the walls of the cracks in which it occurs. When wet it is soft and easily rubbed into a waxy material between the fingers, but when dried becomes tougher and slightly brittle."

The latter part of this description suggests a clay mineral rather than chrysotile.

Garnett (1923, pp. 64-5) was unable to collect this material, owing to the poor condition of the quarry at that time, but he noted its similarity to the chlorites of the Ible Sill.

The veins of fibrous material now to be seen are high at the northern end of the existing quarry face. The fibres range in colour from olive brown to greyish black and have a resinous to silky lustre: they are thus closely comparable with the Calton Hill materials. The fibres range in length from about 5 to 15 mm.

X-ray powder photographs show a considerable admixture of quartz, whose strong pattern masked all weaker lines; however, the 14 Å line could be recognised. The one quartz-free film obtained indicated a mixture of the mineral amesite (a mineral related to the chlorites but differing in molecular structure: see Deer, Howie and Zussman, 1962, pp. 166-7) with montmorillonoids. The Tideswell Dale fibres therefore appear to comprise chlorites, highly altered to amesite and to montmorillonoids and intimately admixed with quartz. It is probable that Arnold-Bemrose saw, and described, them when in much fresher condition and it is regrettable that no analyses are available from that period.

WATERSWALLOWS

The Waterswallows roadmetal quarry, operated by Messrs. Hughes Bros., is situated about 1 mile northwest of Buxton (SK 085750). Arnold-Bemrose (1907, p. 273) considered it to be a sill, on the basis of the slight exposures then available. The structure is now well exposed by quarrying and is undoubtedly a vent (see Moseley, 1966).

Specimens of a grey-black, fibrous mineral were collected here by the author in 1956, from slipped material (briefly referred to in Sarjeant, 1957, p. 217). The fibres, too thick to be taken for asbestos, have a greasy feel and resinous lustre. X-ray powder photographs again indicated a chlorite-montmorillonoid mixture, with a strong admixture of calcite.

Conclusions

Examination of fibrous minerals from four localities in Derbyshire provides no support for the supposition that asbestos occurs in the county. The fibres from Calton Hill, Tideswell Dale and Waterswallows were found to be chlorites, weathered to montmorillonoids and/or amesite; a varying admixture of calcite or quartz, sometimes showing parallel growth, was present. The results of study of fibres from Ible were less satisfactory: the dominant (possibly the only) fibrous mineral present is calcite, but varying proportions of quartz and a darker mineral (chlorite or a clay mineral, or a mixture of both) are present among the calcite fibres. The fibrous chlorite of Calton Hill was found by chemical analysis to be, at least in part, delessite; recognition of the chlorite species elsewhere did not prove possible.

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