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Pyrophyllite and metamorphism in the Carolina slate belt

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Abstract

Exploitable pyrophyllite at Hillsborough, North Carolina, occurs in late Precambrian metavolcanics of the Carolina slate belt as vein and fracture fillings between quartzite and quartz–sericite schist. The host rock forms a lens-shaped body that parallels the regional structural trend. The mineralized area consists of quartz, andalusite, topaz, sericite, pyrophyllite, and kaolinite.

The following paragenesis has been recognized by petrographic and field study: (1) regional prograde metamorphism produced the andalusite–topaz–quartz rock; (2) secondary andalusite reprecipitated during silicification of the andalusite–topaz–quartz rocks; (3) deformation produced both fractures and the regional foliation of the schist and quartzite; (4) sericite, pyrophyllite, and quartz formed fracture fillings in the andalusite–topaz–quartz rocks; (5) retrograde metamorphism formed kaolinite as an alteration product of andalusite and developed a second foliation, and (6) kaolinite was deposited as fracture fillings from low-grade metamorphism and weathering.

The mineral paragenesis and textures at Hillsborough indicate that the mineral assemblages are in disequilibrium and that water, SiO_2 and possibly Al_2O_3 behaved as mobile components during the formation of pyrophyllite. Recent experimental and theoretical work places a maximum temperature and pressure on the formation of the andalusite and topaz (400–450°C, $<$ 2kbar), well within a low-grade metamorphic regime. The geochemical evidence points to the leaching of the andesitic and dacitic volcanic rocks by a hydrothermal or geothermal process before the regional metamorphism to provide the host rock for the pyrophyllite. A comparison of the pyrophyllite occurrences in the northern and southern Appalachians illustrates their striking similarities.

Introduction

Recognition of problems and discrepancies in the determination of aluminosilicate stability fields has generated new interest in pyrophyllite. Pyrophyllite, once thought rare, is a metamorphic mineral often occurring in slates and phyllites in which albite and potassium feldspar are absent (Winkler, 1976), and is also a common mineral in hydrothermal alteration assemblages.

The occurrence of economic pyrophyllite in North Carolina is unique in the United States, but little investigation of these deposits has been attempted. Stuckey (1925, 1928, 1967) and Broadhurst and Councill (1953) have described their gross mineralogy and structure. In a regional study of the kyanite–andalusite–sillimanite occurrences in the Piedmont and Blue Ridge Provinces, Espenshade and Potter (1960) documented kyanite and andalusite occurring as replacement deposits in quartzose rocks along with pyrophyllite, minor topaz, and diaspore. Zen (1961) conducted a petrologic survey of the aluminosilicate assemblages present in seven of the pyrophyllite occurrences in North Carolina.

Past studies have not explained the genesis of the pyrophyllite deposits in relation to the regional geology and metamorphism of the area. This study attempts to establish those relationships based on a detailed field, geochemical, and petrographic investigation of the Hillsborough pyrophyllite deposit. Moreover, recent experimental and theoretical data (Haas and Holdaway, 1973; Day, 1976) delineate the pressure–temperature conditions of formation of the pyrophyllite and related minerals.

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Regional geology

The pyrophyllite deposits of North Carolina occur in the Carolina slate belt, a series of volcanic pyroclastic and epiclastic rocks that have undergone greenschist-facies metamorphism. The northern part of the slate belt has been divided into four stratigraphically and lithologically distinct units without formational names (Allen and Wilson, 1968; Glover and Sinha, 1973). Glover and Sinha, McConnell (1974), and Wright (1974) have established from a detailed mapping and structural analysis the following stratigraphic sequence: Unit I—mixed gneiss, Unit II—intermediate and felsic volcanic rocks, Unit III—tuffaceous epiclastic rocks, and Unit IV—mafic and felsic volcanic rocks.

Several igneous plutons intrude the slate-belt volcanic rocks, which range in composition from felsic to mafic. Volumetrically, the more felsic plutons are the most important. Mesozoic diabase dikes cut both the volcanic and igneous rocks.

Hillsborough pyrophyllite deposit

The host rocks of the deposit are andesitic to dacitic metavolcanic rocks. The deposit is lenticular, about 205 m long and 15 to 60 m wide, and structurally parallels the regional trend. A geologic map of the deposit is shown in Figure 1.

Two foliations are preserved in the schist and breccias. The major foliation averages N70E, 80° NW which approximates the regional attitude of the slate-belt rocks (Butler, 1963; Hauck, 1977). The second foliation, generally sub-horizontal, cuts the regional foliation, but is poorly developed. North–south trending vertical faults are marked by foliated hematite-stained breccias and fine-grained chloritoid-rich gouge. North–south trending vertical joints occur in the massive quartzite, with conjugate pairs developed in some areas.

The rocks of the deposit are divided on the basis of mineralogy, texture, and field relationships into five types: schist, quartzite, pyrophyllite, breccia, and al-

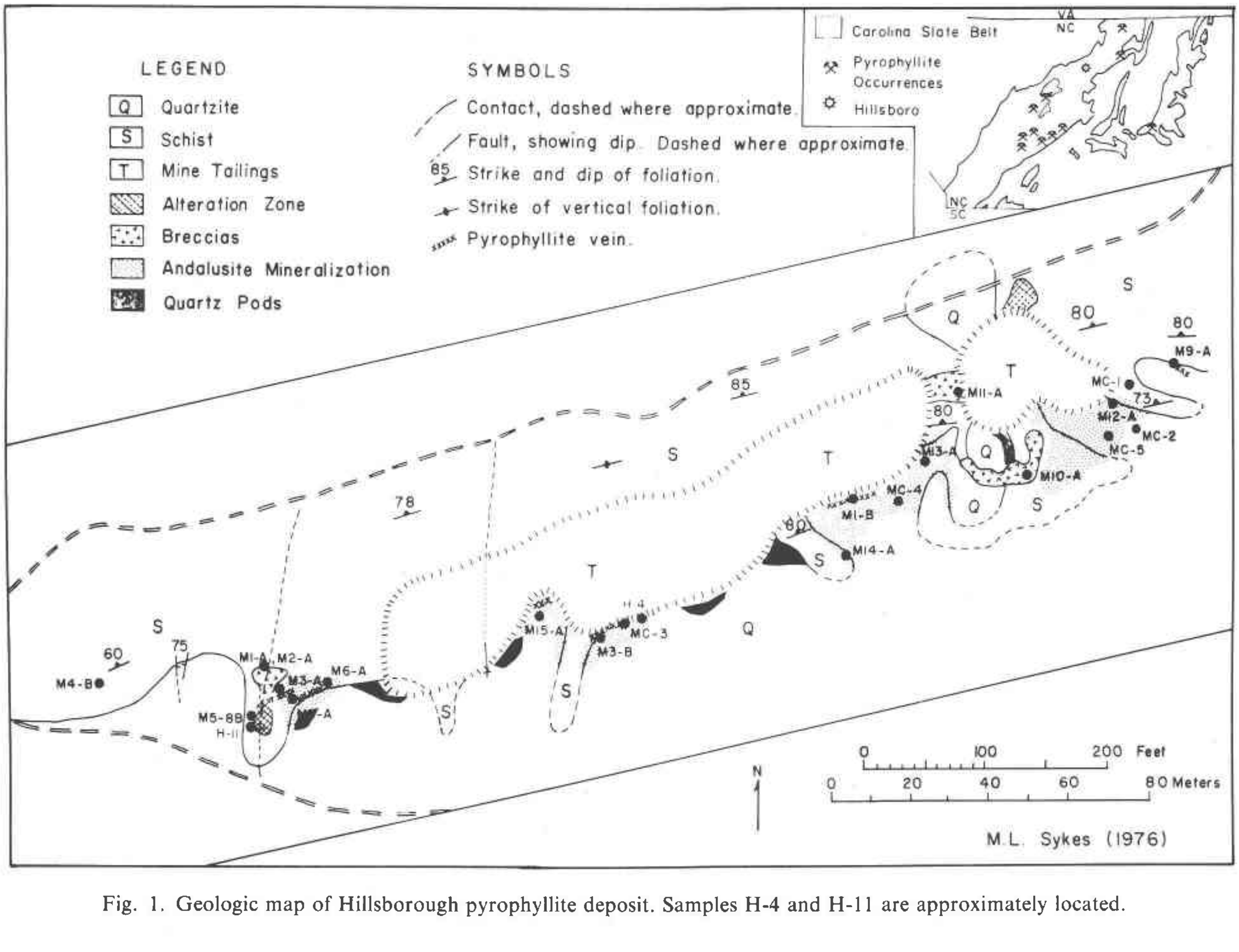

Fig. 1. Geologic map of Hillsborough pyrophyllite deposit. Samples H-4 and H-11 are approximately located.

teration zone rocks. Mineralogy was determined optically and by X-ray diffraction. Results are summarized in Tables 1 and 2. An additional twenty thin sections from Hauck's (1975, unpublished) preliminary study of the pyrophyllite deposit were also examined. Modal analyses of five samples are presented in Table 3.

The andalusite forms blue or gray porphyroblasts (Fig. 2a) in a quartz- or sericite-rich matrix. The blue color is due to a small amount of iron in the mineral (Table 2; Chinner *et al.*, 1969). Topaz also occurs with andalusite as large subhedral porphyroblasts with numerous quartz inclusions. Grain boundaries between the andalusite and topaz are sharp, with no evidence of replacement or alteration of each other (Fig. 2b). Andalusite also occurs as small anhedral grains associated with quartz (Fig. 2c). Fine-grained quartz has partially to totally replaced the andalusite rock. Sericite and pyrophyllite occur as fracture fillings in the andalusite–topaz–quartz rock (Fig. 2d) and may also occasionally replace crystals internally. Radial pyrophyllite is rarely deformed, but the fine-grained aggregates sometimes exhibit kink bands (Hauck, 1975, unpublished). Kaolinite occurs as fracture fillings that cross-cut all other minerals, and as an alteration product of the andalusite and topaz (Fig. 2a). The quartzite is restricted to the footwall of the deposit, and is considered at Hillsborough and

Table 1. Mineralogy of Hillsborough rocks

Sample	Q	A	S	P	K	T	H	Other	Comments
Schist									
M1-A†	X	X	X						Fine-grained quartz-rich schist.
M3-A†	X	X	X	X	X				
M6-A†	X	X	X		X				
M14-A†	X	X	X		X		tr		Sample from contact between foliated sericite quartzite and sericite schist. Shows "flow" in sericite around andalusite, replacement by kaolinite; two planar features.
M4-BI†	X		X		X				Very fine-grained kaolinite-rich schist; rutile is unoriented.
M4-BII†	X		X		X		tr	R(X)	
H-4†	X	X	X		X				
Quartzite									
M12-A†	X	X	X	X	X	X		Ap(tr)	Porphyroblastic andalusite-topaz rock showing quartz replacement, cross cut by pyrophyllite-sericite veins and by kaolinite.
M13-A†	X	X	X		X				Porphyroblastic andalusite quartzite.
M15-A†	X	X		X		X			Porphyroblastic andalusite-topaz quartzite.
M-C1	X	X		X	X	X	tr		Porphyroblastic andalusite-topaz quartzite; andalusite also forms veins.
M-C2†	X	X						Ap(tr)	Foliated equigranular quartzite.
M-C3		X		X	X	X			Andalusite-topaz rock cut by pyrophyllite veins and kaolinite.
M-C4†	tr	X		X	X	X	tr		
M-C5	X	X		X	X	X			Porphyritic andalusite-topaz quartzite.
Pyrophyllite									
M3-A†	X	tr		X					Fine-grained felted pyrophyllite.
M3-B	tr			X					Radial massive pyrophyllite.
Breccias									
M2-A†	X		X		X		X		Foliated relict breccia: white Q-K-S fragments in red Q-K-S-H matrix.
M10-A†			X		X		X		Foliated relict breccia: white K-S fragments in black K-S-H matrix.
M11-A†			X		X		X		Foliated relict breccia: white K-S fragments in red K-S-H matrix, with aggregates of specular hematite crystals 3-5 mm disseminated through matrix.
Alteration zone rocks									
M7-B†*	X		X						Porphyroblastic chloritoid in chlorite Q-S matrix.
M6-B†*	X		X				tr		Weathered porphyroblastic chloritoid in chlorite Q-S matrix.
M5-B†	X		X		X		X		Very fine-grained yellow unfoliated rock.
M8-B†	X				X		X		Very fine-grained red unfoliated rock.
H-11	X								Porphyroblastic chloritoid-chlorite quartz rock.

† Mineralogy determined or verified by X-ray diffractometer traces of whole rock powders.
* Chlorite and chloritoid are major constituents.
Q = Quartz, A = andalusite, S = sericite, P = pyrophyllite, K = kaolinite,
T = topaz, H = hematite, R = rutile, Ap = apatite

Table 2. Direct unit-cell parameters and chemistry of important minerals

Sample	Mineral	a(Å)	b(Å)	c(Å)	V(Å)^3	β	Other
MC-5	topaz	4.6643(5)	8.8414(9)	8.386(1)	345.84(5)		wt% F = 15.6(5)†
MC-4	andalusite	7.7947(3)	7.8973(5)	5.5551(4)	341.96(3)		wt% FeO = 0.53††
M3-A	pyrophyllite	5.163(1)	8.927(3)	18.652(8)	847.3(3)	99°46'(2')	wt% F = 0.35†††
M1-A	muscovite	5.187(1)	8.999(1)	20.805(2)	932.8(1)	95°47'(1')	$2M_1$ polytype††††

X-ray powder data on mineral separates were obtained with Hagg Guinier camera with CuKα_1 radiation (1.5405Å) and NBS#640 Si powder as internal standard (a = 5.43088Å); patterns were read to 0.01 mm; all lines were corrected to internal standard and least squares refinement done with Appleman et al. (1973) program.

†Ribbe and Rosenberg (1971)
††microprobe analysis, courtesty of M. A. Dungan, NASA
†††chemical analysis, courtesy of H. Westrich
††††Carroll (1970)

other North Carolina deposits to be due to silicification of the fault zone (Broadhurst and Councill, 1953; Stuckey, 1967; Sundelius, 1970).

Mineral paragenesis

Interpretation of the field relationships and petrographic evidence results in the following mineral paragenesis, which is summarized in Figure 3.

(1) Andalusite and topaz porphyroblasts were formed during a prograde metamorphic event. The sharp contacts between grain boundaries of these two minerals indicate a stable assemblage (Fig. 2b). Some very small quartz inclusions in these porphyroblasts could be relict.

(2) Partial to complete silicification of the andalusite–topaz rocks occurred next, with secondary formation of andalusite (Fig. 2c) by solution and reprecipitation.

(3) A tectonic event fractured and deformed the andalusite–topaz–quartz rock and produced the foliation in the quartzites and schists.

(4) Sericite, pyrophyllite, and quartz were introduced as fracture fillings in the andalusite–topaz–quartz rocks (Fig. 2d) and as veinlets in the quartzites and schist parallel to the foliation.

(5) A second deformational event caused kink bands in the pyrophyllite and sericite. Fractures (sometimes filled with kaolinite) cross-cutting the foliation were also produced.

(6) Kaolinite formed as an alteration product of andalusite and topaz (Fig. 2a) during very low-grade retrogressive metamorphism.

(7) Weathering also produced kaolinite as fracture fillings in all rock types, and caused the oxidation and dissemination of iron.

Geochemistry

Eighteen samples were analyzed for nine major elements, three trace elements, and loss on ignition. U. S. Geological Survey rock standards were analyzed simultaneously with unknowns. Agreement with accepted values for the standards (Abbey, 1975) was well within five percent. Results of the analyses are presented in Table 4.

The trace-element Harker diagrams (Fig. 4) for the Hillsborough rocks are compared to volcanic rocks

Table 3. Modal analyses of some Hillsborough rocks

Sample	Q	A	S	P	K	T	H	CD	C	Other
M14-A*	42.5	3.7	48.2	-	5.0	-	0.5	-	-	0.1
M12-A*	32.7	36.8	7.9	†	14.0	8.6	-	-	-	-
MC-4*	0.7	65.3	-	26.3	4.4	3.3	-	-	-	-
H-4**	5.2	33.0	47.6	†	14.4	-	0.2			1.0
H-11**	23.4	-	-	-	-	-	-	33.6	39.4	3.6

* 1000 points counted
** 500 points counted, Hauck (1975)
† pyrophyllite point counted with sericite

Attempts to point count the breccia rocks proved to be very difficult due to fine-grain size and hematite masking the other mineral grains.

Mineral abbreviations same as Table 1, CD = chloritoid, C = chlorite.

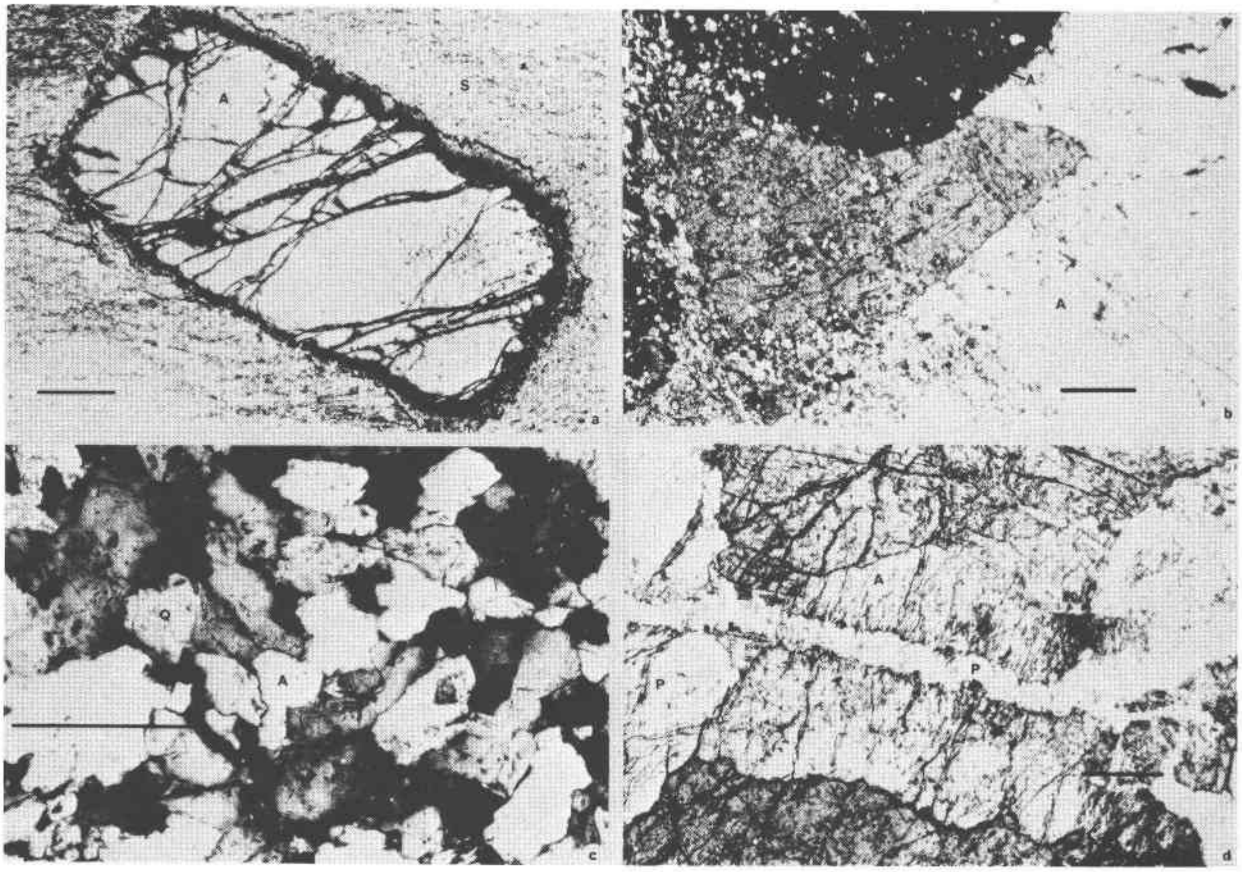

Fig. 2. (a) Fractured andalusite porphyroblasts altering to kaolinite in a sericite matrix, sample H-4. (b) Andalusite and topaz porphyroblasts exhibiting partial silicification, sample M12-A. (c) Secondary andalusite with quartz, sample MC-2. (d) Pyrophyllite as fracture-filling in andalusite porphyroblast, sample MC-4. All photographs taken with crossed nicols; scale is 1 mm.

in the Chapel Hill area (Black, 1977). A Ti *vs.* Zr plot is presented as Figure 5, because those elements have been suggested to be the most resistant to secondary alteration effects in basic rocks (Cann, 1970; Pearce and Cann, 1971, 1973; Kean and Strong, 1975).

Two important points can be discussed with regard to this geochemical data: (1) possible alteration of the slate-belt rocks to produce the rocks at Hillsborough, and (2) the effects of low-grade metamorphism on both Hillsborough and slate-belt volcanic rocks. Considerable scatter is shown in all the geochemical plots for the Chapel Hill area rocks, and can be attributed most probably to the effects of metamorphism on the primary composition of rocks (Smith and Smith, 1976). The Hillsborough rocks show a large variation in SiO_2 (45–98%) compared to the other metavolcanic rocks, suggesting mobility of silica. The slate-belt metabasalts form a distinct group from the more felsic metavolcanics in trace element *vs.* SiO_2 plots, whereas the Hillsborough rocks do not show any such clustering. The Sr and Rb are systematically lower for the Hillsborough rocks in comparison to the Chapel Hill metavolcanic rocks, suggesting removal of these elements before or during the metamorphism and fluid activity. The Zr is more immobile and has not been leached from the Hillsborough rocks. Figures 4 and 5 show that the Hillsborough rocks form two distinct groups: (1) quartzite, schists, and pyrophyllite and (2) alteration zone and breccia rocks. The Ti *vs.* Zr plot suggests that the slate-belt metabasalts are the parent material for the breccias and alteration zone rocks, a point also implied by the mineralogy of the chloritoid–chlorite rocks (Furbish, 1967). Furthermore, the geochemical data are not inconsistent with the hypothesis that the parent material for the aluminous-rich rocks making up the Hillsborough pyrophyllite deposit originated from leaching of the andesitic and dacitic host rocks.

Discussion

Petrologic implications of the mineral assemblages at Hillsborough

Most workers agree that the prograde regional metamorphism of the Carolina slate-belt rocks has reached greenschist facies (Sundelius, 1970; McConnell, 1974; Hauck, 1977). The textural relationship between andalusite and topaz (Fig. 2b) indicates that the two minerals were formed simultaneously and are a stable assemblage, *i.e.* one mineral is not replacing the other. Day's (1976) interpretation of the stability of andalusite indicates that this mineral can be produced during low-grade metamorphism. Rosenberg (1972) cautions against using his experimentally determined curve to determine temperature of formation of topaz solid solutions from natural assemblages. However, the observed assemblage at Hillsborough (andalusite–topaz–quartz) has a bulk composition which is close to one he used in his experiments. Haas and Holdaway (1973) have shown that, at 2 kbar, 380°C is the maximum stability for pyrophyllite, thus Rosenberg's observed assemblage of topaz–quartz–pyrophyllite–vapor below 500°C is a disequilibrium one. For the assemblage topaz–andalusite–quartz, only one phase has a variable F/OH ratio (a trace amount of apatite was found in one of the topaz-bearing assemblages, see Table 1). The topaz F/OH ratio in the Hillsborough assemblage suggests temperatures below 400°C (Δ_{121} = 1.08, Fig. 7, Rosenberg, 1972), which fits well within the temperatures expected for low-grade (greenschist facies) metamorphism (Winkler, 1976).

Zen's (1961) work has been referred to not only as a definitive study on the N. C. pyrophyllite deposits but also as an example of a simple petrologic system which can be defined by the components Al_2O_3–SiO_2–H_2O. Detailed examination of the Hillsborough deposit does not verify Zen's conclusions regarding mutual equilibrium among the phases, or that water behaved as a fixed chemical component during the formation of pyrophyllite. The mineral paragenesis and textures at Hillsborough clearly indicate that disequilibrium is the rule rather than the exception. Pyrophyllite replaces andalusite and topaz (Fig. 2d) along preexisting fractures and later is followed by kaolinite. Water and SiO_2 have behaved as mobile components. Silica has been introduced (re-mobilized?) in the slate belt and resulted in both mineralized and barren quartz veins (Hauck, 1977).

Day's (1976) analysis of the stable assemblages in this system sheds further light on the problem of equilibrium (Fig. 6). Figure 2a shows andalusite altering to kaolinite from the outer rim of the porphyroblasts inward. The reaction of interest is:

$$\underset{\text{andalusite}}{2Al_2SiO_5} + \underset{\text{quartz}}{2SiO_2} + 4H_2O = \underset{\text{kaolinite}}{Al_4Si_4O_{10}(OH)_8}$$

As Day points out, this association represents disequilibrium because "there is no field in phase diagram (Fig. 6) where hydration of kyanite (in our case andalusite) should produce kaolinite directly" without going through a pyrophyllite-bearing divariant field.

Pyrophyllite samples (M3-A and M3-B) have approximately 0.35 weight percent fluorine (Table 2). McDaniel (1976) reported 0.06–0.11 weight percent F in pyrophyllite samples from Glendon deposits in Moore County, North Carolina. Topaz has been reported at those pyrophyllite deposits in Moore County (Stuckey, 1967). The presence of fluorine in the pyrophyllite does not necessarily require addition of fluorine. At Hillsborough the fluorine in pyrophyllite could have been derived from the breakdown of topaz, because topaz has been replaced by pyrophyllite.

Espenshade and Potter (1960) reported minor amounts of diaspore at Hillsborough, but Zen (1961) and we did not observe it. Continuous mining since the 1960's has removed large volumes of rock. Diaspore, if it was present, was a trace mineral in the assemblage, and its possible occurrence could have been related to a very small-scale local enrichment in Al_2O_3. The absence of diaspore at Hillsborough as an essential mineral in the paragenesis is related to bulk composition of the rocks. In an Al_2O_3–SiO_2–H_2O

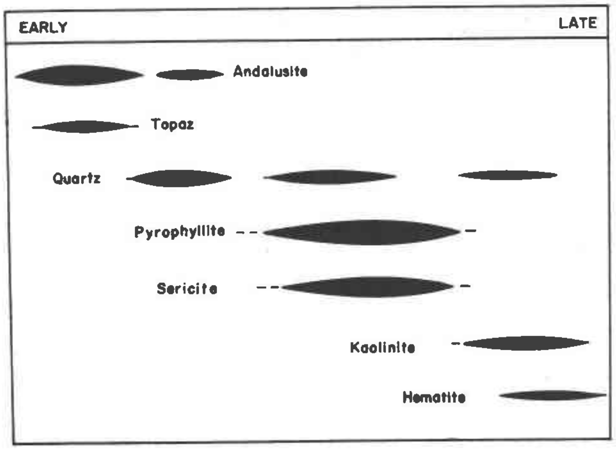

Fig. 3. Mineral paragenesis at Hillsborough as inferred from the petrographic observations.

Table 4. Chemical analyses of rocks in the Hillsborough deposit

	Schist			Quartzite			Pyrophyllite	
Specimen No.	M1-A	M14-A	M4-B	M5-A	M13-A	M15-A	M3-A	M3-B
SiO_2	82.76	46.08	50.82	98.01	56.68	70.21	67.24	63.93
Al_2O_3	9.63	35.80	32.96	1.79	37.19	24.88	26.95	28.28
Fe_2O_3	0.32	0.69	1.35	0.18	0.46	0.30	0.29	0.29
FeO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.45	0.14
MgO	0.04	0.06	0.19	0.03	0.01	tr	0.02	0.02
CaO	0.14	0.17	0.11	0.12	0.12	0.11	n.m.	0.11
Na_2O	0.03	0.39	0.48	0.12	tr	tr	tr	tr
K_2O	2.53	8.74	9.24	0.44	0.77	0.03	0.01	0.02
TiO_2	0.40	0.30	0.32	0.30	0.31	0.29	n.m.	0.31
L.O.I.	2.84	5.81	4.73	0.58	2.93	3.30	4.64	6.14
Total	98.69	98.02	100.20	101.01	98.47	99.12	99.15	99.10
Zr ppm	375	189	204	162	272	270	25	233
Sr ppm	141	266	73	30	163	132	3	161
Rb ppm	42	117	167	10	16	7	<1	2

Analyst: M.L. Sykes

n.d. = not detected, n.m. = not measured, tr = trace, <0.01%

SiO_2 determined colorimetrically (Shapiro,1975 ; Fritz,1976) ; Al_2O_3, Fe_2O_3, MgO, Na_2O, K_2O by atomic absorption (Bernas,1968) ; FeO by titrimetry (Schafer,1966) ; CaO, TiO_2, Zr, Sr, Rb by X-ray fluorescence (Butler and Ragland,1969 ; Fritz,1976) ; L.O.I. (Fritz,1976).

plot, all the Hillsborough rocks plot to the right of the tie-line between andalusite and diaspore, indicating that the rocks did not have enough Al_2O_3 to produce diaspore as a distinct mineral in the assemblage. The reactions:

$$\underset{\text{kaolinite}}{3Al_4Si_4O_{10}(OH)_8} = \underset{\text{andalusite}}{4Al_2SiO_5} + \underset{\text{pyrophyllite}}{Al_4Si_8O_{20}(OH)_4} + 10H_2O \qquad (2)$$

$$\underset{\text{kaolinite}}{Al_4Si_4O_{10}(OH)_8} + \underset{\text{quartz}}{4SiO_2} = \underset{\text{pyrophyllite}}{Al_4Si_8O_{20}(OH)_4} + 2H_2O \qquad (3)$$

define the breakdown of andalusite and pyrophyllite. As a result, the reaction:

$$\underset{\text{diaspore}}{4AlO(OH)} + \underset{\text{kaolinite}}{Al_4Si_4O_{10}(OH)_8} = \underset{\text{andalusite}}{4Al_2SiO_5} + 6H_2O \qquad (4)$$

is *not* applicable because of the lack of diaspore.

In light of the above statements of non-equilibrium and diaspore's absence as a critical mineral in the assemblage, most of Day's (1976) discussion about Hillsborough does not apply. However, the concern of Day (1976) and Burt (1977) over the pressure position of the invariant point (*Q*) is relevant to Hillsborough. If (*Q*) lies at very low pressures, then neither reactions (2) or (4) would define the breakdown of pyrophyllite (Day, 1977, personal communication), which would then occur by reaction (3). Day's equilibrium analysis does put some pressure–temperature limits on the pyrophyllite formation: pyrophyllite was formed at less than 350°C and less than 2 kbar total pressure. The effect of fluorine substitution for hydroxyl in the pyrophyllite would be to extend its stability to a slightly higher temperature than Day's analysis suggests (S. Ludington, oral communication, 1977). The mineral paragenesis determined at Hillsborough does not support the experimental work of Tsuzuki and Mitzutani (1971), because kaolinite was an alteration product of andalusite, topaz, or pyrophyllite or as a late-stage mineral in fractures. No evidence for the reaction path:

$$\text{sericite} \rightarrow \text{kaolinite} \rightarrow \text{pyrophyllite}$$

was observed.

Relationship of the deposit to regional geology

The sequence of events at the Hillsborough pyrophyllite deposit fits well with what is known of the

Table 4. continued

	Breccia			Alteration zone rocks			
Specimen No.	M2-A	M10-A	M11-A	M7-B	M6-B	M5-B	M8-B
SiO_2	53.35	41.99	49.19	56.71	49.92	59.73	58.26
Al_2O_3	24.68	14.33	24.27	14.88	20.13	20.43	18.29
Fe_2O_3	9.53	36.48	12.23	3.48	3.24	8.68	11.44
FeO	n.d.	0.45	0.14	8.79	9.83	n.d.	0.73
MgO	0.08	0.13	0.20	6.45	5.89	0.08	0.04
CaO	0.10	0.12	0.11	0.14	0.12	0.16	0.31
Na_2O	n.d.	0.06	n.d.	n.d.	tr	0.10	0.03
K_2O	1.78	1.25	1.71	0.10	0.03	1.59	1.31
TiO_2	0.93	0.94	0.66	2.94	1.94	1.14	0.49
L.O.I.	11.34	2.15	10.21	6.25	7.54	7.89	8.68
Total	101.79	98.90	98.72	98.85	98.64	99.80	99.54
Zr ppm	68	64	41	118	119	73	71
Sr ppm	26	72	46	197	196	131	200
Rb ppm	28	25	35	<1	<1	27	6

geologic history of the Carolina slate belt (Table 5). Radiometric age determinations (Rb/Sr whole rock and zircon U–Pb) indicate that the slate-belt rocks in the southern part of North Carolina are 40–200 m.y. younger than those in the north. Geologic evidence suggests that the radiometric age difference between those two parts of the slate belt may reflect an unconformity or a difference in stratigraphic level (Seiders and Wright, 1977). Fossil evidence (St. Jean, 1973; Cloud *et al.*, 1976) substantiates the radiometric data within their uncertainty. Plutons which intrude the volcanic rocks in the northern slate belt have the same range in age (550–705 m.y.) as the volcanic rocks (Table 5), except for some post-metamorphic gabbros and ~300 m.y. granitic plutons (Fullagar and Butler, 1977).

Structurally, the northern slate belt has undergone several periods of deformation. Glover and Sinha (1973) propose the formation of the Virgilina synclinorium as a deformation event (D_1) 575–620 m.y. The alteration zone in the Chapel Hill pluton at 613 m.y. gives additional support for the Virgilina deformation (Hauck, 1977). Glover and Sinha (1973), McConnell (1974), and Wright (1974) do not recognize in their areas a slaty cleavage accompanying the Virgilina folding event (F_1). Therefore, the penetrative regional cleavage (S_1) correlates with their F_2 folding event. Ages from Avalonian to Acadian have been suggested for the regional metamorphism associated with F_2 folding event from radiometric and geologic data; however, the weight of the evidence for the timing of metamorphism appears to be Taconic or younger. Taconic metamorphism is evidenced in the Rb/Sr ages of a dacite metalithic-tuff near Chapel Hill, North Carolina (Table 5).

The Hillsborough pyrophyllite deposit is located in a major fault zone that was probably formed post F_1–pre F_2 structures (Glover and Sinha, 1973). Reconnaissance mapping by Glover and Wright extended the major wrench fault system from the Durham North quadrangle into the Hillsborough quadrangle through the pyrophyllite deposit (Wright, 1977, personal communication). The pronounced foliation observed in the rocks of the deposit parallels the regional foliation (S_1). The pyrophyllite mineralization is clearly after the regional metamorphism and deformation, but how much later is difficult to postulate without additional data. Some evidence for the timing of the pyrophyllite mineralization can be inferred from muscovite K–Ar dates (Bell *et al.*, 1972) obtained from three hydrothermal areas in the slate belt of South Carolina, which yielded apparent (minimum) ages of 317 and 430 m.y. The Hillsborough rocks also show evidence of a weakly developed but definite third deformational event of uncertain age: (1) rotation of the andalusite porphyroblasts in a sericite matrix which may be permissive evidence for deformation (Spry, 1969), (2) kink bands and deformation of the pyrophyllite, and (3) fractures cross-cutting the regional foliation.

Pyrophyllite from the northern Appalachians in Avalon Peninsula of Newfoundland (Papezik and Keats, 1976) is strikingly similar to its occurrence in the Carolina slate belt (Table 6). At the Foxtrap deposit in Avalon Peninsula andalusite and topaz are missing, but barite and minor kaolinite are present.

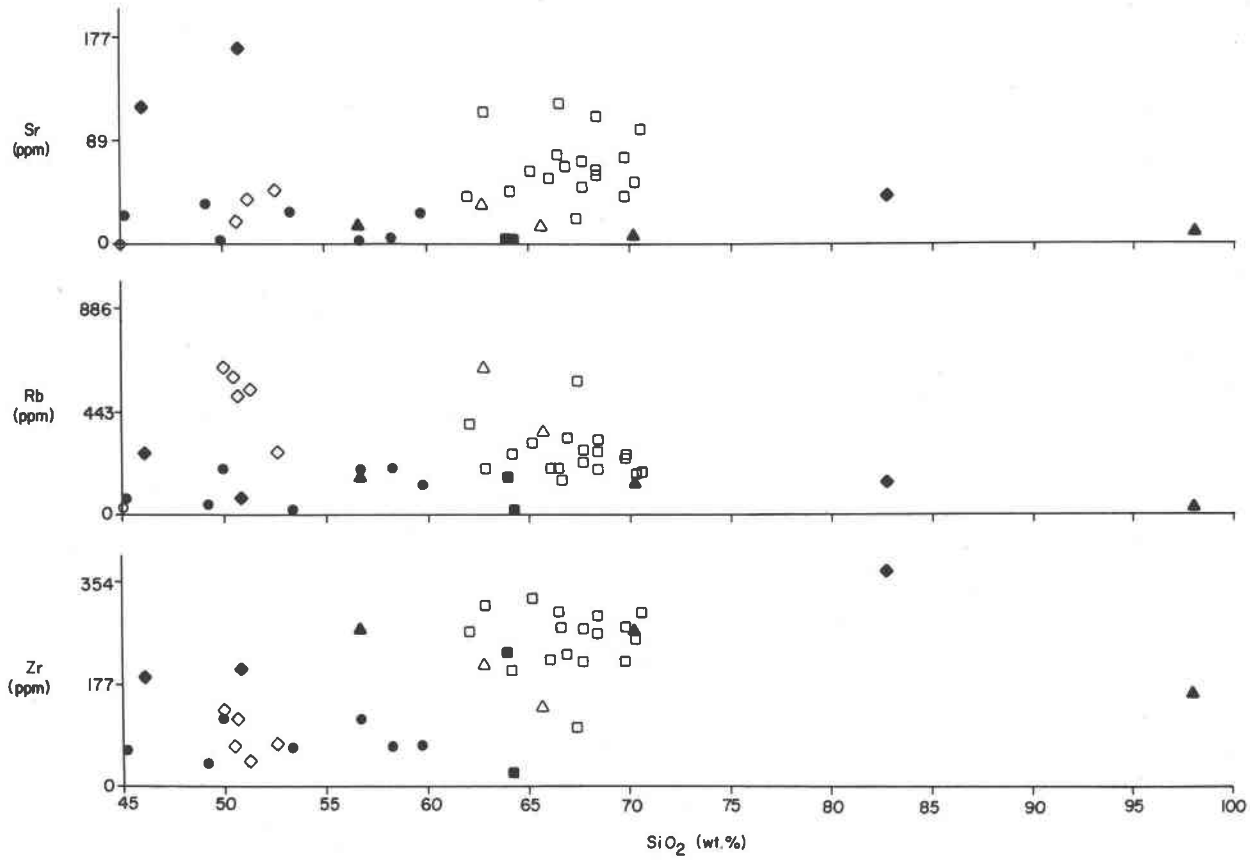

Fig. 4. Harker plots of trace elements *vs.* SiO_2 for Hillsborough rocks and Chapel Hill area metavolcanic rocks (Black, 1977). Filled symbols represent Hillsborough rocks and open symbols the Chapel Hill area metavolcanic rocks: ◆ = schist, ▲ = quartzite, ■ = pyrophyllite, ● = breccias and alteration zone rocks, ◇ = basalt, △ = andesite, □ = dacite.

Origin of the deposit

As stated above, the mineralogy and petrology of the Hillsborough pyrophyllite deposit indicate that a leaching process must have been active, which produced the high-alumina and silica rocks from the parent volcanic rocks. The possible leaching mechanisms are weathering, hydrothermal or geothermal alteration.

A plot of silica against alumina for the schists, quartzites, and pyrophyllite at Hillsborough follows a linear trend that intersects 100 percent SiO_2 at 0 percent Al_2O_3. Such a linear trend is typical of classical weathering profiles, in which silica is leached out and the alumina content relatively enriched. Zen (1961) proposed that weathering produced the protolith for the pyrophyllite deposits. The tropical

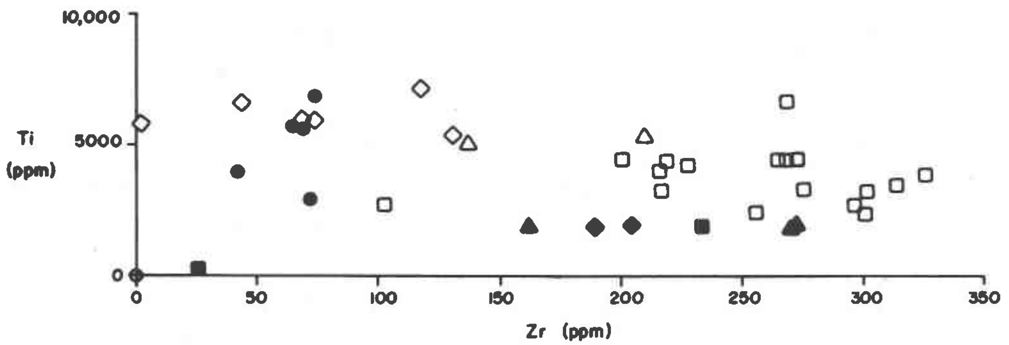

Fig. 5. Ti *vs.* Zr for Hillsborough and Chapel Hill area metavolcanic rocks. Symbols are same as in Fig. 4.

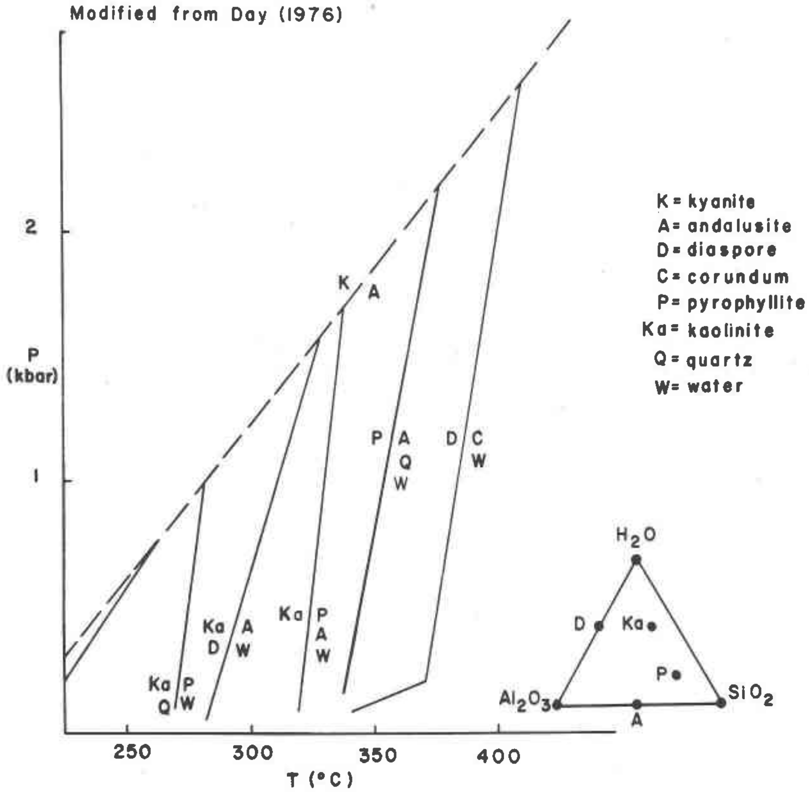

Fig. 6. Equilibrium relationships in Al_2O_3–SiO_2–H_2O system as a function of temperature and pressure.

weathering of volcanic rocks does produce soils of the appropriate bulk composition, *i.e.,* laterite and bauxite. However, tropical soils do not appear in the geologic record until Devonian time, because terrestrial vegetation is necessary to provide increased silica solubility (Blatt *et al.,* 1972). Further, development of a soil horizon seems unlikely, since the leaching must have occurred before the regional metamorphism. Also, the occurrence of topaz with andalusite cannot be explained using this model, as fluorine would be removed from the system during weathering.

Hydrothermal alteration is developed in areas of geothermal activity and in hot-spring systems. Ellis (1967) summarizes the chemistry and alteration products of geothermal areas in New Zealand, Iceland, Japan, the United States, and the Soviet Union. Kaolin minerals form at the surface under acid conditions, and grade into zeolite minerals, adularia, and hydromicas with depth. Iwao (1970) describes clay and silica deposits occurring in both active and extinct hot-spring systems in Japan. Quartz, alunite, kaolinite, montmorillonite, sericite, and pyrophyllite are the major consituents. The deposits are zoned, with a central silicified or alunitized zone grading outward into kaolinite and montmorillonite zones. Fluorine is often present in geothermal systems low in calcium (Ellis, 1967), and may be precipitated along the wall rocks as a fluorine-mica such as lepidolite (Bargar *et al.,* 1973). At Hillsborough, such geothermal or hot-springs activity could cause the leaching of the country rocks to produce the fluorine-bearing high-alumina and silica rocks, which were then metamorphosed to produce andalusite–topaz rocks.

Spence (1975) and McDaniel (1976) developed a hot spring-fumarole alteration model in a study of the pyrophyllite deposits at Glendon. The only point of difference between McDaniel's model and this study is that the hot-spring system would provide the leaching mechanism for enriching the rocks in Al_2O_3 and SiO_2 by producing kaolinite. At Hillsborough, that parent material (kaolinite) was metamorphosed to produce the andalusite, topaz-bearing rocks, *not* pyrophyllite. Later introduction of silica-rich fluids reacted with the andalusite and topaz to produce pyrophyllite. The presence of relatively pure quartz (*i.e.,* quartz pods) in mineralized zones is evidence for high activity of silica in the fluid phase at the time of pyrophyllite mineralization.

Advanced argillic alteration, sericitic alteration, and silicification as defined by Meyer and Hemley (1967) could provide both the appropriate mineral assemblages and the silica–alumina distribution. The schists represent sericitic alteration, which grades into argillic alteration, as represented by the andalusite–topaz-rich zone. Silicification would be the major process forming the quartzite. Hildebrand (1961a) describes an assemblage of hydrothermally altered felsic volcanic rocks in eastern Puerto Rico. The altered rocks consist of intermixed massive quartzose rocks, and softer rocks composed of quartz, sericite, alunite, pyrophyllite, and kaolinite. Hildebrand (1961b) also cites the occurrence of a muscovite, andalusite, quartz, and topaz greisen in eastern Puerto Rico. The assemblage occurs in an area of argillic hydrothermal alteration. Thus, a possible greisen origin for the Hillsborough deposit could be asserted. The pyrophyllite–andalusite–topaz assemblage, as seen locally at Butte, for example, would be analogous to the Hillsborough assemblages, yet would not have an origin related to a metamorphic history (J. Hemley, personal communication, 1977). The andalusite–topaz assemblage would have originated before the regional metamorphism and persisted through it.

Table 5. Sequence of events in the Carolina slate belt of North Carolina

Event	Age (m.y.)	Reference
Northern slate belt volcanoclastic rocks (Chapel Hill and Durham area)	550-740	Glover & Sinha (1973), Black et al. (1975), McConnell & Sinha (1976), Sinha (1976), Black & Fullagar (1976)
Chapel Hill pluton	705	Black & Fullagar (1976)
Flat River Complex	650	McConnell & Sinha (1976)
Meadow Flats pluton	638	Black & Fullagar (1976)
Virgilina deformation (D_1)	575-620*	Glover & Sinha (1973)
Alteration zone in Chapel Hill pluton	613	Black & Fullagar (1976), Black (1977, pers. comm.)
West Farrington pluton	550	Fullagar (1971, pers. comm. 1976)
Central slate belt felsic volcanic rocks	580	Wright & Seiders (1977)
Southern slate belt volcaniclastic rocks (Albemarle area)	494-535(?)	Hills & Butler (1969), Butler & Fullagar (1975), Black et al. (1975)
Taconic metamorphism		
1) dacite meta-tuff from Chapel Hill area	459	Black & Fullagar (1976)
2) re-crystallization of andalusite-topaz and chlorite-chloritoid rocks**		
3) silification		
4) regional fracturing and foliation (S_1)		
Pyrophyllite mineralization with associated quartz		
1) deformation of pyrophyllite-sericite veins		
2) fractures and foliation (S_2?) cutting regional foliation		
Kaolinitization		

*not an absolute age, bracketing from geologic evidence

**A preliminary date (sample M14-A) derived from the whole rock and a muscovite mineral separate yields an age of 469 ± 47 m.y. using a decay constant of 1.39×10^{-11} years^{-1} for Rb^{87}. The very large uncertainity in the age is due to the very small variation in the Sr^{87}/Sr^{86} ratios. Courtesy of S. Kish and W. Black.

Table 6. Comparison of the pyrophyllite occurrences in the northern and southern Appalachians

	Hillsborough	Avalon Peninsula*
host rock:	andesitic and dacitic metavolcanic rocks	rhyolite flows and pyroclastics
structure:	NE trending fault zone	E-NE trending fault zone
mineralogy:	quartz, muscovite, andalusite, topaz, kaolinite, pyrophyllite	quartz, muscovite, pyrophyllite, diaspore, barite, trace kaolinite
paragenesis:	pyrophyllite younger than topaz and andalusite, kaolinite youngest	muscovite → kaolinite → pyrophyllite
metamorphism:	low grade, well-developed regional foliation (S_1), weaker cross-cutting S_2 (?)	low grade, unfoliated, except locally in shear zones
origin:	leached felsic volcanics, followed by low-grade metamorphism, then introduction of silica-rich fluids	alteration of rhyolite by acid fluids derived from igneous pluton
age:	Taconic or younger	late Precambrian or younger

*Papezik and Keats (1976)

Thus either a hydrothermal or geothermal system could have produced the protolith of the Hillsborough pyrophyllite deposit. Due to the extensive metamorphism and deformation of the deposit, choosing between the two alternatives may be impossible.

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