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Résumé de l'article

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# Geochemistry of the Annidale Group: implications for the tectonic setting of Lower Ordovician volcanism in southwestern New Brunswick

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Chemical analyses from volcanic rocks in the Lower Ordovician Annidale Group in southern New Brunswick indicate that it contains two main suites. The volumetrically more abundant suite is bimodal, and consists of within-plate tholeiitic basalt and rhyolite. The other suite contains rocks that exhibit features indicative of oceanic or possibly subduction-related magmatism. The chemistry of the former suite is consistent with the current interpretation that Ordovician volcanism in southwestern New Brunswick occurred in a back-arc basin. The latter suite, situated near the highly-sheared southeastern margin of the Annidale Group, apparently contains remnants of a different magmatic series near the suture zone between the Gander Zone and the surface expression of the Avalon Zone to the southeast.

Les analyses chimiques des roches volcaniques du Groupe d'Annidale, de l'Ordovicien inférieur, dans le sud du Nouveau-Brunswick indique que celui-ci comprend deux suites principales. La suite la plus abondante en termes de volume est bimodale et comprend des basaltes tholéïtiques intraplaques et des rhyolites. L'autre suite contient des roches qui montrent des caractéristiques indiquant un magmatisme océanique ou possiblement relié à la subduction. La chimie de la première suite est en accord avec l'interprétation prévalant actuellement voulant que le volcanisme ordovicien du sud du Nouveau-Brunswick ait eu lieu dans un bassin d'arrière-arc. La seconde suite, située près de la bordure sud-est, fortement cisailée, du Groupe d'Annidale, contient apparemment des reliques d'une série magmatique différente près de la zone de suture entre la zone de Gander et l'expression en surface de la zone d'Avalon vers le sud-est.

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## INTRODUCTION

New Brunswick is underlain by three (Avalon, Gander and Dunnage; Fig. 1) of the five Appalachian tectonostratigraphic zones defined by Williams (1979). The Gander Zone is generally considered to represent a Cambro-Ordovician sedimentary apron deposited off the western margin of the Avalonian microcontinent as the Iapetus Ocean opened to the west. The Dunnage Zone consists of marine, Early to Middle Ordovician volcano-sedimentary sequences that developed within the Iapetus system. The Gander and Dunnage zones in New Brunswick were modified and divided into subzones by van Staal and Fyffe (1991), who assigned the Cookson Group (St. Croix Subzone) to the Gander Zone (Fig. 1). McLeod *et al.* (1992) demonstrated that volcanic units in the recently recognized Annidale Group are contemporaneous with the Cookson Group (Ludman, 1987; Fyffe and Riva, 1990) of the St. Croix Subzone and that tentative correlations can be established between these two groups. Hence, the Annidale Group is also provisionally assigned to the Gander Zone and the area in which it occurs is termed the Annidale Subzone.

Recent studies of Ordovician rocks in New Brunswick (e.g., Fyffe *et al.*, 1988, 1990; Dostal, 1989; van Staal and Fyffe, 1991; van Staal *et al.*, 1991) underscore the significance of geochemical characteristics in interpreting the tectonic history of the Dunnage and Gander zones. Based partially on chemistry, recent models for the Lower to Middle Ordovician in New Brunswick

(e.g., van Staal *et al.*, 1991) invoke development of a Lower to Middle Ordovician arc (the Woodstock-Meductic arc, Dostal, 1989) above a southeastward-dipping subduction zone. According to this model, the arc subsequently rifted and most of it migrated northwestward to form the Popelogan Arc, leaving remnants (westernmost part of the Hayesville Subzone, Fig. 1) on the southeastern side of a developing back-arc basin. The extensive, mainly Middle Ordovician, volcanic belts of the northern Miramichi Highlands and the Elmtree inlier thus include rocks with field relationships and chemical signatures suggesting both rifted continental margin and oceanic back-arc environments (the Tetagouche and Fournier groups, respectively, of the Bathurst Subzone) erupted during the formation of a mid-Ordovician back-arc basin (van Staal *et al.*, 1991).

Geological mapping and preliminary chemical studies of the Annidale Group (McLeod *et al.*, 1991a, 1992; van Staal and Fyffe, 1991) indicated the presence of possible arc-related (back-arc and ophiolitic) volcanic rocks. The volcanic rocks could be associated with the "Woodstock-Meductic arc" (van Staal and Fyffe, 1991), or more likely could include vestiges of a separate arc associated with the St. Croix Subzone (McLeod *et al.*, 1991b). This paper presents additional chemical data from the Annidale Group, compares it with the chemistry of other Ordovician volcanic groups in southern New Brunswick and Maine, and proposes a model for the tectonic setting during their formation.

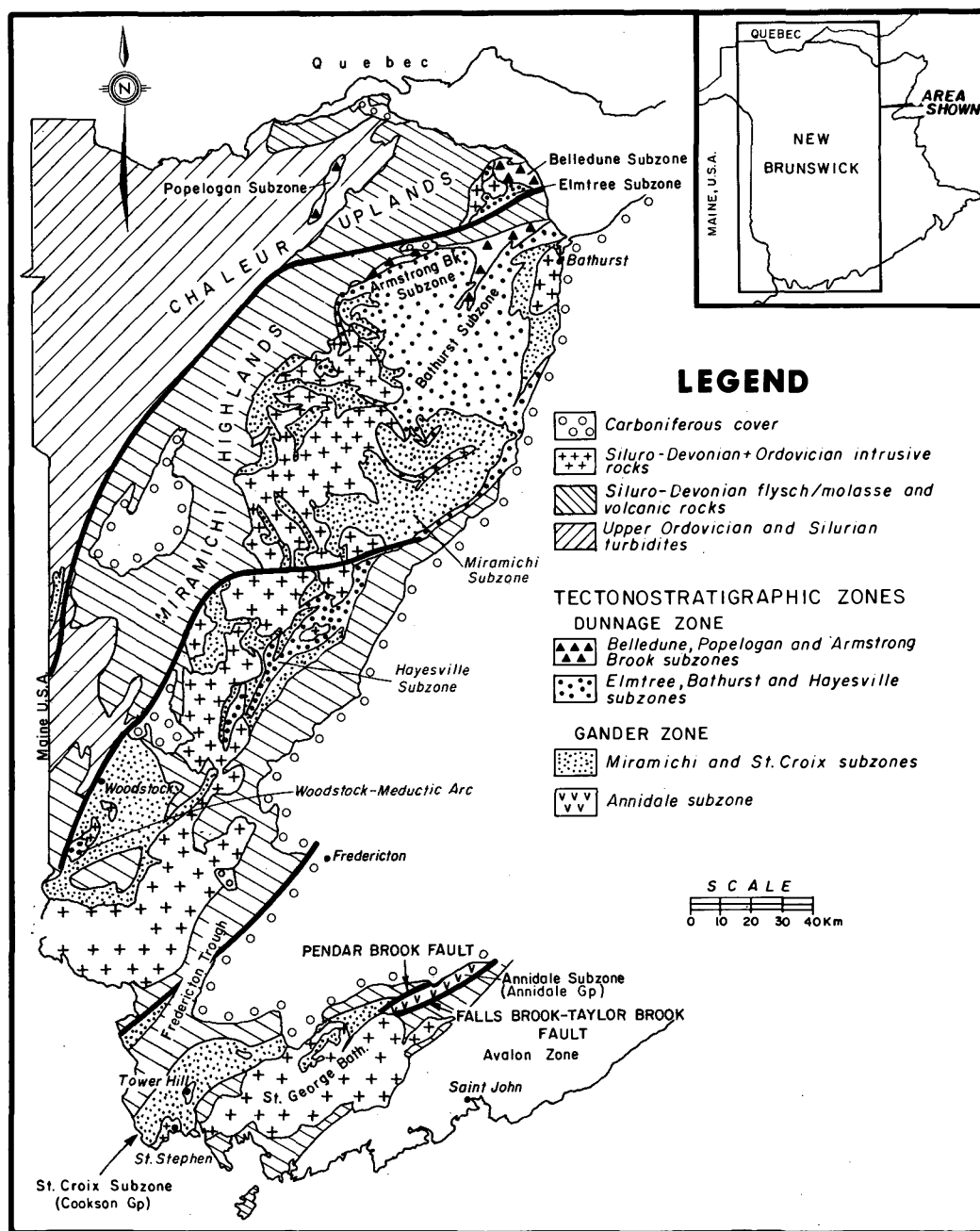


Fig. 1. Generalized geology of New Brunswick illustrating major tectonostratigraphic subdivisions (modified after van Staal and Fyffe, 1991).

### GEOLOGY OF THE ANNIDALE GROUP

The Lower Ordovician Annidale Group, from which U-Pb dates of  $493 \pm 2$  Ma and  $497 \pm 10$  Ma were obtained (McLeod *et al.*, 1992), consists of a variety of marine volcanic and sedimentary rocks. It occupies a position analogous to the Cookson Group, situated north of the northernmost exposures of the Avalon Zone and south of the Siluro-Devonian cover sequence of the Fredericton Trough (Fig. 1). In the Annidale area, the sedimentary and minor volcanic rocks of the Queen Brook Formation (McCutcheon and Ruitenberg, 1987), of unknown affinity, separates the Annidale Group from the Avalon Zone to the south. The southeastern and northwestern boundaries of the Annidale Group are marked by the Falls Brook - Taylor Brook Fault and the Pendar Brook Fault, respectively. The northeast-

ern extension is buried beneath Carboniferous cover rocks and the group is terminated to the southwest by the Siluro-Devonian Saint George Batholith (Fig. 1).

The Annidale Group comprises three main units (Fig. 2), each of which contains distinctive lithologies and/or structures. The two southern units, the East Scotch Settlement and Lawson Brook formations, contain all of the volcanic rocks in the group. The northern unit, the Canaan Forks sequence, is devoid of volcanic rocks and is not considered further here. It is emphasized that determination of stratigraphic relationships between and within these units is hampered by paucity of outcrops, by numerous northeast- and northwest-trending faults, shear zones and alteration zones that typify the group in general, and by Carboniferous cover.



# PETROGRAPHY AND GEOCHEMISTRY

## Petrography of analyzed samples

Mafic volcanic rocks were sampled from undeformed, amygdaloidal pillow lavas and flows in the lower part of the East Scotch Settlement Formation (7 samples), from slightly deformed amygdaloidal flows in the upper part of the East Scotch Settlement Formation (4 samples) and the Dick Mine (3 samples), and from deformed amygdaloidal pillow lava in the Lawson Brook Formation (1 sample) (Fig. 2). The sampled units are representative of demonstrable mafic flow units in the Annidale Group. Primary interstitial textures are faintly preserved in some of the mafic rocks, but most of the primary mineralogy has been variably obliterated by regional metamorphism

and carbonatization. During regional metamorphism, the mafic minerals were altered to chlorite, the feldspars to muscovite and the remaining matrix to a fine-grained chlorite-muscovite aggregate. Ilmenite (now largely replaced by leucoxene) is ubiquitous, and carbonate and quartz occur in veins, as replacements of larger feldspar crystals, or in places as wholesale replacement of the rocks. The mafic flows contain rare (< 5%) altered feldspar phenocrysts and abundant (up to 20-25%) amygdales filled with calcite or chlorite. Sulphide minerals commonly accompany the carbonate in veins and amygdales.

Four samples of felsic volcanic rocks were taken from high-level, massive rhyolitic domes in the East Scotch Settlement Formation and from a massive to flow-banded rhyolite in the Lawson Brook Formation (Fig. 2). These rocks are variably porphyritic and contain unaltered phenocrysts (up to 15%), mostly

Table 1. Analytical data.

Sample Number	Lower East Scotch Settlement Formation							Upper East Scotch Settlement Formation			
	HB74 224	H-12 25-89	H-13 36-90	WS681	WS682	WS683	WS684	BF-1 67.5m	BF-1 68.0m	BF-1 71.0m	TB-1 81.2m
SiO <sub>2</sub>	43.66	44.25	46.95	50.34	45.22	45.30	45.28	31.29	42.56	34.72	52.68
TiO <sub>2</sub>	2.06	1.55	2.36	2.07	1.81	1.84	1.66	2.85	2.14	1.81	3.60
Al <sub>2</sub> O <sub>3</sub>	15.29	16.17	15.12	17.35	16.76	16.45	15.53	13.56	16.01	16.72	14.65
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	10.02	13.36	12.22	10.30	9.88	10.64	13.12	9.93	12.15	5.00	14.69
MnO	0.16	0.20	0.25	0.12	0.15	0.16	0.18	0.17	0.13	0.13	0.27
MgO	5.13	8.83	8.32	6.21	9.28	7.75	8.88	4.09	7.65	2.70	3.87
CaO	11.76	8.71	7.57	5.15	9.43	11.18	8.94	17.61	6.68	17.27	1.95
Na <sub>2</sub> O <sub>3</sub>	4.62	3.64	3.80	4.31	2.98	2.04	2.71	3.78	1.94	2.31	3.22
K <sub>2</sub> O	0.38	0.08	0.07	0.04	0.27	0.09	0.29	0.88	0.93	3.74	0.35
P <sub>2</sub> O <sub>5</sub>	0.23	0.18	0.30	0.24	0.19	0.17	0.18	0.42	0.28	0.23	0.35
L.O.I.	7.07	3.69	3.45	4.24	4.47	5.22	3.38	15.56	9.52	13.60	4.07
Total	100.38	100.66	100.41	100.37	100.44	100.84	100.15	100.14	99.99	98.23	99.70
Ba	339	53	72	42	423	163	131	260	323	958	174
Cl	116	105	145	93	93	105	95	108	195	271	99
Cr	372	218	229	274	147	153	311	38	22	151	bdl
Cu	50	38	49	31	58	63	45	72	79	62	124
Ga	13	14	18	15	14	17	16	20	20	19	21
Nb	9	5	10	8	6	6	6	13	10	7	5
Ni	166	124	127	132	104	97	128	39	51	81	17
Pb	bdl	2	1	bdl	3	4	3	5	2	bdl	7
Rb	7	bdl	1	2	4	3	5	23	24	94	13
Sr	260	239	220	274	210	213	325	404	147	250	65
V	338	355	370	301	245	260	352	422	338	258	442
Y	40	29	39	27	28	28	31	37	26	25	43
Zn	86	117	102	69	65	69	105	139	82	100	156
Zr	164	88	172	189	152	155	99	265	198	156	105

bdl = below detection limit

composed of potassium feldspar, less commonly quartz, and rarely plagioclase. The matrix, which is composed of a fine-grained mosaic of quartz, feldspar and scattered Fe-Ti oxides, contains minor amounts of secondary muscovite and chlorite.

Four samples collected south of Annidale at the fuchsite zone are all extensively altered and variably deformed. They retain little of their original mineralogy and now consist of sheared domains of serpentinite and/or chlorite, separated from one another by broad anastomosing shear zones filled with re-crystallized granular quartz which thus provides evidence of later silicification. Locally, fine-grained segregations of magnetite or chrome-spinel occur in aggregates with quartz. No original textures were seen in thin section. The overall appearance of these rocks compared to the identifiable metasedimentary

rocks in the fuchsite zone, however, indicates an igneous protolith.

#### Analytical procedures and effects of alteration

Analytical results are shown on Tables 1 and 2. Analyses for major elements and most trace elements were done at Keele University using XRF spectrometry. Representative samples were also analysed by INAA for Cs, Hf, Sc, Ta and Th and by ICP for rare earth elements (REE). Analytical methods are described in Winchester *et al.* (1992). At some localities more than one sample was collected to determine intra-unit variation.

Table 1 Continued.

Sample Number	Dick Mine			Lawson Brook Formation		Felsic Volcanics Annidale Group					Fuchsitic Zone	
	WS676	WS677	WS678	H-13 21-90	H-12 13-89	H-13 25-90	H-13 26-90	H-13 9-90	BH83901 225m	BH83901 229m	WS679	WS680
SiO <sub>2</sub>	53.85	41.16	48.20	53.20	80.55	78.44	77.11	84.35	70.96	68.80	65.48	59.03
TiO <sub>2</sub>	1.43	0.67	0.71	3.53	0.12	0.13	0.17	0.10	0.48	0.61	0.45	0.55
Al <sub>2</sub> O <sub>3</sub>	16.14	15.79	14.80	16.15	9.75	11.22	11.88	8.38	11.67	11.07	9.37	10.94
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	10.70	10.54	11.06	10.46	0.24	1.17	1.29	0.31	6.41	8.54	8.13	9.09
MnO	0.13	0.18	0.19	0.33	0.01	0.02	0.01	0.01	0.20	0.23	0.26	0.28
MgO	8.61	9.83	8.01	1.78	0.01	0.22	0.28	0.02	1.90	2.45	11.25	13.73
CaO	0.61	8.65	10.20	3.64	0.03	0.00	0.00	0.00	0.61	0.41	0.10	0.03
Na <sub>2</sub> O <sub>3</sub>	3.73	1.67	2.91	4.30	0.48	1.64	0.56	1.93	0.03	0.02	0.00	0.00
K <sub>2</sub> O	0.03	0.49	0.02	1.65	7.66	6.34	7.33	3.92	3.25	2.72	0.02	0.01
P <sub>2</sub> O <sub>5</sub>	0.14	0.06	0.07	0.84	0.03	0.04	0.03	0.04	0.04	0.05	0.05	0.06
L.O.I.	4.61	10.85	3.54	4.20	0.37	0.52	0.84	0.29	4.07	5.14	5.04	5.99
Total	99.98	99.89	99.91	100.08	99.25	99.74	99.50	99.35	99.62	100.04	100.15	99.71
Ba	73	93	10	460	386	346	211	253	717	449	53	523
Cl	103	104	106	117	95	149	99	101	85	86	66	85
Cr	5	456	407	bdl	28	20	22	29	1631	1757	1861	2239
Cu	20	15	22	32	15	5	5	bdl	11	27	22	13
Ga	14	10	10	19	7	18	22	7	9	13	6	12
Nb	9	3	3	26	12	49	40	48	2	3	1	2
Ni	54	142	104	8	2	2	6	4	334	483	674	1015
Pb	bdl	bdl	2	4	10	bdl	bdl	bdl	6	29	17	14
Rb	4	22	2	25	63	142	177	76	121	104	4	4
Sr	19	95	133	126	24	29	23	44	16	12	4	8
V	429	248	250	415	8	10	bdl	10	210	307	215	260
Y	35	21	26	53	53	108	93	152	13	17	8	6
Zn	113	83	71	137	47	35	76	21	98	78	311	334
Zr	157	32	34	444	192	581	427	261	26	37	27	29

bdl = below detection limit

Table 2. Trace element and REE data for selected samples.

Sample Number	WS681	WS682	WS678
Cs	0.27	0.44	0.18
Hf	4.20	3.30	0.89
Sc	37	39	133
Ta	0.51	0.32	0.10
Th	0.50	0.23	0.05
La	8.6	6.2	0.5
Ce	23.3	17.5	1.5
Pr	3.35	2.75	0.36
Nd	16.5	13.9	3.1
Sm	4.29	3.77	1.36
Eu	1.27	1.23	0.66
Gd	4.66	4.39	2.45
Dy	5.08	4.87	3.97
Ho	0.91	0.87	0.80
Er	2.53	2.49	2.61
Yb	2.22	2.23	2.63
Lu	0.31	0.32	0.39

Because of the intensity and pervasiveness of deformation, carbonatization, metamorphism and, locally, silicification which commonly characterises the volcanic rocks of the Annidale Group, most samples were not fresh. Evidence of considerable major element mobility in the mafic rocks is provided by a Na<sub>2</sub>O-CaO diagram (Fig. 3a), which shows that all but a few samples from the Lower East Scotch Settlement Formation plot outside the rectangle depicting the field of "normal" basalt. Several samples show CaO depletion and some Na<sub>2</sub>O enrichment characteristic of spilitization. Also, the metasomatised rocks from the fuchsite zone show effects of silica enrichment. Hence the relatively immobile high field strength elements (HFSE) are mainly used here to interpret the nature and tectonic setting of the volcanic rocks. Also shown on the chemical variation diagrams (Figs. 3, 4) for comparison are analyses from Lower Ordovician rocks in other parts of southern New Brunswick and Maine after Dostal (1989) and Fyffe *et al.* (1988).

### Chemical characteristics

On the FeO/MgO-SiO<sub>2</sub> discriminant diagram (Fig. 3b), the mafic samples plot in the iron-enriched tholeiitic field. The Zr/TiO<sub>2</sub>-Nb/Y diagram shows that the mafic samples are subalkalic basalts, whereas the felsic samples have rhyolitic compositions (Fig. 3c). Volcanism was essentially bimodal. A MgO-FeO(total) diagram (Fig. 3d) indicates that the mafic magmas are high-magnesian basalts with some scattering toward low-Mg basalt and ferrobasalt.

On the Zr-TiO<sub>2</sub> diagram (Fig. 4a), most samples plot in the overlapping mid-ocean ridge or within-plate basalt fields. The main exceptions are two samples from sheared flows from

the Dick Mine, which plot in the island arc tholeiite field. A Zr-Zr/Y diagram (Fig. 4b) shows the within-plate nature of most samples, with the exception of the same two samples from the Dick Mine. This diagram indicates that contrasting Zr/Y values typify mafic rocks from both the lower and upper East Scotch Settlement Formation, suggesting that different magmas are present in each part of the formation. A Ti-V diagram (Fig. 4c) shows that mafic rocks in the Annidale Group have high Ti and V, indicative of a within-plate origin, except the Dick Mine samples which plot in the arc-related field. Classification of the samples from the fuchsite zone is hampered by intense alteration. High concentrations of compatible immobile elements (Cr and Ni), however, suggest a possible ultramafic protolith.

A chondrite-normalized rare earth element (REE) plot (Fig. 5a) shows that mafic volcanic rocks from the lower part of the East Scotch Settlement Formation display a gently sloping REE profile, with no Eu anomaly, whereas the Dick Mine basalt displays marked LREE depletion. These differences are also shown on a multielement plot (Fig. 5b), on which the profile of the sample from the Dick Mine reveals depletion of most elements relative to mid-ocean ridge basalt. The apparent Nb peak may be spurious, as the recorded value of 3 ppm is below the limit of detection by XRF and is unlikely to be precise. The felsic rocks broadly support the tectonic setting indicated by the mafic rocks across most of the area. On a Nb-Y discriminant diagram (Fig. 4d), they plot in the within-plate field, suggesting that they were emplaced in an extensional setting.

### COMPARISONS AND DISCUSSION

Coeval mafic volcanic rocks from the St. Stephen and Penobscot (Maine) areas (Fyffe *et al.*, 1988) in the St. Croix Subzone are plotted on Figures 3 and 4 for comparison. The mafic rocks from the St. Croix Subzone have been interpreted to represent volcanism in an extensional environment marginal to an ocean basin, and display alteration and chemical modification similar to those in the Annidale Subzone (Fyffe *et al.*, 1988). They consistently plot as tholeiitic basalts in the within-plate field on most discriminant diagrams, like most mafic samples from the Annidale Group (Figs. 3, 4).

The calc-alkaline volcanic rocks from the Woodstock-Meductic area, which were extruded in an arc or backarc environment (Dostal, 1989), are also plotted for comparison on the tectonic setting discrimination diagrams (Fig. 4). The mafic samples plot in the arc field on Figure 4a and c, as do the low-Ti Dick Mine samples. The felsic volcanic rocks plot in the arc field (Fig. 4d), consistent with arc affinities for the suite. This contrasts with felsic rocks from the Annidale Group which plot in the within-plate field.

The main problem in interpreting the chemical data from the Annidale Group is reconciling the mixed chemical signatures of the Dick Mine samples with the rest of the samples. The presence of intensely metasomatized rocks in adjacent major shear zones (e.g., the fuchsite zone) indicates that some of the Dick Mine rocks could have been brought by shearing to their present position and, accordingly, could be genetically unrelated to the rest of the group. Although meagre, available field evidence indicates that this is not the case. Stratigraphy in the

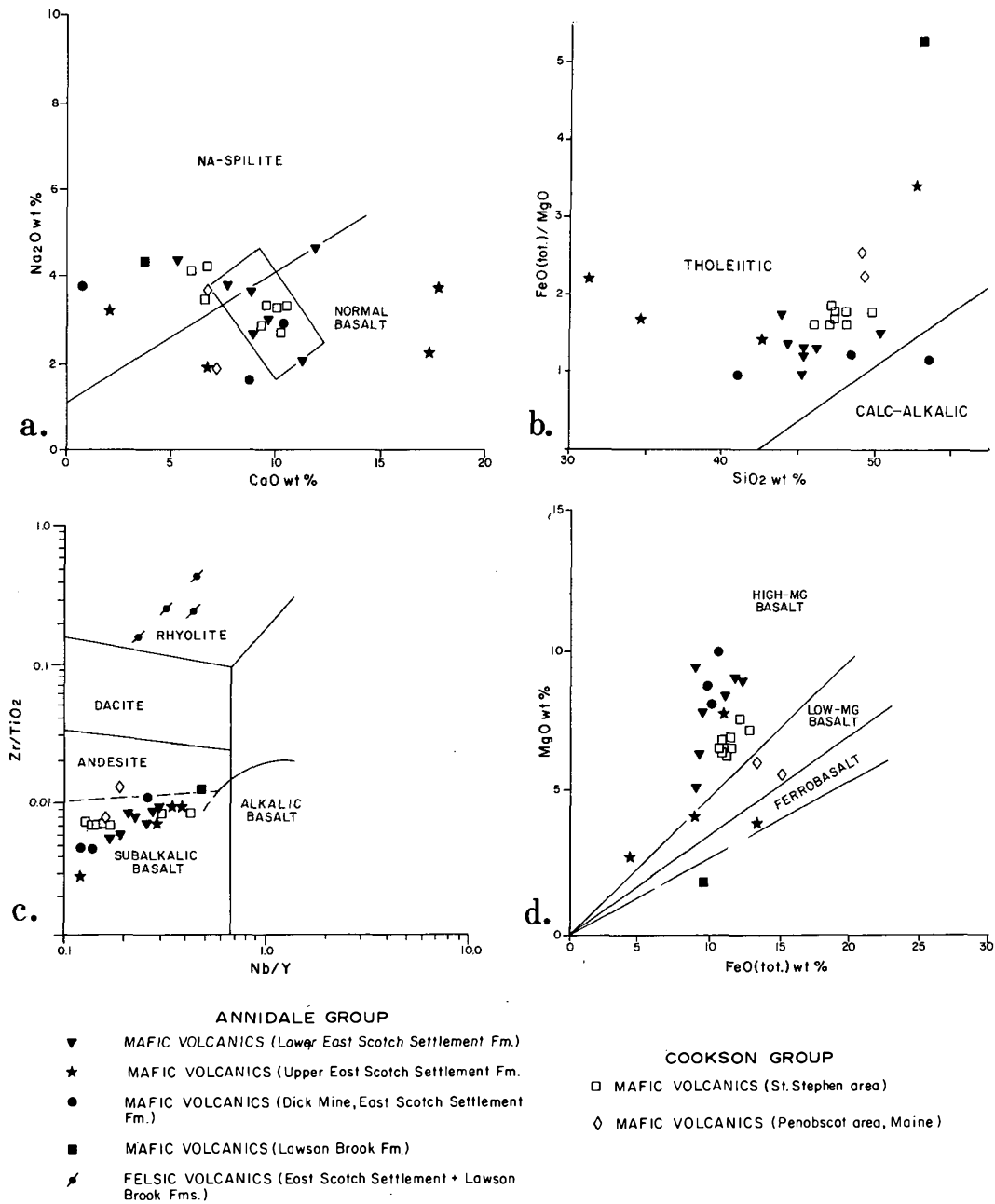


Fig. 3. Diagrams illustrating chemical classification of mafic and felsic volcanic samples from the Annidale Group and of contemporary volcanic suites in the Cookson Group. (a)  $\text{Na}_2\text{O}$ -CaO diagram illustrating mobility of these elements relative to unaltered basaltic rocks (fields after Graham, 1976; Stillman and Williams, 1979). (b)  $\text{FeO (total)}/\text{MgO}$ - $\text{SiO}_2$  diagram (fields after Miyashiro, 1974). (c)  $\text{Zr}/\text{TiO}_2$ -Nb/Y discriminant diagram (fields after Winchester and Floyd, 1977). (d)  $\text{MgO}$ - $\text{FeO (total)}$  diagram showing compositional range of the basalts (fields after Wood, 1978).

Dick Mine area appears too be continuous with the rest of the East Scotch Settlement Formation, and available drill core from the area does not reveal major structural discontinuities. Two additional samples from mafic flows in closely spaced drill holes at the Dick Mine were analyzed for partial chemical data by XRF spectrometry. These samples also yielded contrasting low and high HFSE concentrations ( $\text{TiO}_2 = 1.07\%$  versus  $0.55\%$ ;  $\text{Zr} = 333$  ppm versus 39 ppm.). Similar extreme variations in chemistry may occur within individual formations in back-arc basins, and discrimination diagrams may also give mixed signatures for tectonic setting (Barker *et al.*, 1989).

Volcanic rocks in the Annidale Group (except possibly those

from the Dick Mine and the fuchs site zone) were emplaced in an extensional basin, which may have been a back-arc basin behind a developing arc. This arc could have been the Early Ordovician Woodstock-Meductic arc to the northwest or an as yet unrecognized or buried volcanic belt.

The volcanic rocks of the Dick Mine and possibly ultramafic rocks represented by the fuchs site zone suggest the existence of a suture zone along the southeastern margin of the Annidale Group. Only in these rocks was a LREE-depleted REE profile displayed, together with depletion of HFSE, possibly indicating an arc affinity. If so, the relationship of these rocks to those in coeval arcs in the area remains unknown. The tectonic situa-



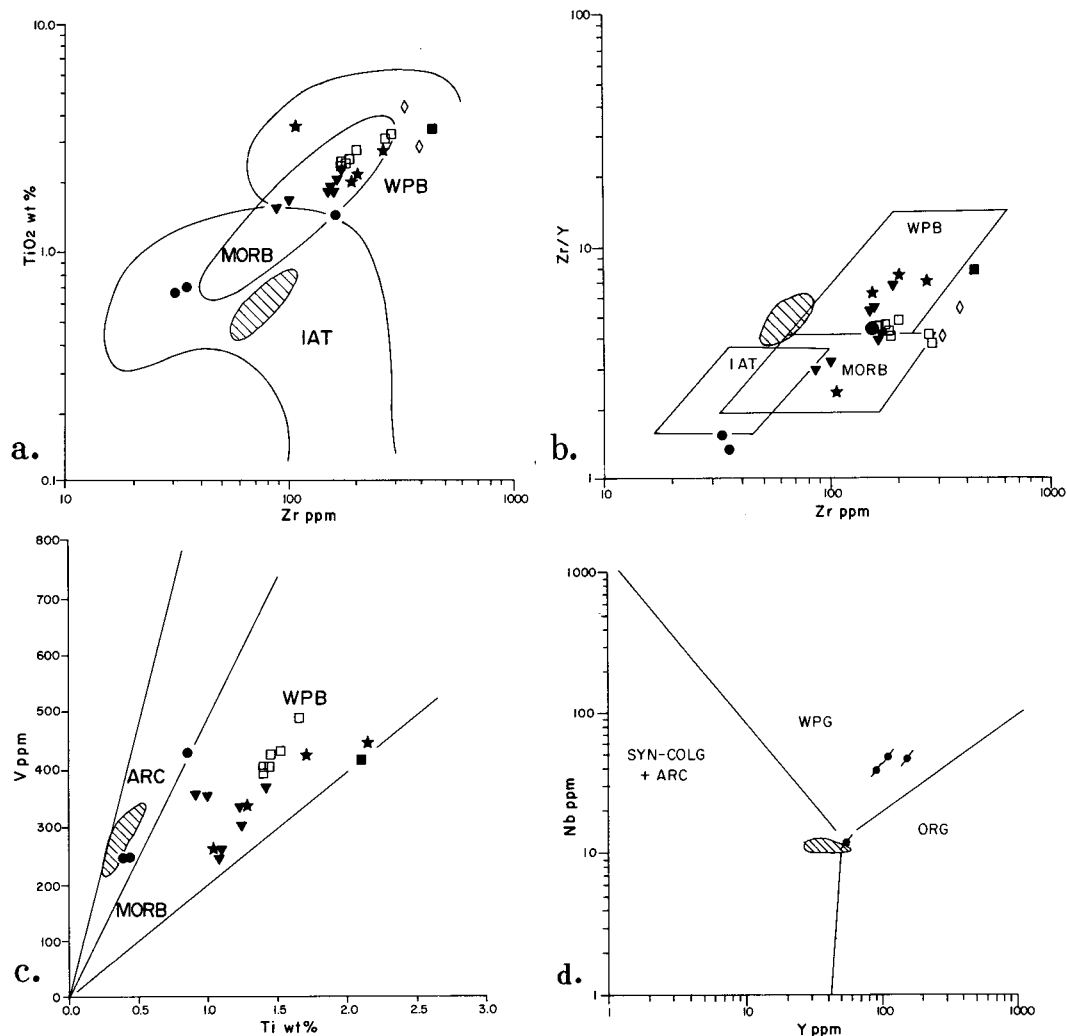


Fig. 4. Diagrams illustrating tectonic setting of the mafic and felsic volcanic rocks in the Annidale Group and contemporary volcanic suites in the region. Symbols as on Figure 3. Diagonal ruled area includes samples from the Woodstock-Meductic arc (after Dostal, 1989). (a) Zr-TiO<sub>2</sub> discriminant diagram (fields after Pearce, 1975). (b) Zr/Y-Zr discriminant diagram (fields after Pearce and Norry, 1979). (c) Ti-V discriminant diagram (fields after Shervais, 1982). (d) Nb-Y discriminant diagram for granites applied to felsic volcanic rocks from the Annidale Group (fields after Pearce *et al.*, 1984). MORB = mid-oceanic ridge basalt, WPB = within-plate basalt, IAT = island arc tholeiite, SYN-COLG = syn-collision granite, VAG = volcanic arc granite, WPG = within-plate granite, ORG = oceanic ridge granite.

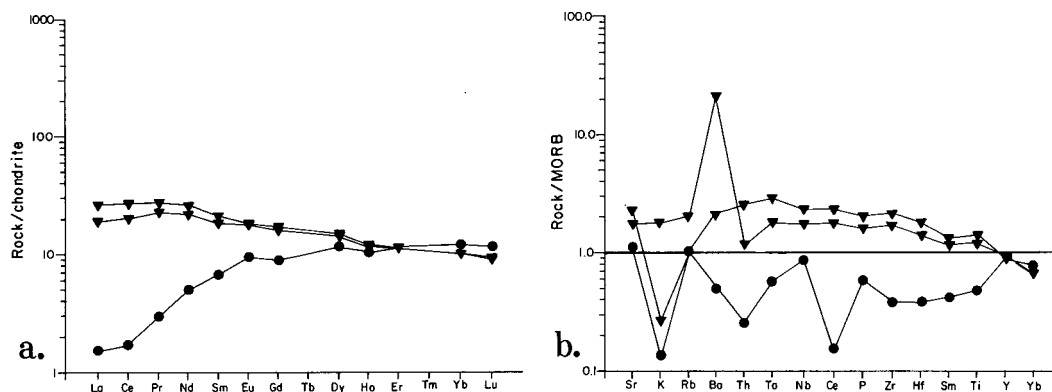


Fig. 5. Rare earth element and multielement profiles of selected samples from the Annidale Group. Symbols as on Figure 3. (a) Chondrite-normalized rare earth profile (normalization values from Nakamura, 1974). (b) MORB-normalized (Pearce, 1982) multielement diagrams for Annidale Group.

tion envisaged is similar in some respects to that in central Newfoundland where complexes of mafic and ultramafic rocks exhibit chemical characteristics indicating complex magmatic histories. These complexes define major zonal and subzonal boundaries between the Gander and Dunnage zones, and, along with other associated sequences of volcanic and sedimentary rocks, represent vestiges of Iapetus Ocean (O'Neill, 1991; Jenner and Swinden, 1993). The rocks of the fuchsite zone and the Dick Mine area may define a similar boundary, but in this case, between the surface expression of the Avalon Zone and the Gander Zone. The Annidale Subzone probably represents a remnant of the Iapetus Ocean.

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