Notes on a new occurrence of stilpnomelane from North Wales

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Summary. An occurrence of stilpnomelane in calcite veins cutting an Ordovician sedimentary iron-ore body has yielded good material for optical and chemical study; data for both ferro- and ferri-stilpnomelane are presented. Associated pyrrhotine, ilmenite, and apatite are briefly described, and a chemical analysis of the apatite shows it to be an extremely pure fluorapatite.

STILPNOMELANE has been recorded from several localities in north Wales, mostly associated with sedimentary iron-ores; the new locality is similar in this respect. It is situated approximately 2 miles south-west of Drws-y-nant station (near Dolgelley) at an altitude of 1950 ft. Exposure is very poor, and no mapping was attempted, the only available map being the original survey sheet (74.SW).

The iron-ore occurs as a lenticular mass some 8 feet thick, and several hundred feet long; the lens is near vertical and strikes approximately SW.–NE. The lens occurs in Ordovician ashes, and by analogy with similar bodies near the foot of the Cader Idris escarpment where fossil evidence has been found (e.g. Cross Foxes and Arthog) it probably belongs to the *N. Gracilis* zone. The mass is terminated abruptly at its west end, probably by a fault (Survey Memoir), and the ore appears to have been richest at this end. Under the name Tyllau Mwn, the first recorded working was in 1838, and ore yielding as much as 52 % Fe was being raised until working stopped in the 1930's. The workings are now flooded and inaccessible, but the tip heaps yield adequate specimens of ore, and, in one place particularly, a lot of vein calcite. This was probably the last material to be brought out of the mine, and could well indicate that the fault was reached. No calcite veins have been found in surface outcrops.

There is a record of stilpnomelane 'in feathery bunches and veins, disseminated throughout the rock' in the Survey Memoir. This is confirmed by the authors to some extent, but the more interesting and hitherto unrecorded occurrence is in vein calcite where this cuts the iron-rich rock. The ore rock itself shows a coarse pisolitic structure, with individual pisoliths up to 3 mm in diameter, often elliptical and cracked. Concentric layers of the pisoliths are formed of very finely crystalline magnetite in a chamosite matrix, while larger magnetite octahedra (approx. 0·1 mm) are scattered throughout in varying amount.

The calcite veins vary in thickness from approx. ½ mm up to 1 ft. The thinner veins can be seen to cut individual pisoliths, the separated fragments having no lateral displacement. Stilpnomelane commonly grows out into the calcite perpendicular to the vein walls; in veins less than approx. 1 in. thick, thin laminae (1 mm) of stilpnomelane crystals have formed right across the vein, dividing the vein into rectangular (in cross-section) spaces, which are filled to varying degrees with small crystals of stilpnomelane growing from the laminae and perpendicular to them. In thicker veins, and therefore more obvious in hand specimen, stilpnomelane is seen to grow as platy crystals as much as 2 cm across and 2 mm thick. The crystals are usually perpendicular to the vein walls and tend to form lines of crystals in this direction, often with associated stringers of pyrrhotine. It is rare for there to be any stilpnomelane more than 2 in. from the vein wall, and 3 in. was the maximum observed.

In thin section the stilpnomelane shows strong pleochroism either from dark brown to light golden-yellow or from light apple-green to light yellow. The green form occurs most commonly in the thin veins and feathery patches in the wall rock, while the brown form constitutes the bulk of the coarsely crystalline stilpnomelane in the larger veins. In a few cases, individual large crystals or coarse aggregates show green patches enclosed in brown; also brown patches have developed in the finer grained green stilpnomelane of some thin veins (but not in the thinnest). The transition from brown to green is often independent of crystal boundaries, and is diffuse (fig. 1). Both forms show a strong (001) micaceous cleavage, and a (100) fracture—the latter being markedly stronger in the brown form, which is in effect very brittle.

Samples of green and brown stilpnomelane were separated from crushed material using heavy liquids, and were used for chemical and optical study. Refractive indices proved to be very difficult to measure accurately, due to the dense colour, micaceous habit, and high birefringence. It was also found that each separation included grains over a small range of compositions. The results are summarized in tables I and II. Assuming that the measured refractive indices are representative of the analysed material, the values do not lie on Hutton's curves (1945), but approach more closely those given in Deer, Howie, and Zussman (1962).

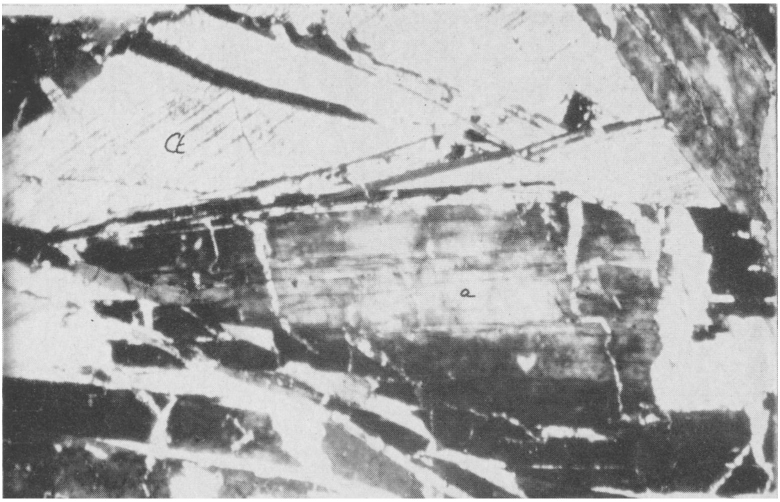

FIG. 1. Core of ferro-stipnomelane (*a*) in dark ferri-stilpnomelane crystal. Ct, calcite. Crossed nicols. ×40.

The minerals associated with stilpnomelane in the calcite veins also proved to be of interest; they are apatite, ilmenite, and pyrrhotine.

Apatite occurs as small, flat crystals, 'floating' free in calcite or attached to the vein walls. These crystals commonly occur in the thinner veins, and are occasionally found on the walls of an otherwise empty fissure. The crystals show a basal pinacoid and a flat hexagonal bipyramid; no prism faces are visible. Their size varies from almost $\frac{1}{2}$ in. in diameter down to less than 1 mm, and the crystals have an average breadth:length ratio of approximately 5:1. Separation of pure apatite was easily achieved, and the results of chemical and spectrographic analyses are given in tables I and II. It can be seen that the composition corresponds remarkably closely with that of an ideal fluorapatite $Ca_5(PO_4)_3F$.

One specimen of *ilmenite* was found quite by chance, and further searching has failed to reveal any more. This one consists of two flat rhombohedral crystals approx. $\frac{1}{2}$ in. across, in parallel composite growth. They occur floating in a calcite vein that is only slightly wider than the crystals, together with some apatite. Identification was by powder photograph because of the unusual habit.

TABLE I. Chemical analyses of stilpnomelane and associated minerals (J. H. Scoon, anal.)

	1	2	3	3*	4
SiO_2	44·37	45·45	23·27	30·17	nil
Al_2O_3	5·06	4·95	7·40	9·59	0·08
Fe_2O_3	8·78	23·86	14·13	—	0·03
FeO	28·99	13·21	38·81	42·07	—
MnO	0·05	0·06	0·05	0·06	0·01
MgO	1·91	1·91	1·59	2·06	0·02
CaO	0·55	0·65	3·54	1·48	55·88
Na_2O	0·39	0·06	0·37	0·48	—
K_2O	0·45	0·51	0·35	0·45	—
H_2O^+	6·32	5·66	6·71	8·70	0·05
H_2O^-	3·12	3·54	0·77	1·00	nil
TiO_2	0·24	0·18	0·62	0·80	—
P_2O_5	n.d.	n.d.	0·53	0·69	42·00
F	—	—	—	—	3·73
CO_2	—	—	1·88	—	nil
Total	100·23	100·04	100·02	100·00	100·22†

	1 (a)	1 (b)	2 (a)	2 (b)
Si	11·85	8·00	11·89	8·00
Al	1·60	1·08	1·21	1·02
Fe‴	1·76	1·19	4·68	3·15
Fe″	6·45	4·35	2·88	1·94
Mn	0·01	0·01	0·01	0·01
Mg	0·77	0·52	0·75	0·50
Ca	0·16	0·11	0·18	0·12
Na	0·20	0·14	0·03	0·02
K	0·15	0·10	0·17	0·11
Ti	0·05	0·03	0·03	0·02
OH^-	42·00 (OH, O)	3·80	42·00 (OH, O)	3·32
O		28·36		28·26

1. Green stilpnomelane.
2. Brown stilpnomelane.
3. Chamosite–magnetite rock.
3*. Anal. 3 recalculated to 100 % after deduction of Fe_2O_3 as magnetite and CO_2 as calcite.
4. Fluorapatite. ω 1·633±0·001, ϵ 1·630±0·001.
1*a*, 2*a*. Atomic ratios of stilpnomelanes 1 and 2, on a basis of 42 (O, OH).
1*b*, 2*b*. Atomic ratios on a basis of 8 Si.
† After deduction of 1·57, O for F; CO_2, SO_3, and Cl nil.

	1	2
Fe″	78·6 at. %	38·1
Fe‴	21·4	61·9
$\frac{100\,(Fe''' + Al)}{Fe'' + Mn + Mg + Fe''' + Al}$	= 31·75	62·99
α	1·577±0·002	1·596±0·002
$\gamma = \beta$	1·623±0·002	1·705±0·005
$\gamma - \alpha$	0·046	0·109
2*V*	0°	0°

Pyrrhotine is abundant as thin veins and streaks through the ore, and less commonly as poorly developed tabular hexagonal crystals in some calcite veins. It also occurs as thin strings growing perpendicular to the vein walls in thinner veins, where stilpnomelane usually forms a sheath round the pyrrhotine.

Low quartz was also found, especially where the veins cut siliceous ash. Again the crystals are discrete individuals embedded in calcite.

Discussion

Some general conclusions may be made on the conditions under which the stilpnomelane formed, although no precise experimental evidence is available. Such late-stage (i.e. post-regional metamorphism) veins are emplaced at low temperatures and under low hydrostatic pressures, as a fluid; either as aqueous solution in equilibrium with vapour or as a vapour. The change chlorite → stilpnomelane is characteristic of the fourth subzone of the chlorite grade in Otago greywackes (Hutton and Turner, 1936), while in lower grade subzones chlorite and stilpnomelane coexist. A roughly analogous sequence may be traced from calcite veins into chamosite–magnetite rock, where stilpnomelane is sometimes found for several inches from the vein wall (it is always green ferro-stilpnomelane except in the 1 to 5 mm immediately adjacent to the

TABLE II. Trace constituents of stilpnomelanes and associated minerals, parts per million

	1	2	3	4	5
Ga	4	4	20		
Cr			35		
V	40	40	120		
Mo			5		
Ni			20		
Co	10	10	10		
Zr			260		
Yt			35	140	
Sr	20	40	28	430	1000
Ba	64	72	20		
Li	6	6			

1. Green stilpnomelane.
2. Brown stilpnomelane.
3. Chamosite–magnetite rock.
4. Fluorapatite.
5. Vein calcite.

vein, and the magnetite is unaffected). Presumably this change in assemblage in the present case is due to a temperature gradient rather than pressure variation.

The origin of the minerals present in the calcite is fairly clear. An analysis of the chamosite–magnetite rock is given in table I. If all CO_2 is subtracted as calcite and Fe_2O_3 as magnetite, the remainder must represent approximately the composition of the chamosite although as such it has slightly high SiO_2 and low Al_2O_3. A reaction forming stilpnomelane from chamosite involves a considerable increase in SiO_2 and slight decrease in Al_2O_3, but no other major changes (magnetite does not enter into the reaction). In view of the fact that free quartz is found where calcite vein cuts siliceous ash, it is reasonable to assume an abundance of available SiO_2, which could enter into the reaction. It can be seen from analyses 1 and 2 (table I) that the change from green to brown stilpnomelane involves only the state of oxidation of Fe; a similar conclusion was reached by Hutton (1938).

It seems reasonable to assume that the wall rock is also the source of P_2O_5 and TiO_2 for apatite and ilmenite respectively, and of Fe for pyrrhotine, which must indicate a certain amount of S in the vein fluids. On the whole, however, the condition of the fluids must have been strongly oxidizing. A complete lack of *in situ* material has prevented a more complete study of the metamorphic and metasomatic effects.

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