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STILPNOMELANE IN METASOMATIC ROCKS ASSOCIATED WITH STEATITE AND IN REGIONAL SCHISTS, QUEBEC APPALACHIANS

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ABSTRACT

Stilpnomelane is widespread at St-Pierre-de-Broughton and Robertsonville in the Quebec Appalachians, 65 km south of Quebec City. The mineral occurs in regionally metamorphosed, intermediate-pressure, biotite-grade rocks of appropriate bulk chemical composition, and in metasomatic rocks adjacent to blackwall that encloses steatitized parts of the ultrabasic Pennington sheet. The ratio $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ in the stilpnomelane ranges from 0 to 0.83. All Fe^{3+} probably represents primary Fe^{2+} oxidized during weathering. Stilpnomelane coexists with iron-rich biotite and chlorite in which the $Fe^*/(Fe^* + Mg)$ ratio exceeds 0.57 and 0.53, respectively. Other minerals commonly associated are albite, phengite, quartz and titanite. The X_{Fe^*}/X_{Mg} partition coefficient of mineral pairs and the distribution of tie lines lines on the AFM projection suggest that regional metamorphism and metasomatism were coeval. The blackwall formed during steatitization is considered a residue whose volume is about half that of its precursor rock. Postmetamorphic deformation, possibly of Acadian age, has in places sheared the steatitized ultrabasic rocks from their blackwall shell at St-Pierre-de-Broughton.

Keywords: stilpnomelane, blackwall, Quebec, Appalachians.

SOMMAIRE

La stilpnomélane est répandue à St-Pierre-de-Broughton et à Robertsonville, à 65 km au sud de Québec, dans les Appalaches québécoises. On la rencontre dans des roches de composition appropriée métamorphisées à l'échelle régionale, à pression moyenne, jusqu'au stade de la biotite, ainsi que dans l'enveloppe métasomatique des salbandes chloriteuses ("blackwall") qui renferment les parties stéatitisées de l'écaille ultrabasique de Pennington. Le rapport $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ de la stilpnomélane varie de 0 à 0.83; le Fe^{3+} serait surtout dû à l'oxydation du Fe^{2+} primaire par altération atmosphérique. La stilpnomélane coexiste avec biotite et chlorite riches en fer dans lesquelles le rapport $Fe^*/(Fe^* + Mg)$ dépasse 0.57 et 0.53, respectivement. Sont aussi présents: albite, phengite, quartz et titanite. Le coefficient de partage X_{Fe^*}/X_{Mg} entre minéraux et l'attitude des assemblages coexistants dans les projections AFM indiquent que le métamorphisme régional et le métasomatisme étaient contemporains. Le "blackwall" serait un résidu occupant environ la moitié du volume de la roche originelle. À St-Pierre-de-Broughton, un épisode de déformation postérieur au métamorphisme, peut-être d'âge acadien, a détaché çà et là les roches stéatitisées ultrabasiques de leur enveloppe métasomatique.

Mots-clés: stilpnomélane, salbandes chloriteuses, Appalaches québécoises.

GENERAL STATEMENT

Stilpnomelane is a dark brown to black layer-silicate mineral found in some low-grade regionally metamorphosed terranes. Although particularly well developed in iron formations, stilpnomelane may also occur in pelitic, quartzofeldspathic and mafic rocks. The megascopic appearance and optical properties of stilpnomelane mimic closely those of other, more common minerals, and in cursory studies, it may easily be overlooked. In hand specimen, for example, stilpnomelane resembles biotite, whereas in thin section, it is easily mistaken for biotite, oxidized chlorite or green phengite.

From the Quebec Appalachians, stilpnomelane has been reported heretofore only as an accessory mineral in weakly metamorphosed rocks located 30 km southwest of Quebec City (Zen 1974) and near the town of Richmond (Trzcienski 1976). The intent of the present report is to indicate that stilpnomelane occurs widely in low-grade rocks of Early Paleozoic age in the Quebec Appalachians, and that the mineral is a major constituent of schists in an area from St-Pierre-de-Broughton to Robertsonville. Although some exposures occur in modern quarries, others are found in wooded outcrops where, for more than a century, coarse-grained stilpnomelane presumably has been misidentified as biotite.

GEOLOGICAL SETTING

Sedimentary and metamorphic rocks of the Quebec Appalachians are divided broadly into two parts separated from one another by a regional fault or unconformity. Rocks of Cambrian and Ordovician age in the north constitute the "Taconian orogen" (St-Julien & Hubert 1975); rocks of Silurian and Devonian age of the Connecticut Valley – Gaspé synclinorium occur to the south. Stilpnomelane is apparently restricted to low-grade metamorphic rocks of the Taconian orogen.

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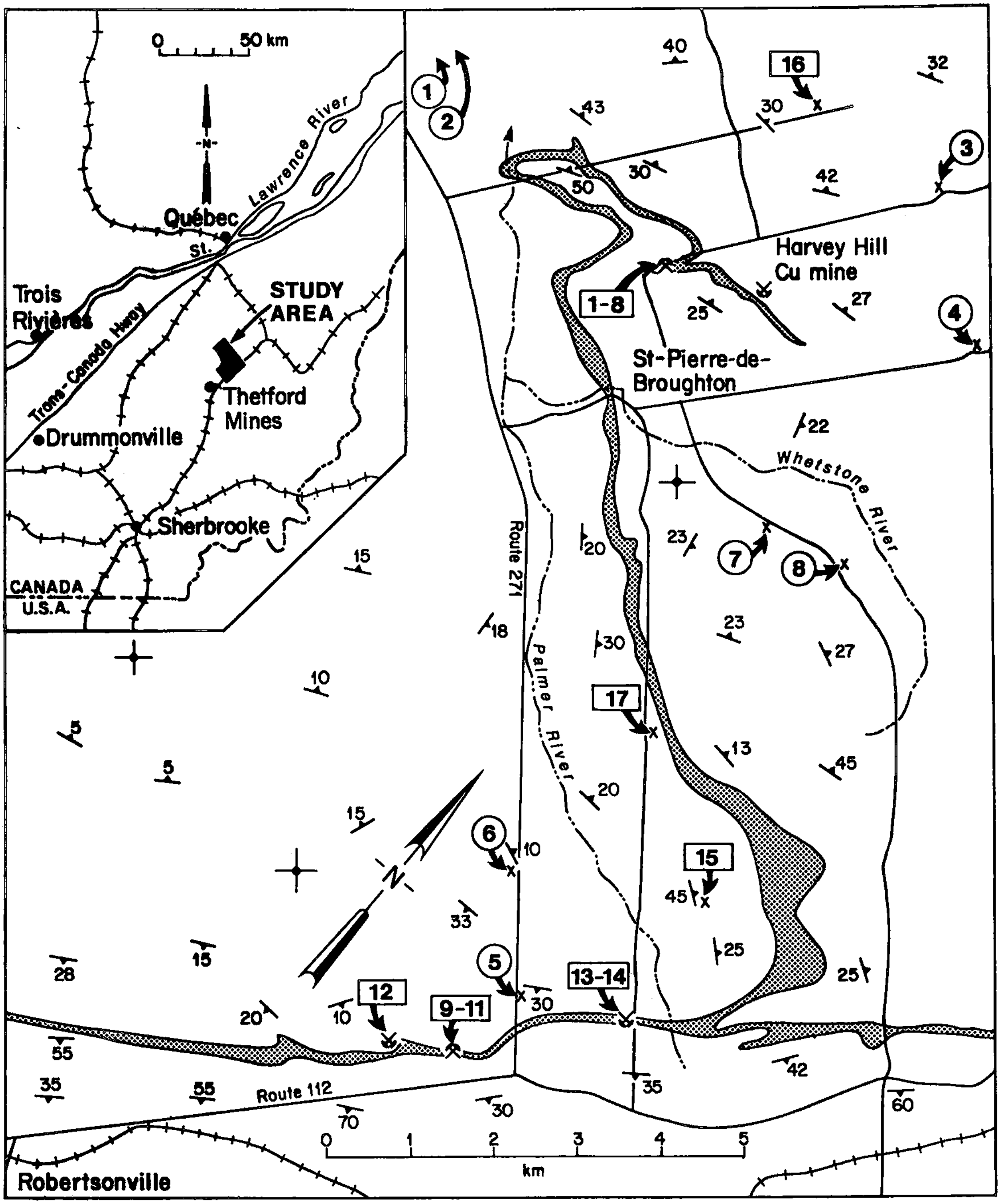

FIG. 1. Generalized map of the St-Pierre-de-Broughton – Robertsonville area, showing part of the Pennington sheet (grey), Bennett Schist (blank), and sample sites (large numbers; those in circles are the composite samples of schist listed in Table 5). Geology simplified from unpublished map by Pierre St-Julien.

In the St-Pierre-de-Broughton – Robertsonville area, located 65 km south of Quebec City (Fig. 1), stilpnomelane occurs in two contrasting settings. It is found in a strictly regional environment in schists of appropriate bulk chemical composition and metamorphic grade. Stilpnomelane also occurs in a metasomatic environment in rocks that have undergone major chemical exchanges with abutting ultramafic bodies during their alteration to talc–carbonate rock and steatite.

STILPNOMELANE-BEARING ROCKS

Regional environment

Stilpnomelane in regionally metamorphosed rocks has been identified by the author in the Bennett Schist in the St-Pierre-de-Broughton – Robertsonville area (Fig. 1 and Group E in Table 1) and in the St-Daniel Formation near Sherbrooke.

Dark brown stilpnomelane in flakes 5 mm in diameter is concentrated in laminae in a fine-grained, light yellow-green epidote schist, 4 km north of St-Pierre-de-Broughton (loc. 16, Fig. 1). Layers of coarse-grained chlorite schist in the same outcrop contain flakes of stilpnomelane as much as 1 cm in diameter. Brown, medium-grained, somewhat gneissic stilpnomelane schist constitutes small outcrops on a hillside overlooking the Palmer River valley, 6 km southeast of St-Pierre-de-Broughton (loc. 15, Fig. 1). The rock is complexly deformed and contains sericitized albite. Fine- to medium-grained biotite schist in a roadcut 4 km southeast of St-Pierre-de-Broughton (loc. 17, Fig. 1) contains minute flakes of stilpnomelane less than 0.1 mm long. One hundred km southwest of St-Pierre-de-Broughton, a massive to faintly laminated, deep brown to black metavolcanic rock in the Lower Ordovician St-Daniel Formation is exposed along autoroute 55, 10 km northwest of Sherbrooke. The rock contains 10% stilpnomelane as nearly colorless (*Z* pale green) flakes 0.6 mm long, but only 0.015 mm thick. The flakes are arranged in radial aggregates set in a muddy-appearing matrix composed of finely granular (< 0.02 mm) albite and epidote, with accessory chlorite, sericite, rutile and titanite.

Metasomatic environment

Unusual stilpnomelane-rich metasomatic rocks are associated spatially with the ultramafic Pennington sheet at St-Pierre-de-Broughton, and between that village and Robertsonville (Fig. 1, Groups A to D in Table 1). Active and abandoned talc quarries afford exceptional exposures.

The Pennington sheet is a relatively thin, gently dipping, areally extensive ultramafic body that marks the sole of a regional thrust-fault. The sheet was emplaced tectonically as serpentinite and subsequently was altered (steatitized) in many places to

TABLE 1. GENERALIZED MODAL COMPOSITIONS OF 17 SCHISTS FROM THE ST-PIERRE-DE-BROUGHTON - ROBERTSONVILLE AREA

	Sample	Quartz	Albite	Muscovite	Biotite	Chlorite	Stilpnomelane	Actinolite	Epidote	Zircon	Titanite	Rutile	Apatite	Opaque	Calcite	Field number and comments	
A	1	▲	■		■	△		▲	■		△			△	■	159A	Hanging-wall schist. Biotite pseudomorphic after stilpnomelane.
	2	▲	■		■	■					▲		△	▲	■	174Q	Hanging-wall schist.
	3	△	■			■	△			△	△	△	▲	▲		174AD	Small tectonic inclusion. Late recrystallization of some albite.
	4					■				△		▲	△		△	174AH1	Blackwall shell of large tectonic inclusion in talc-carbonate rock.
	5		■	△		■				△	▲		▲	▲		174AJ1	Inner shell of same tectonic inclusion.
	6	△	■			▲	■			△	▲		▲	▲		174AK	Core of same tectonic inclusion.
	7	▲	■			△	■				▲	△	△	△		174AL1	Idem.
	8		■	▲		■				△	△	▲	△			174AV	Footwall schist. Na-metasomatized.
B	9	△	■	▲	▲		■			△	▲		△	△		177A	Hanging-wall schist.
	10	▲	■	▲	△	▲	■			△	▲		△			177F	Footwall schist.
	11	▲	■	▲	▲	△	■			△	▲		△	△		177J	Hanging-wall schist.
C	12	▲		■	△	■	■			△	▲		▲	▲		231A	Very mafic rock.
D	13	■	■	■		▲	■			△	▲		△			178E	
	14	▲	■	▲		■				△	▲		△			178I	
E	15	■	■	▲	▲	■	■			△	▲		△	△		774-64	
	16	■	■			△	▲		■		▲		△	△		207C	
	17	■	■		■	▲	△	▲			▲		△	△	▲	228	Stilpnomelane is not in textural equilibrium with other phases.

A, Talc-carbonate rock quarry, 2 km northwest of St-Pierre-de-Broughton; B, Steatite quarry north of route 112, 5 km northeast of Robertsonville; C, Abandoned steatite quarry, 0.7 km southwest of B; D, Abandoned steatite quarry at the Broughton Soapstone Co. mill, 7 km southeast of St-Pierre-de-Broughton; E, Samples not associated with ultrabasic rocks. See Fig. 1 for localities.

■ Major mineral (>10%); ▲ Minor mineral (1-10%); △ Accessory mineral (<1%).

talc–carbonate rock or to steatite composed of talc alone. Contact relationships of the Pennington sheet with the surrounding country-rocks mimic those of small ultramafic bodies to the south in the Appalachians of Vermont and Massachusetts; these were described in detail by Chidester (1962), Jahns (1967) and Sanford (1982).

Alteration of serpentinite to talc-bearing assemblages involves major chemical exchanges with siliceous host-rocks, and leads to a regular succession of metasomatic zones from a few centimetres to several metres thick and disposed outward from the ultramafic body. The thickness and composition of each zone are determined by the original composition of the host rock, the composition and availability of hydrothermal fluids, and the metamorphic T and P that prevailed during the talc-forming reactions (Sanford 1982). Two well-defined zones of metasomatic rocks envelop talc-rich parts of the Pennington sheet. The innermost zone is blackwall, composed nearly entirely of chlorite. As in many New England examples (Jahns 1967, p. 147; Sanford

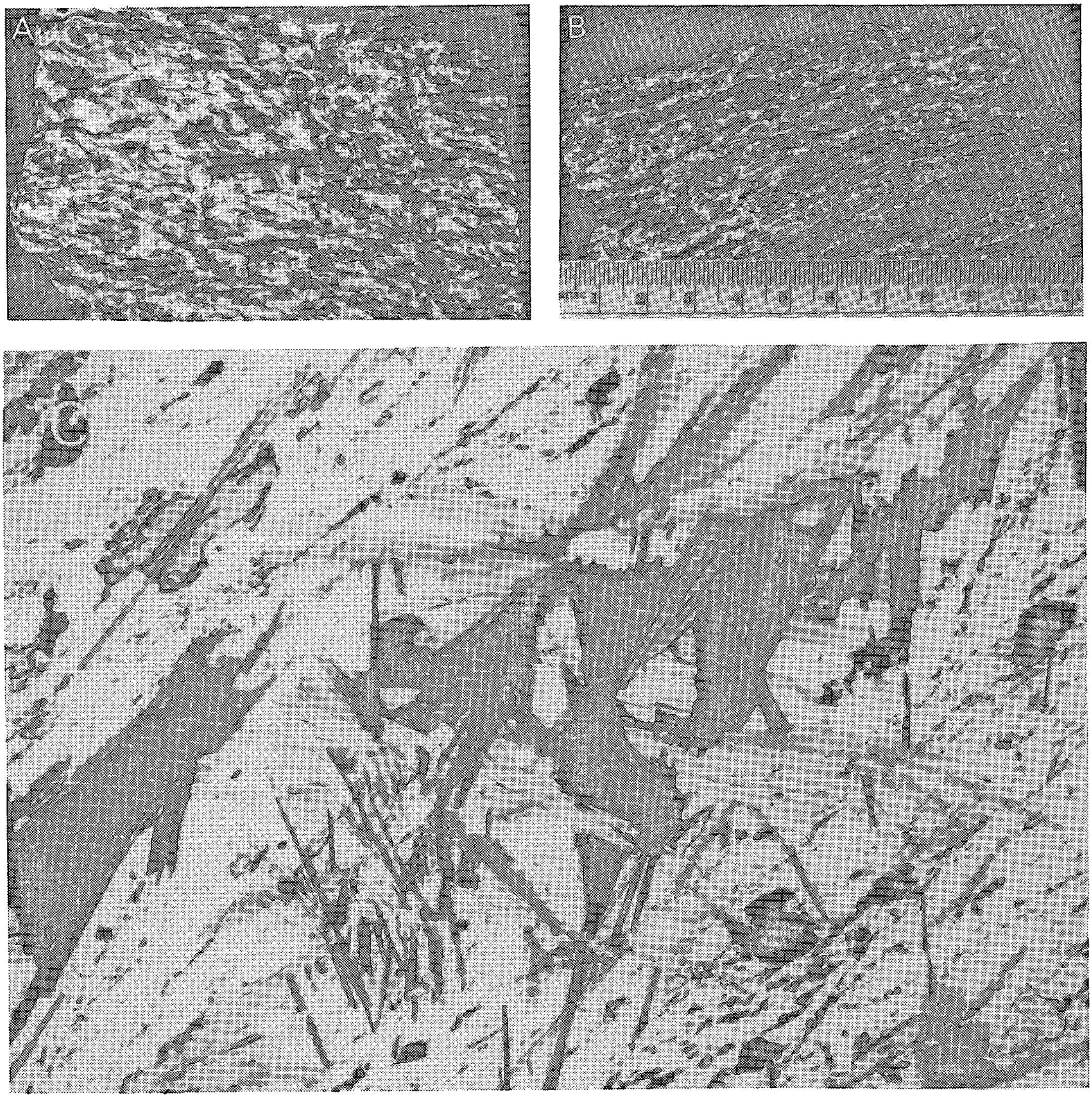

FIG. 2. Two albite–stilpnomelane schists from the metasomatic environment, talc–carbonate rock quarry, St-Pierre-de-Broughton. A. Hand specimen from the hanging wall (scale as in B). B. Hand specimen from the core of a tectonic inclusion in talc–carbonate rock (sample 5, Tables 1 and 4). C. Photomicrograph of B showing coarse stilpnomelane plates in fine-grained albitic matrix. Plane light, width of field of view 4 mm.

1982, p. 605-606), blackwall is succeeded by a zone enriched in Na, comparable to the albite-porphyroblast rock of Chidester (1962, p. 64-65). The accompanying enrichment in iron, which in New England is manifested by an abundance of biotite (Chidester 1962, p. 123) or by a relatively higher Fe*/(Fe* + Mg) ratio in biotite and amphibole (Sanford 1982, p. 560, 565, and Figs. 18, 20, 22), in Quebec is expressed in the crystallization of stilpnomelane.

TALC–CARBONATE-ROCK QUARRY AT ST-PIERRE-DE-BROUGHTON

A singular, fine-grained albite–stilpnomelane schist makes up a discontinuous layer as much as 30 cm thick, admixed with albite-porphyroblast rock immediately overlying blackwall on the hanging wall of the Pennington sheet. The schist is composed of untwinned, saccharoidal, white albite in grains <0.1 mm in diameter, and subhedral to euhedral black stilpnomelane in bent plates from 5 to 10 mm across and arranged in radial aggregates (Fig. 2A). Other minerals are titanite (about 4% modally) and minor chlorite, apatite and pyrite. The associated albite-porphyroblast rock is fine- to medium-grained, dark green-grey muscovite schist peppered with euhedral porphyroblasts of dusted white albite 1 to 3 mm in diameter. Ilmenite, iron-rich chlorite, titanite and apatite are accessories.

Talc–carbonate rock in the quarry contains numerous tectonic inclusions of host rock. Most of the inclusions have the form of thin slabs tens of metres long and have been altered wholly to blackwall. However, two bulky inclusions are concentrically zoned and contain a core of more felsic rock with stilpnomelane (samples 6 and 7, Table 1) that differs from stilpnomelane-rich rock on the hanging wall in that it contains grey quartz, is relatively darker colored, and is layered and gneissic (Fig. 2B) rather than schistose. Stilpnomelane occurs as undeformed plates more than 5 mm across, some of which are arranged in radial aggregates (Fig. 2C). Other minerals present are titanite, zircon, rutile, apatite and pyrite.

OTHER LOCALITIES

Stilpnomelane is a major phase in fine- to medium-grained, dark brown to black, salt-and-pepper albite-rich schist just outside the blackwall of both the hanging wall and footwall of the active steatite quarry (localities 9 to 11, Fig. 1) 5 km northeast of Robertsonville. On the hanging wall of an abandoned talc pit (locality 12, Fig. 1), 0.7 km southwest of the active quarry, chlorite and stilpnomelane make up 35 and 30%, respectively, of a dark, fine- to medium-grained mafic schist similar to blackwall. Stilpnomelane occurs sporadically in fine-grained, dark brown schist adjacent to blackwall and talc-rich ultramafic rocks at the large abandoned quarry at the Broughton Soapstone Co. mill (localities 13 and 14, Fig. 1). The schist contains bent flakes of muscovite and is more quartzose than stilpnomelane schist elsewhere in the metasomatic environment.

MINERALOGY

Microprobe analyses were carried out on 11 grains of stilpnomelane, 7 of biotite, 16 of chlorite, 8 of

TABLE 2. ELECTRON-MICROPROBE ANALYSES OF STILPNOMELANES IN 11 SCHISTS FROM THE ST-PIERRE-DE-BROUGHTON - ROBERTSONVILLE AREA, QUEBEC

Sample no.	3		6		7		9		10		11		12		13		15		16		17	
SiO_2	46.5		45.0		45.5		44.3		46.6		46.7		43.3		45.1		45.5		45.6		46.5	
TiO_2	0.1		tr		0.0		tr		0.0		0.0		0.2		0.0		tr		tr		tr	
Al_2O_3	6.2		6.0		6.0		6.6		6.5		6.9		6.7		6.6		7.1		5.6		5.6	
Fe_2O_3	16.7		0.1		0.0		0.4		2.0		15.5		26.1		23.0		26.6		21.6		14.5	
FeO	15.1		27.5		27.4		27.8		27.0		12.7		5.4		8.8		6.4		8.4		12.1	
MnO	0.5		0.6		0.4		0.3		0.5		0.4		0.4		0.9		0.7		0.6		1.6	
MgO	5.7		6.7		7.2		6.0		6.3		7.6		5.0		5.3		5.4		6.0		6.6	
CaO	0.1		0.2		0.2		0.2		0.1		0.0		0.4		0.3		tr		0.1		0.1	
Na_2O	---		0.2		0.3		0.2		0.6		0.0		0.0		---		0.0		0.0		0.0	
K_2O	0.6		1.2		1.5		1.7		2.2		0.4		0.9		1.1		1.3		0.7		1.0#	
	91.5		87.5		88.5		87.5		91.8		90.2		88.4		91.1		93.0		88.6		88.0	
Number of ions on the basis of 11 (O)																						
Si	3.53	4.00	3.66	4.00	3.65	4.00	3.62	4.00	3.62	4.00	3.53	4.00	3.37	3.98	3.42	4.00	3.37	3.99	3.52	4.00	3.62	4.00
Al^{iv}	0.47		0.34		0.35		0.38		0.38		0.47		0.61		0.58		0.62		0.48		0.38	
Al^{vi}	0.08	2.74	0.23	3.12	0.22	3.17	0.26	3.16	0.22	3.18	0.14	2.75	0.00	2.59	0.01	2.67	0.00	2.64	0.03	2.63	0.14	2.91
Ti	0.01		0.00		0.00		0.00		0.00		0.00		0.01		0.00		0.00		0.00		0.00	
Fe^{3+}	0.95		0.01		0.00		0.02		0.12		0.88		1.53		1.31		1.48		1.25		0.85	
Fe^{2+}	0.96		1.87		1.84		1.90		1.76		0.80		0.32		0.56		0.40		0.54		0.77	
Mn	0.03		0.04		0.03		0.02		0.03		0.03		0.03		0.06		0.04		0.04		0.11	
Mg	0.64		0.81		0.86		0.73		0.73		0.86		0.58		0.60		0.60		0.69		0.77	
Ca	0.01		0.02		0.02		0.02		0.01		0.00		0.03		0.02		0.00		0.01		0.01	
Na	---		0.02		0.05		0.03		0.09		0.00		0.00		---		0.00		0.00		0.00	
K	0.06		0.12		0.15		0.18		0.22		0.04		0.09		0.11		0.12		0.07		0.10	
$\frac{Fe^*}{(Fe^* + Mg)}$	0.749		0.699		0.681		0.725		0.720		0.661		0.761		0.757		0.758		0.722		0.678	
$\frac{Fe^{3+}}{(Fe^{3+} + Fe^{2+})}$	0.497		0.005		0.000		0.010		0.064		0.524		0.827		0.701		0.787		0.698		0.525	
N_z	1.66		1.579		1.576		1.58		1.589		1.655		1.709		1.687		1.703		1.680		1.65	

See Table 1 for locations and generalized modal compositions. Fe^{3+}/Fe^{2+} ratios calculated following Deer et al. (1962, Fig. 26).

\# Potassium analyses gave erratic results for sample 17; the value K_2O = 1.0% was assigned. See text for discussion.

muscovite, 2 of actinolite and 3 of calcite. Stilpnomelane compositions are given in Table 2, whereas remaining compositions are available, at nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Stilpnomelane

The author has used the nomenclature of Hashimoto (1969) to distinguish ferristilpnomelane from ferrostilpnomelane, with a division between the two at a value of the atomic ratio $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ of 0.50. The term stilpnomelane is reserved for the entire series. Fe^{3+} contents were calculated by solving the following pair of simultaneous equations:

$$Fe^* = Fe^{2+} + Fe^{3+} \qquad (1)$$

$$(100 - \text{ferrostilpnomelane}) = (Fe^{3+} + Al)/(Fe^{3+} + Al + Fe^{2+} + Mg + Mn) \qquad (2)$$

The value (100 - ferrostilpnomelane) was determined graphically (Deer *et al.* 1962, p. 106) based on the n_z of each grain of stilpnomelane measured in sodium light.

In the Quebec rocks, stilpnomelane constitutes euhedral to subhedral plates that in most samples have a porphyroblastic habit and a radial arrangement (Fig. 2C). Color and pleochroism range widely, and depend on the $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ ratio of the mineral. Ferrostilpnomelane with little or no Fe^{3+} (samples 6 and 7, Table 2) is weakly pleochroic: X colorless, $Y = Z$ pale grey-green. With only slightly higher Fe^{3+} contents (samples 9, 10), pleochroism becomes pronounced: X light yellow-tan, $Y = Z$ medium olive-brown. Grains of ferristilpnomelane are strongly pleochroic: X medium bright yellow, $Y = Z$ deep orange-brown to opaque.

The role of Fe^{3+} in stilpnomelane has been deliberated extensively (Dobretsov *et al.* 1973). Based on evidence from crystal chemistry (Eggleton & Bailey 1965), phase equilibria (Zen 1960, Craw 1981) and field relationships (Robinson 1969), agreement is general (but not unanimous: see Eggleton 1972) that stilpnomelane forms as ferrostilpnomelane that subsequently may undergo oxidation, commonly by weathering. This view is supported by observations in the Quebec Appalachians. Samples 6 and 7, containing pure ferrostilpnomelane, were taken from the core of the largest tectonic inclusion, riven by blasting only months prior to sampling in the quarry at St-Pierre-de-Broughton. Ferrostilpnomelane from the hanging wall of the active steatite quarry northeast of Robertsonville (sample 9) comes from schist uncovered by quarrying in the past few years, whereas ferristilpnomelane from the hanging wall (sample 11) is from a natural outcrop enlarged by quarrying. All rock is weathered in the shallow pit to the southwest, where sample 12, containing ferristilpnomelane, was taken. Sample 13, also containing ferristilpnomelane, is from a near-surface site exposed by quarrying in the last century. All stilpnomelane in natural outcrops (samples 15 to 17) is ferristilpnomelane. Furthermore, pale green ferrostilpnomelane commonly is encased in thin shells of light brown stilpnomelane easily interpreted as the product of incipient oxidation, a relationship also reported by Hutton (1938), Brown (1971) and Craw (1981).

Some authors have proposed that progressive leaching of K accompanies the oxidation of ferro- to ferristilpnomelane. Frey *et al.* (1973) found that green (ferro-)stilpnomelane contains as much as ten times the amount of K in brown (ferri)stilpnomelane. Brown (1971, p. 282-283) went further and, basing his argument on the composition of stilpnomelane coexisting with the chemically equivalent pair chlorite–minnesotaite (on an Al–Fe–Mg plot) in an iron formation, suggested that the minimum content of potassium in natural occurrences of stilpnomelane is 1.88% K_2O.

The Quebec stilpnomelane sheds some light on these problems, but one must first emphasize the erratic behavior of potassium and the uncertainty associated with its analysis in stilpnomelane (Graham 1976, Craw 1981). Comments on the present analyses (Table 2) are in order. The microprobe at the Université Laval is a model 121000 ARL fitted with two crystal spectrometers. Spots to be analyzed were selected beforehand and located precisely on thin section drawings by the author. Analyses by repeated ten-second integrations, two elements at a time, were carried out on each spot. Potassium was analyzed on the third or fourth run. By completion of the five required runs (for nine elements), target spots on ferrostilpnomelane (except sample 3) were darkened to a deep red-brown color, and many had strongly enhanced birefringence. Target spots on ferristilpnomelane were unchanged. Alterations of potassium content may have taken place at target spots in the course of analysis, particularly in ferrostilpnomelane. For example, whereas analysis of ferrostilpnomelane in sample 7 by electron microprobe gave 1.5% K_2O, analysis of a concentrate (>95% stilpnomelane) from the same sample gave 0.86% K_2O by atomic absorption, and 0.92% K_2O by X-ray fluorescence. Stilpnomelane in sample 17 behaved in a particularly unusual fashion: under the electron beam during analysis, potassium counts increased progressively. Nowhere on the mineral were counts stable, and a value of 1% K_2O, the approximate value at the onset of analysis, was assigned (Table 2). The mechanism proposed by Graham (1976) and modified by Craw (1981) best explains this behavior: OH^- ions

TABLE 3. ANHYDROUS FORMULAE OF STILPNOMELANE

IDEAL STILPNOMELANE	QUEBEC STILPNOMELANES		
	Average stilpnomelane	Average ferrostilpnomelane(1)	Range
$(K, Na, Ca)_{0.00-0.84}$ $(Al, Fe, Mg, Mn)_{2.64-3.11}$ $Si_{3.10-3.75}\,Al_{0.90-0.25}$*	$(K, Na, Ca)_{0.15}$ $(Al, Fe, Mg, Mn)_{2.71}$ $Si_{3.54}\,Al_{0.46}$	$(K, Na, Ca)_{0.23}$ $(Al, Fe, Mg, Mn)_{2.93}$ $Si_{3.64}\,Al_{0.36}$	$(K, Na, Ca)_{0.04-0.34}$ $(Al, Fe, Mg, Mn)_{2.46-2.96}$ $Si_{3.37-3.66}\,Al_{0.62-0.34}$
$(K, Na, Ca)_{4^{**}\text{ or }5^{***}}$ $(Ti_{0.1}\,Al_{2.3}\,Fe_{35.5}\,Mg_{9.3}\,Mn_{0.8})$ $(Si_{63}\,Al_{9})$**	$(K, Na, Ca)_{2.6}$ $(Al_{2.1}\,Fe_{32.6}\,Mg_{12.7}\,Mn_{0.7})$ $(Si_{63}\,Al_{8.3})$	$(K, Na, Ca)_{4.1}$ $(Al_{3.9}\,Fe_{32.6}\,Mg_{13.5}\,Mn_{0.5})$ $(Si_{63}\,Al_{6.3})$	$(K, Na, Ca)_{0.7-5.6}$ $(Al_{0.0-4.5}\,Fe_{28.2-35.1}\,Mg_{10.8-15.3}\,Mn_{0.3-1.9})$ $(Si_{63}\,Al_{5.9-11.6})$

(1) Samples 6, 7, 9 and 10; * Chauvel (1972) based on 11 (0); ** Eggleton (1972) based on Si = 63; *** Eggleton & Chappell (1978) based on Si = 63.

volatilized by the beam are replaced by nearby, loosely bound K^+ ions that migrate to fill the structural vacancies created. The problem of charge balance remains unresolved.

The correlation between K and $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ is erratic in the Quebec occurrences of stilpnomelane. On average, ferrostilpnomelane contains more K than ferristilpnomelane (respectively 1.4 and 0.9% K_2O by weight). Nevertheless, the most oxidized ferristilpnomelane (in sample 12) contains more K (0.9% K_2O) than ferrostilpnomelane in sample 3 (0.6%). The data do not support the minimum K_2O content of unaltered stilpnomelane proposed by Brown (1971).

The ideal formula of stilpnomelane is in dispute. Stilpnomelane from Quebec (Table 3) shows general agreement with formulae proposed by Chauvel (1973) and Eggleton (1972).

Biotite

Biotite is anhedral, with *Z*-direction colors that range from olive to dark red-brown with increasing $Fe^*/(Fe^* + Mg)$ ratio. Iron-rich biotite [$Fe^*/(Fe^* + Mg) \geq 0.57$] coexists with stilpnomelane, although relatively magnesian biotite [$Fe^*/(Fe^* + Mg) = 0.50$] coexists with stilpnomelane in sample 17.

Chlorite

Prograde anhedral chlorite occurs in 15 of the 17 samples. It is secondary after biotite in sample 1, and is absent in sample 9. Compositions vary chiefly in the ratio $Fe^*/(Fe^* + Mg)$. Strongly pleochroic, bright grey-green, iron-rich chlorite [$Fe^*/(Fe^* + Mg) \geq 0.53$] coexists with stilpnomelane. More magnesian chlorite is pale green, and the chlorite in the blackwall [sample 4; $Fe^*/(Fe^* + Mg) = 0.19$] is nearly colorless.

Muscovite

Phengitic muscovite, mostly as robust, subhedral flakes, is the only white mica in the samples studied. In the metasomatic environment it is widespread at the three southernmost quarries (samples 9 to 14). Based on 22 oxygen atoms, Si ranges from 6.12 to 6.73. The value of $X_{\text{paragonite}}$ is between 0.04 and 0.10, and even lower, 0.03, in the only albite-free sample (no. 12). Although generally common in the Bennett Schist, muscovite is present in only one sample (no. 15) from the regional environment. It is weakly phengitic, with Si = 6.09 and $X_{\text{paragonite}} = 0.06$. Relatively iron-rich muscovite [$Fe^*/(Fe^* + Mg) \geq 0.53$.] is found with stilpnomelane. In stilpnomelane-free sample 8, the ratio is 0.32.

Actinolite

Actinolite occurs in two samples. In sample 1, actinolite is bright blue-green in thin section [$Fe^*/(Fe^* + Mg) = 0.46$; $Al_2O_3 = 2.6\%$], whereas in sample 17 it forms nearly colorless anhedra [$Fe^*/(Fe^* + Mg) = 0.30$; $Al_2O_3 = 0.9\%$].

Calcite

Anhedral carbonate, in part present as porphyroblasts, is a major constituent in the hanging wall at the St-Pierre-de-Broughton quarry. It is also a common accessory mineral in the regional schists. Carbonates in samples 1, 2 and 17 consist of nearly pure calcite (>97% $CaCO_3$), with minor $MgCO_3$ (0.2 to 0.6%), $FeCO_3$ (0.5 to 1.2%) and $MnCO_3$ (0.8 to 1.5%).

PETROLOGY

The discussion that follows aims to establish: (1) that the grade of regional metamorphism is uniform throughout the St-Pierre-de-Broughton – Robertsonville area, (2) that conditions of T and P adjacent to the Pennington sheet during steatitization resembled those in surrounding host-rocks during regional metamorphism, and (3) that metamorphism of the Bennett Schist and steatitization in the Pennington sheet were coeval.

Unfortunately, the petrology of stilpnomelane-bearing rocks is not without pitfalls. Firstly, the chemical composition of stilpnomelane is known imprecisely, and K_2O may be in error in many analyses. Secondly, the role of Fe^{3+} in the mineral is uncertain. Finally, the porphyroblastic habit characteristic of stilpnomelane is open to multiple interpretations.

Prograde stilpnomelane typically occurs as boldly discordant porphyroblasts that locally are filled with tiny inclusions (Fig. 2C). Such a texture dominates the Quebec rocks in both the metasomatic and regional environments, although stilpnomelane may also be bent or lie weakly oriented with respect to schistosity. In only one sample (no. 13) is stilpnomelane rigorously parallel with schistosity.

The porphyroblastic textures are open to two interpretations. Either stilpnomelane postdates the regional metamorphism and records a later, static, thermal overprint, or it formed late in the metamorphic episode after virtually all deformation had ceased. A history of repeated stilpnomelane-forming events that differentially affected rocks in the restricted St-Pierre-de-Broughton - Robertsonville area, particularly in the absence of intrusive igneous rocks, is improbable. Rather, the author interprets the textures, varied as they are, to be consonant with mineralogical equilibrium achieved during a single metamorphic episode. Stilpnomelane constitutes undeformed porphyroblasts in rocks where metamorphic recrystallization outlasted deformation. Bent porphyroblasts occur where the reverse held, *i.e.*, where deformation outlasted metamorphic recrystallization. Stilpnomelane plates are aligned with schistosity where deformation and metamorphic recrystallization were coeval.

Two samples were judged on textural grounds alone to represent disequilibrium assemblages. Sample 1, without stilpnomelane, contains cross-cutting, lathlike porphyroblasts of anhedral biotite pseudomorphic after stilpnomelane. In sample 17, stilpnomelane occurs as minute plates no more than 0.005 mm thick that are not commensurate with the grain size of the schist, where biotite forms flakes from 0.1 to 0.35 mm thick.

Metamorphic grade

Metamorphic grade appears constant in passing from the more or less isochemical metamorphism of the regional environment to the metasomatic environment characterized by substantial chemical exchanges. The widespread occurrence of biotite, albite and actinolite, the presence of chloritoid in highly aluminous pelites at the Harvey Hill Cu mine, and the absence of staurolite or garnet, even in iron-rich pelites, all point to regional metamorphism having taken place in the biotite zone of an intermediate-pressure facies series. Stilpnomelane itself is of little use as an isograd mineral (Zen & Thompson 1974). It may appear in the lowest-temperature part of the greenschist facies (Dobretsov *et al.* 1973), or

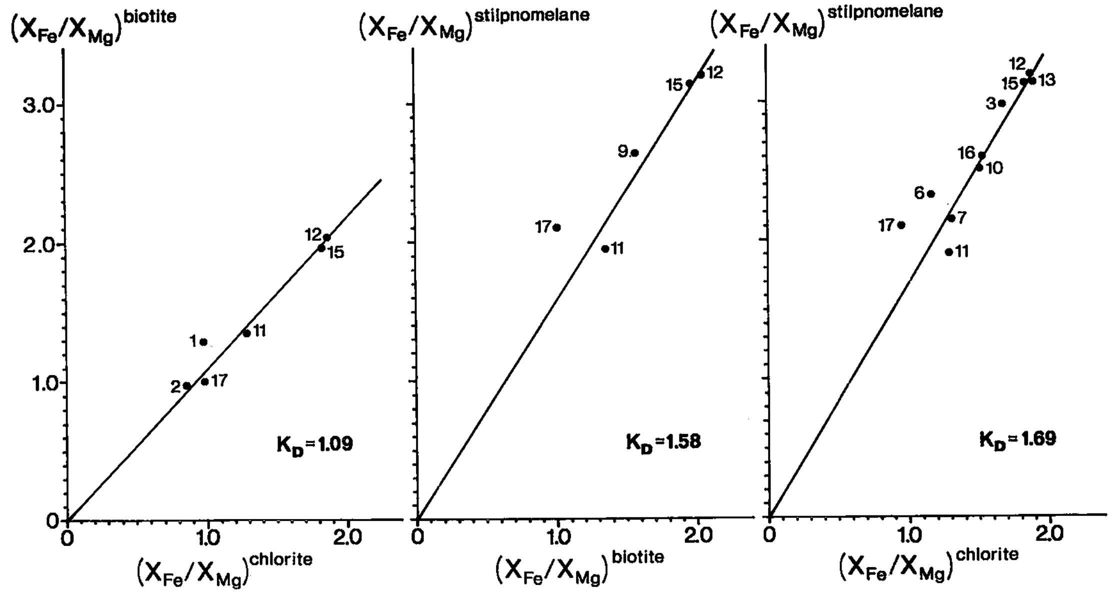

FIG. 3. Fe/Mg partitioning in biotite–chlorite, stilpnomelane–biotite and stilpnomelane–chlorite pairs. All Fe calculated as Fe^{2+}. Sample numbers are from Table 1.

even at lower grades (Seki 1961), and persists into the amphibolite facies (Brown 1971, Korikovskiy *et al.* 1975).

Phase equilibria

Three ferromagnesian silicates, chlorite, biotite and stilpnomelane in order of increasing Fe*/(Fe* + Mg) ratio, are widely dispersed in the study area. X_{Fe^*}/X_{Mg} partition coefficients, K_D, have been plotted for the mineral pairs biotite-chlorite, stilpnomelane—biotite and stilpnomelane-chlorite (Fig. 3). Samples 1 and 17, judged already on textural grounds to be disequilibrium assemblages, depart significantly.

In sample 1, biotite is relatively too iron-rich with respect to coexisting chlorite. The biotite is in part pseudomorphic after an earlier stilpnomelane, which

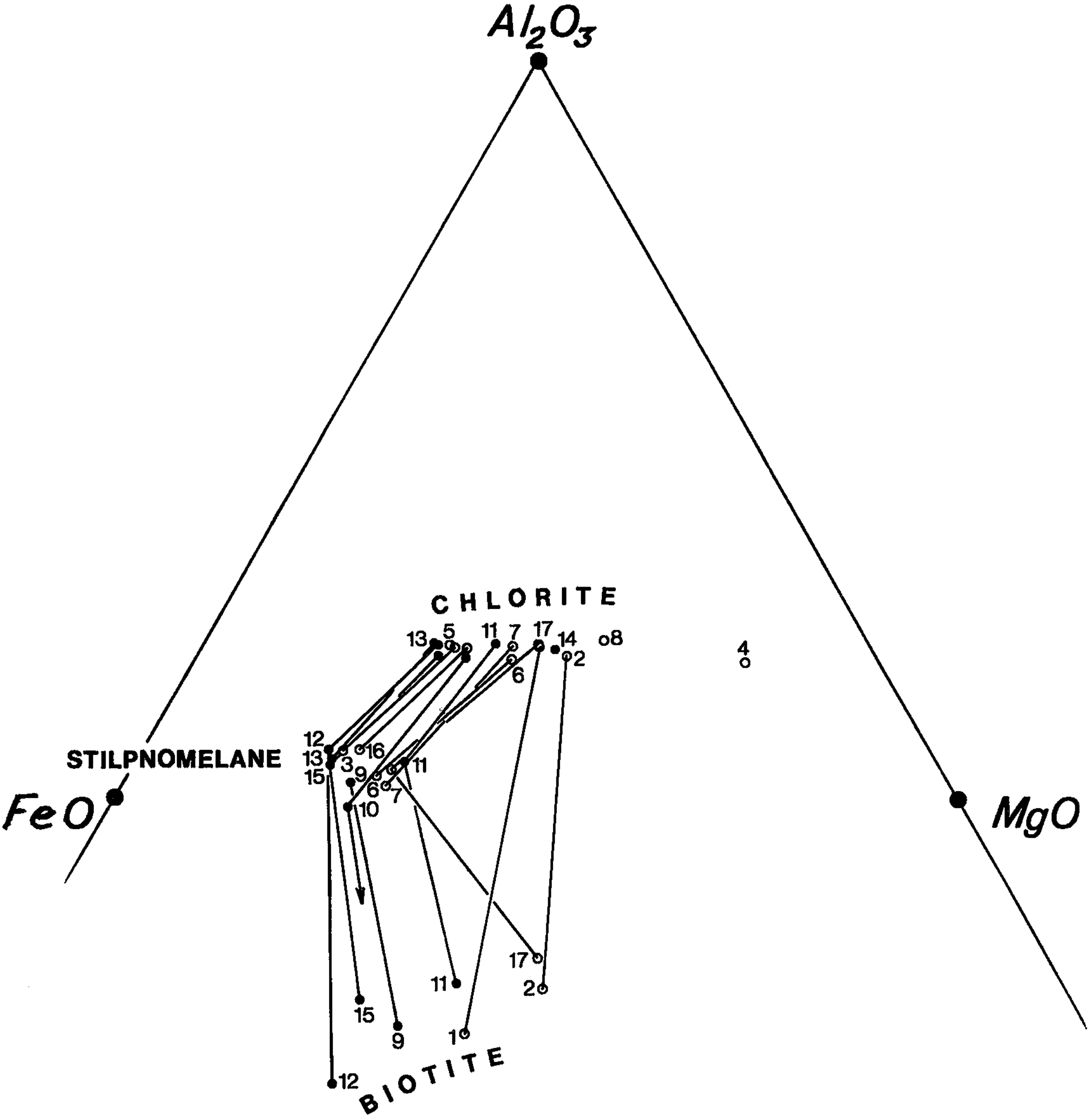

FIG. 4. AFM (Thompson) projection of chlorite, stilpnomelane and biotite compositions. All Fe calculated as Fe^{2+}. Sample numbers are from Table 1. Filled circles, samples with quartz + muscovite; open circles, samples lacking quartz or muscovite or the two minerals and therefore not compatible topologically with the projection. Biotite in sample 10 is too fine grained to permit analysis.

may have influenced its X_{Fe*}/X_{Mg} ratio during the replacement reaction (Brown 1971):

$$\text{muscovite} + \text{stilpnomelane} \rightarrow \text{biotite} \; (+ \text{chlorite} + H_2O) \qquad (3)$$

Ideally, to be in equilibrium with the chlorite (X_{Fe*}/X_{Mg} = 0.98) of sample 1, a biotite should have an X_{Fe*}/X_{Mg} ratio of 1.06, whereas the ratio of a coexisting stilpnomelane should be 1.62 (Fig. 3). The ratio of the biotite in sample 1 is 1.30, an intermediate value. Presumably, the newly formed biotite, during the replacement reaction, equilibrated continuously with matrix biotite to achieve the medial value. Why the chlorite did not react to become more iron-rich and reach equilibrium with the new biotite is not clear. Some of the chlorite is secondary and replaces biotite. Perhaps the late chlorite formed during cooling and equilibrated with prograde chlorite under conditions unlike those of the prograde metamorphism.

Fine-grained, accessory stilpnomelane in sample 17 is not in equilibrium with coexisting magnesian biotite or chlorite (Fig. 3). The stilpnomelane-forming reaction, which postdates the prograde regional metamorphism, may have been (Dobretsov *et al.* 1973):

$$\text{biotite} + \text{quartz} + \text{magnetite} + H_2O \rightarrow \text{stilpnomelane} + \text{chlorite} + \text{muscovite} \qquad (4)$$

The presence of two generations of chlorite, one primary and the other a secondary replacement of biotite, supports the proposed reaction, although the absence of muscovite is unexplained. As in sample 1, retrograde reactions are ambiguous.

All compositions determined for chlorite, stilpnomelane and biotite have been plotted on an AFM (Thompson) projection (Fig. 4). The following observations are pertinent: (1) All iron in stilpnomelane was calculated as Fe^{2+}. The restricted scatter of points that represent stilpnomelane with $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratios from 0 to 0.83 (Table 2) lends support to the view that primary iron in stilpnomelane is largely or wholly ferrous (Zen 1960, Robinson 1969). (2) Stilpnomelane that coexists with iron-rich chlorite, iron-rich biotite, or with both minerals, defines a narrow fan of tie lines. Small departures are interpreted as artifacts that result from unreliable analyses for potassium, preferential leaching of potassium from ferristilpnomelane by weathering, or a combination of the two. The widely divergent tie-lines of samples 1 and 17 confirm the nonequilibrium nature of these samples established earlier. The tie line joining coexisting chlorite and biotite in stilpnomelane-free sample 2 falls beyond the most iron-poor side of the three-phase field chlorite – stilpnomelane – biotite. (3) The concordance of partition coefficients and the congruence of mineral tie-lines from widely spaced samples provide further evidence that temperature was broadly uniform during the peak of prograde metamorphism throughout the area. Moreover, the overlap of samples from the regional and metasomatic environments is in keeping with the view that prograde regional metamorphism and steatitization in the Pennington sheet were coeval.

Stilpnomelane and blackwall

The association of stilpnomelane-rich rocks with blackwall is conspicuous in all the talc quarries. Especially significant examples are afforded by tectonic inclusions with cores of albite–stilpnomelane rock that are enclosed in talc–carbonate rock in the quarry at St-Pierre-de-Broughton. The unique spatial setting of the inclusions permits semiquantitative mass-transfer calculations of the chemical and volumetric changes that may have accompanied formation of the blackwall.

The largest tectonic inclusion has the form of an ellipsoid of revolution. It is made up of a core of albite–stilpnomelane rock (no. 7, Table 4) whose major and minor axes are 6 and 2 m, respectively. The core is enveloped by a shell 0.4 m thick, com-

TABLE 4. CHEMICAL AND MODAL COMPOSITIONS AND BULK DENSITIES OF THREE ROCKS THAT COMPOSE A TECTONIC INCLUSION OF COUNTRY ROCK IN TALC-CARBONATE ROCK AT ST-PIERRE-DE-BROUGHTON

Sample no.	4	5	7
SiO_2	30.13	60:02	63.20
TiO_2	1.60	1.40	1.40
Al_2O_3	18.68	18.36	14.85
Fe_2O_3	1.75	1.39	1.33
FeO	8.75	3.73	3.80
MnO	0.08	0.05	0.06
MgO	25.87	1.45	1.45
CaO	0.06	0.58	1.18
Na_2O	0.13	9.84	8.76
K_2O	0.00	0.05	0.46
P_2O_5	0.02	0.32	0.21
CO_2	0.02	0.13	0.07
H_2O^+	12.30	1.80	1.82
H_2O^-	0.22	0.13	0.14
	99.61	99.25	98.73
Quartz			5.4
Albite		82.9	66.5
Muscovite		0.1	
Chlorite	97.8	12.3	0.2
Stilpnomelane			23.0
Zircon	0.3	0.2	
Titanite		1.0	4.3
Rutile	1.9		0.1
Apatite	tr	1.8	0.1
Opaque		1.7	0.5
Calcite	tr		
	100.0	100.0	100.1
D (g/cm^3)	2.79	2.71	2.67

4, Blackwall shell that surrounds the tectonic inclusion; 5, Inner shell of albite-chlorite schist; 7, Core of stilpnomelane schist. Wet-chemical analyses by Centre de Recherches Minérales, Québec. Modal analyses based on 1435, 1445, and 1289 points, respectively, on standard thin sections by the author. Proportions of quartz and albite determined by relative peak intensities on whole-rock diffractograms.

posed of albite–chlorite rock (no. 5, Table 4). A 1.5-m-thick shell of blackwall (no. 4, Table 4) constitutes the exterior of the inclusion. The core and shells of the inclusion have chemical compositions unlike those of common rocks, and all are metasomatic replacements of a precursor rock. Isolation of the inclusion in the Pennington sheet, 30 m below the hanging wall and 75 m above the footwall, makes it likely that metasomatic exchanges were limited exclusively to the tectonic inclusion and enclosing ultramafic rocks. Gradients of chemical potential were restricted to inwardly and outwardly directed radial paths, more or less normal to the surface of the inclusion. Diffusion away from the ultramafic rock was restricted to a confined space, and components could not disperse imperceptibly into vast volumes of host rock as presumably took place at the hanging wall and footwall.

The assumption is made here that the chemical composition of the precursor rock of the inclusion was similar to that of the pelitic to semipelitic host Bennett Schist exposed beyond the metasomatic influence of the Pennington sheet. Accordingly, eight composite samples of Bennett Schist were taken from fresh roadcuts and stream-bank exposures within a few km of St-Pierre-de-Broughton (Fig. 1). Two elements, sodium and titanium (expressed as Na_2O and TiO_2) were selected for analysis because of their respective mobility and immobility during the metasomatic reactions (Table 5).

Three cases are considered (Table 6). Case A is the present state of the inclusion: its core of albite–stilpnomelane rock (volume 37.7 m^3), inner shell of albite–chlorite rock (30.1 m^3), and shell of blackwall (223.9 m^3). Based on the chemical compositions and densities of the three rocks, the inclusion contains 17.6 tonnes of Na_2O and 12.5 tonnes of TiO_2. In B, it is assumed that metasomatism occurred at constant volume; that is, the body of precursor rock had the volume of the presently exposed inclusion (291.7 m^3), a density of 2.7 g/cm^3, and the tenors of Na_2O and TiO_2 in average host-rock (Table 5). The contents of Na_2O and TiO_2 (respectively 10.8 and 7.0 tonnes) of such an inclusion fall far short of the amounts of the oxides actually present in the metasomatized rocks (Table 6). An equal volume of precursor rock contains less than two thirds of the required Na_2O, and just over one half the TiO_2. Case C assumes that the blackwall shell represents a residue whose volume is only one half of the precursor rock. Here the calculated contents of Na_2O and TiO_2 are remarkably close (within 10 and 1%, respectively) to the contents of these oxides observed in the inclusion.

TABLE 5. Na_2O AND TiO_2 IN COMPOSITE SAMPLES OF BENNETT SCHIST

Sample *	Na_2O	TiO_2
1	1.04 wt.%	1.02 wt.%
2	2.57	2.08
3	1.83	0.70
4	1.48	1.03
5	0.42	0.06
6	1.09	0.35
7	0.93	0.83
8	1.69	1.02
Average	1.38	0.89

* See Figure 1 for sample sites, which are all from the St-Pierre-de-Broughton - Robertsonville area.

TABLE 6. DENSITY, VOLUME, BULK WEIGHT, Na_2O AND TiO_2 IN A TECTONIC BLOCK IN TALC-CARBONATE ROCK AT THE QUARRY, ST-PIERRE-DE-BROUGHTON, AND POSSIBLE PRECURSOR ROCKS OF THE INCLUSION

	Rock type	Density	Volume	Bulk weight	Na_2O	TiO_2
A.	Core	2.67	37.7	100.7	8.8	1.4
	Inner shell	2.71	30.1	81.6	8.0	1.1
	Blackwall shell	2.79	223.9	624.7	0.8	10.0
	Total		291.7	807.0	17.6	12.5
B.	Core - inner shell precursor schist	2.7	67.8	183.1	2.5	1.6
	Blackwall precursor schist	2.7	223.9	604.5	8.3	5.5
	Total		291.7	787.6	10.8	7.0
C.	Core - inner shell precursor schist	2.7	67.8	183.1	2.5	1.6
	Blackwall precursor schist	2.7	447.8	1209.0	16.7	10.8
	Total		515.6	1392.1	19.2	12.4

A. The inclusion as exposed. Core of albite-stilpnomelane rock: a 6 m, b 2 m, D 2.67 g·cm^{-3}; Table 4, no. 7. Inner shell of albite-chlorite rock: 0.4 m thick, D 2.71 g·cm^{-3}; Table 4, no. 5. Blackwall shell: 1.5 m thick, D 2.79 g·cm^{-3}; Table 4, no. 4. Volume in m^3, Na_2O and TiO_2 in tonnes.
B. Volume-for-volume replacement of precursor schist by blackwall. Precursor schist: a 9.8 m, b 5.8 m, D 2.7 g·cm^{-3}, Na_2O 1.38%, TiO_2 0.89%.
C. Volume of blackwall is 50% of the volume of precursor schist. Block of precursor schist: a 11.5 m, b 7.5 m, D 2.7 g·cm^{-3}, Na_2O 1.38%, TiO_2 0.89%.

The figures used in the calculations above are semi-quantitative at best. Their purpose is solely to show the likelihood that significant volume-loss accompanied the metasomatic formation of blackwall at St-Pierre-de-Broughton. At first glance it may appear improbable that a volume loss perhaps as great as 50% could be unaccompanied by direct structural evidence. However, the *linear* shrinkage of the inclusion during metasomatism and volume loss would have been much less. For example, the long axis of the inclusion in the quarry is about 9.8 m; with a shell of precursor rock of twice the volume in place of the present blackwall shell, the long axis would be 11.5. This is a diminution of less than 15%, an amount perhaps easily passed unnoticed. Sanford (1982) has already remarked on this relationship in a study of blackwalls in New England.

Why stilpnomelane?

Stilpnomelane is not common in metamorphic terranes. Its surprising abundance in the area of this report is due to a fortuitous combination of favorable metamorphic conditions and appropriate composition of the rocks. Around the world, stilpnomelane is restricted chiefly to low-grade and high- or medium-pressure metamorphic rocks (Miyashiro 1973). In the St-Pierre-de-Broughton - Robertsonville area, the Bennett Schist is in the greenschist facies. Contiguous rocks to the southwest with blue amphibole (Trzcienski 1976) and omphacite (Laird & Albee 1981) show the high-pressure affinities of the metamorphic belt.

Among pelites and psammites, only rocks with high Fe*/(Fe* + Mg) ratios and low contents of Al and K can contain stilpnomelane. As illustrations, even though iron-rich, aluminous pelites contain chloritoid in place of stilpnomelane, and K-rich rocks contain biotite. Thus biotite in samples 10 and 11 is restricted to small flakes adjacent to aggregates of muscovite, the only K-rich domains in the respective rocks. Mineralogical evidence points to the Bennett Schist being poor in K relative to Na. Accordingly, in the alkali metasomatic rock adjacent to blackwall, enrichment was chiefly in Na, and stilpnomelane is the ferromagnesian mineral observed rather than biotite, which is characteristic in some Vermont occurrences (Chidester 1962, p. 123, 125). In fact, molar $Na_2O/(Na_2O + K_2O)$ ratios of albite-rich metasomatic rocks at St-Pierre-de-Broughton range from 0.97 to 0.99 (Table 4), whereas an albite-porphyroblast rock with biotite from Vermont has the ratio 0.83 (Chidester 1962, Table 3, no. 24).

ACADIAN(?) DEFORMATION

The history of deformation and metamorphism in the St-Pierre-de-Broughton – Robertsonville area is complex and incompletely understood. Nevertheless, the fact that multiple deformation and the main episode of metamorphism took place during the Taconic orogeny is well established (St-Julien & Hubert 1975). Postmetamorphic shearing has separated the Pennington sheet from its blackwall shell along the footwall in the quarry at St-Pierre-de-Broughton. The former presence of blackwall is recorded by trains of coarse, mechanically broken grains of pyrite on the surface of the host schist where overlain by steatite or talc–carbonate rock. Pyrite is prominent only in blackwall, where commonly it forms euhedral cubes several mm across that may reach 3% modally.

The shearing may be of Acadian age. St-Julien *et al.* (1983) have speculated that Acadian deformation in the Notre Dame anticlinorium (site of the Pennington sheet), heretofore unrecognized, may be widespread. Evidence in the quarry at St-Pierre-de-Broughton supports this view.

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