



Petrogenesis of Siluro-Devonian rhyolites of the Tobique Group in the northwestern Appalachians (northern New Brunswick, Canada): tectonic implications for the accretion history of peri-Gondwanan terranes along the Laurentian margin

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Abstract: Uppermost Silurian–Lower Devonian felsic rocks in the bimodal volcanic suite of the Tobique Group in the northwestern mainland Appalachians (northern New Brunswick, Canada) form part of an overstep sequence deposited across the accreted vestiges of Iapetus Ocean on composite Laurentia. Whereas the mafic rocks of the bimodal volcanic suite are continental tholeiites, the felsic rocks are peraluminous and possess geochemical characteristics of A2-type granites emplaced in post-collisional extensional settings. The major and trace element compositions of the felsic rocks indicate that they were generated by dehydration melting of late Precambrian granitoid rocks triggered by heat derived from the rising mafic magma. Unlike the basalts, which have positive $\varepsilon_{Nd}(t)$ values, the felsic rocks have values close to chondrites (-1.6 to $+1.1$), which is consistent with derivation from a crustal source. The rapid transition from compressional to extensional magmatism in latest Silurian–Early Devonian times in this part of Ganderia is probably due to Late Silurian Ganderia–Laurentia collision followed by slab breakoff. Based on Sm–Nd isotopic characteristics in their respective igneous rocks, both Ganderia and Avalonia are underlain by similar Neoproterozoic lower–middle crust and subcontinental lithospheric mantle.

The Appalachian–Caledonide accretionary orogen was formed by the Paleozoic closure of the Iapetus, Tornquist and Rheic oceans (e.g. Williams and Hatcher 1982). The northern Appalachian part of this orogen records the closure of the early Paleozoic Iapetus Ocean, and the collision and accretion of island arcs, seamounts and microcontinents that were located in the Iapetus Ocean between Laurentia and Gondwana (e.g. van Staal *et al.* 2009, 2012). However, the details of terrane accretion and deformational events are still under discussion. Much of the critical information on these processes can be obtained from the investigation of successor basins that overstep and link major elements of the orogen.

In the northwestern mainland Appalachians (Fig. 1), abundant uppermost Silurian–Lower Devonian sedimentary and volcanic rocks form the upper part of an overstep sequence (the Matapedia cover sequence: MCS) deposited across the accreted vestiges of Iapetus on composite Laurentia. These volcanic rocks can provide clues regarding the regional Late Silurian–Early Devonian geological setting and the tectonic events that resulted in the accretion of terranes to the eastern margin of Laurentia. The rocks were emplaced after the Middle–early

Late Silurian Salinic Orogeny (*c.* 430–422 Ma) but prior to the beginning of the Early–Middle Devonian Acadian Orogeny, which is attributed to the accretion of the peri-Gondwanan microcontinent of Avalonia (van Staal *et al.* 2009; Zagorevski *et al.* 2010; Tremblay and Pinet 2016 and references therein). The abundant uppermost Silurian–Lower Devonian volcanic rocks of the MCS in central and northern New Brunswick and southeastern Quebec occur dominantly as bimodal suites. The mafic volcanic types are considered to be rift-related (Dostal *et al.* 1989, 1993, 2016). However, as with many other similar bimodal suites, the origin of the felsic members has been under debate and, in fact, the petrogenetic aspects of the uppermost Silurian–Lower Devonian felsic volcanic rocks in this part of Canada have not yet been investigated in detail. The origin of the felsic rocks in bimodal suites is also an important key to the understanding of the evolution of the continental crust (e.g. McBirney 2006). In this paper, we present whole-rock major and trace element data, as well as Nd isotopic data, for volcanic rocks of the Tobique Group in the MCS (Fig. 2). The focus of this paper is on the felsic rocks of the bimodal suite; specifically, the aim is to (1) constrain their

From: Murphy, J. B., Strachan, R. A. and Quesada, C. (eds) 2021. *Pannotia to Pangaia: Neoproterozoic and Paleozoic Orogenic Cycles in the Circum-Atlantic Region*. Geological Society, London, Special Publications, **503**, 391–407.

First published online June 1, 2020, <https://doi.org/10.1144/SP503-2019-229>

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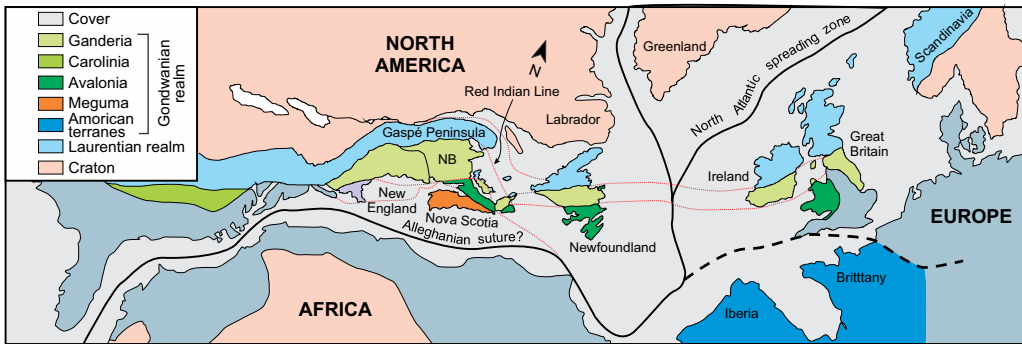


Fig. 1. The major lithotectonic units of the Appalachian–Caledonian orogenic belt in an Early Mesozoic restoration (modified after van Staal and Barr 2012; Dostal *et al.* 2016).

evolution and origin, and, together with data on the associated mafic rocks, to (2) interpret their tectonic setting and contribute to the debate on geodynamic models for the closure of the Iapetus Ocean. The investigation of the felsic rocks can also help to evaluate the nature of crustal basement.

Geological setting

As noted earlier, Upper Silurian–Lower Devonian volcanic rocks of northern New Brunswick are part of the MCS (Fig. 2), which extends from the eastern Gaspé Peninsula of Québec to northern and central Maine. The MCS is an Upper Ordovician–Lower Devonian successor basin deposited unconformably on Ordovician volcanic rocks of the Popelogan terrane, which in turn rests on Early Paleozoic and older continental substrate of Ganderia, a peri-Gondwanan microcontinent. Closure of the main tract of the Iapetus Ocean by southeasterly subduction led to construction of the Andean-type Popelogan arc, and culminated in accretion of Ganderia's leading edge to Laurentia in Late Ordovician time (van Staal 1994; Wilson *et al.* 2004; van Staal *et al.* 2009, 2016; Zagorevski *et al.* 2010). Extension and rifting of the Popelogan arc in the Middle Ordovician led to the opening of the Tetagouche back-arc basin and separation of Ganderia's leading edge from an outboard 'trailing margin' (van Staal *et al.* 2016). NW-directed subduction of the Tetagouche back-arc basin between 450 and 425 Ma was accompanied by development of the Brunswick subduction complex in northeastern New Brunswick, and culminated in the collision of Ganderia's trailing margin with composite Laurentia in the Middle–early Late Silurian (Salinic Orogeny) (van Staal 1994; van Staal *et al.* 2009; Wilson *et al.* 2017).

Upper Silurian–Lower Devonian volcanic rocks emplaced on Ganderian basement are widespread in

the northern mainland Appalachians (Fig. 2). They are primarily found in three volcanic belts in Maine and New Brunswick: the Piscataquis, Tobique-Chaleur and Coastal. The Piscataquis belt stretches discontinuously across north-central Maine (Osberg *et al.* 1989; Hon *et al.* 1992; Schoonmaker *et al.* 2011), whereas the Tobique-Chaleur belt extends in a SW–NE direction from west-central New Brunswick to Chaleur Bay (Dostal *et al.* 1989, 2016; Wilson and Kamo 2008, 2012; Wilson 2017), and farther to the NE in the Gaspé Peninsula of Québec (Dostal *et al.* 1993; D'hulst *et al.* 2008). The Coastal belt extends for over 500 km along the coast of Massachusetts, Maine and New Brunswick but strikes inland in the vicinity of Saint John (Seaman *et al.* 1999; Van Wagoner *et al.* 2002; Llamas and Hepburn 2013). The volcanic centres are frequently associated with coeval intrusions.

The detailed stratigraphy and structural evolution of the MCS was presented by Wilson (2017). The MCS has been divided into three structural zones, from NW to SE these are: the Connecticut Valley–Gaspé Synclinorium, Aroostook–Percé Anticlinorium and Chaleur Bay Synclinorium (Wilson *et al.* 2004). The Chaleur Bay Synclinorium is subdivided by the Rocky Brook–Millstream Fault into two parts (Fig. 2): the Chaleur zone to the north and the Tobique zone (the focus of this study) to the south. The Tobique zone is mainly occupied by the Tobique Group (Fig. 3), which is composed of marine sedimentary rocks (including turbidites) and bimodal volcanic rocks that were emplaced in subaerial to submarine environments. The lower part of the Tobique Group (the dominantly volcanic Costigan Mountain, Cameron Mountain and Pentland Brook formations) has been estimated to be as much as 5000–6000 m thick, whereas the upper part of the group (the dominantly sedimentary Wapske Formation) is *c.* 8000 m thick (Wilson 2017). The felsic rocks include rhyolite flows, felsic hyaloclastites,

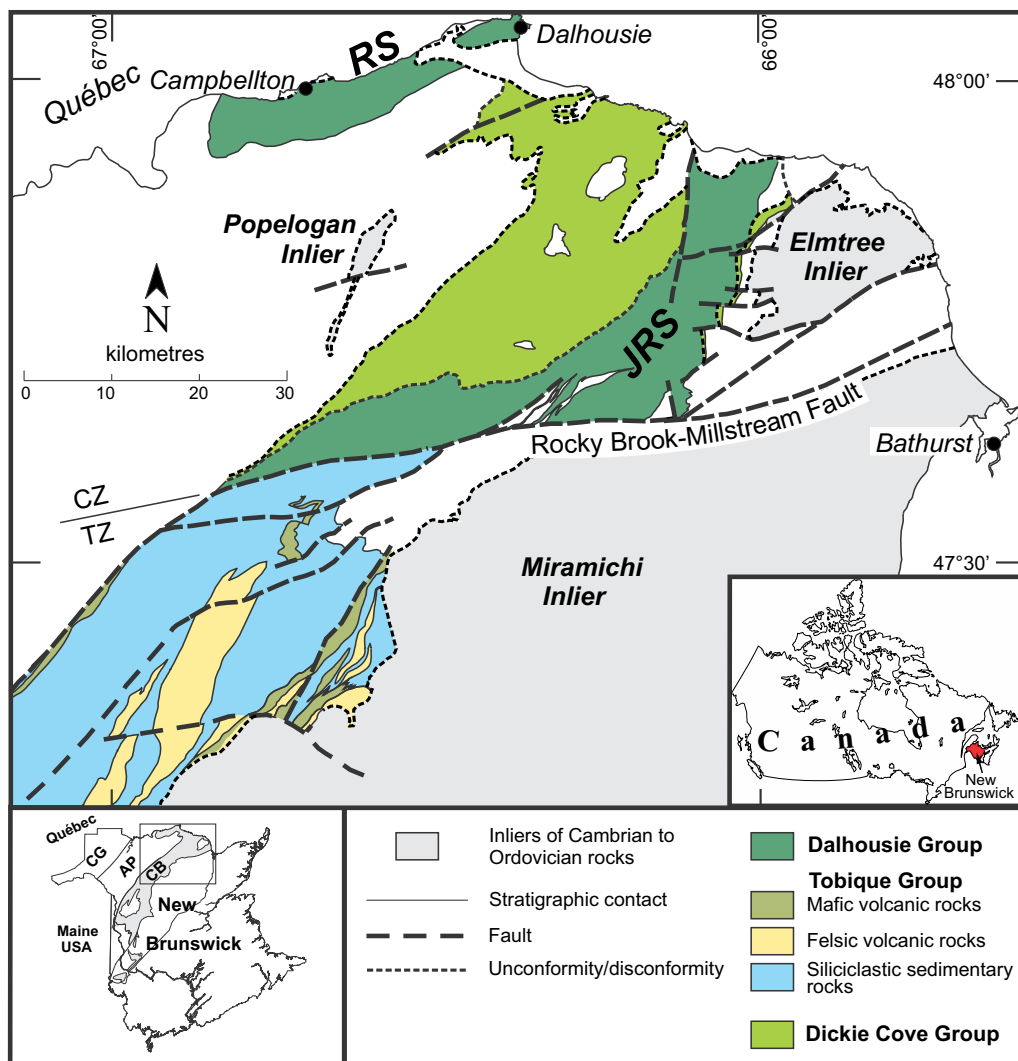


Fig. 2. Simplified geology of the northern part of the Chaleur Bay Synclinorium (modified after [Wilson *et al.* 2017](#)). The Chaleur zone (CZ) is located north of the Rocky Brook–Millstream Fault and the Tobique zone (TZ) is south of the fault. Abbreviations: RS, Restigouche Syncline, JRS, Jacquet River Syncline; uncoloured areas represent Late Ordovician–Silurian rocks and rarely also Carboniferous rocks. The inset in the lower left shows the location of the geological map and the three subdivisions of the Matapedia cover sequence: CB, Chaleur Bay Synclinorium; AP, Aroostook–Percé Anticlinorium; CG, Connecticut Valley–Gaspé Synclinorium. The inset in the right shows the location of New Brunswick.

quartz porphyry and various pyroclastic rocks. The mafic rocks are mainly massive to amygdaloidal, commonly pillowed basalts but locally include scoriaeous flows and interbedded mafic volcanoclastic rocks. The bimodal volcanic rocks are overlain by, and locally interbedded with, deep shelf to outer slope sedimentary rocks ([Wilson 1992, 2017](#)). Based on mainly brachiopods and spores, sedimentary rocks of the Tobique Group are Lower Devonian

(Lochkovian, spanning from 419.2 to 410.8 Ma; [Boucot and Wilson 1994](#); [Wilson and Burden 2006](#); [Wilson *et al.* 2017](#)). However, U–Pb zircon dating of volcanic rocks in the lower part of the Tobique Group have yielded mainly latest Silurian (Pridolian) ages (420.8 ± 0.6 – 418.6 ± 0.9 Ma; [Wilson and Kamo 2008](#); [Wilson *et al.* 2017](#)).

The Central plutonic belt (CPB) of New Brunswick, a c. 250 km-long, NE-trending string of mainly

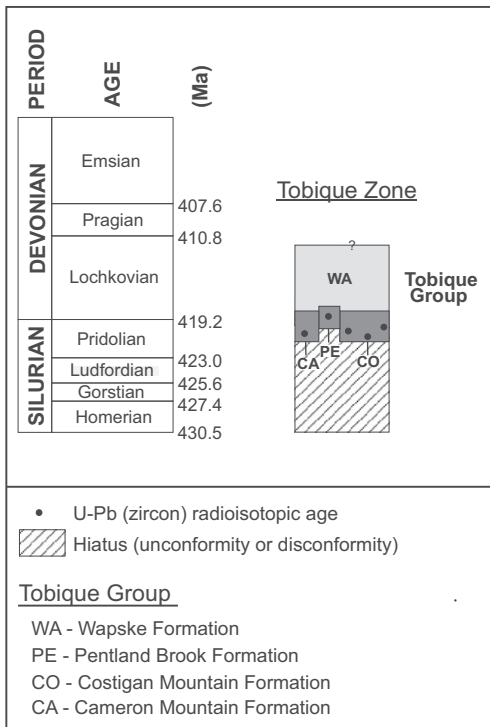


Fig. 3. Stratigraphic columns showing the age of Upper Silurian–Lower Devonian volcanic rocks of the Tobique Group. Abbreviations for volcanic rocks: PE, Pentland Brook Formation; CA, Cameron Mountain Formation; CO, Costigan Mountain Formation; WA, Wapske Formation.

granitic rocks ranging in age from Early Ordovician to Late Devonian, extends from southwestern New Brunswick to Chaleur Bay in the NE. The granitic rocks, which include several Late Silurian–Early Devonian plutons, intrude Cambro-Ordovician metasedimentary rocks in the Miramichi Inlier (Fig. 2). Wilson and Kamo (2016) documented that the Late Silurian–Early Devonian plutons in central New Brunswick are made up typically of peraluminous, calc-alkaline, S-type granites and postulated that the protolith of these plutons was the Cambrian–Ordovician metasedimentary rocks (Miramichi Group and Trousers Lake Metamorphic Suite) that form the core of the Miramichi Inlier. The exception is the Redstone Mountain Granite, which lies along the western margin of the Miramichi Inlier adjacent to the volcanic rocks of the Tobique belt. The Redstone Mountain Granite appears to have a genetic connection to the Tobique volcanic rocks. This A2-type granite is the same age as the Costigan Mountain Formation and has been interpreted as the subvolcanic equivalent of the Tobique volcanic

rocks (Walker and Clark 2012; Wilson and Kamo 2016).

Petrography

Felsic volcanic rocks in the central part of the Tobique Group are massive to flow-banded, aphyric to feldspar-phyric and, in places, vesicular and/or spherulitic. Massive to flow-banded rhyolites commonly pass into hyaloclastic breccias composed of angular rhyolitic fragments enclosed in a finely granulated groundmass. Conversely, felsic volcanic rocks near the exposed margins of the Tobique ‘basin’ are dominantly pyroclastic rocks containing rounded clasts of rhyolites, vitric crystals, vitric lapilli and polymict lithic fragments.

Porphyritic rocks contain potassium feldspar phenocrysts, which are typically euhedral to subhedral and up to *c.* 2 mm in size. Subordinate phenocrysts of quartz are commonly embayed. Phenocrysts rarely comprise more than 25% of the volume. They are set in a fine-grained or a devitrified glassy groundmass, and both phenocrysts and their groundmass are locally sericitized and altered. All these rocks underwent sub-greenschist facies metamorphism as indicated by mineral assemblages in the associated basaltic rocks (e.g. Mossman and Bachinski 1972; Wilson 1992), although the felsic rocks contain only sericite and chlorite as secondary minerals.

Analytical methods

The analysed rhyolitic samples from the Tobique Group were selected from a set of several hundred volcanic rocks that were collected during regional mapping projects in northern and western New Brunswick (e.g. Walker and Wilson 2013; Wilson 2017). The analysed samples are from the Pentland Brook and Costigan Mountain formations. The analyses of whole-rock major and trace elements (Table 1) were done via lithium metaborate–tetraborate fusion at the Activation Laboratories Ltd in Ancaster, Ontario, Canada. Major elements were analysed by an inductively coupled plasma-optical emission spectrometer, whereas trace elements were determined by an inductively coupled plasma mass spectrometer. The accuracy for each element was monitored by analysing international standards, which were run as unknown. Based on replicate analyses, the precision is generally better than 3% for most major elements, and between 5 and 10% for trace elements.

Sm and Nd concentrations, and Nd isotope ratios of the rhyolitic rocks (Table 2) were determined at the Atlantic Universities Regional Facility at the Department of Earth Sciences of Memorial

Table 1. Representative analyses of the volcanic rocks of the Tobique Group

Sample No.	Rhyolite																Basalt			
	238	173	5	f-34	56	20	195	141	59	6	107	201	207	263	278	67	99	1	34	
	CMF	CMF	CMF	CMF	CMF	CMF	CMF	CMF	CMF	CMF	CMF	CMF	PBF	PBF	PBF	PBF				
wt%																				
SiO ₂	71.95	71.96	72.34	72.32	73.04	72.36	74.99	70.44	73.52	76.13	73.20	74.70	74.06	72.60	70.96	69.50	52.19	44.81	48.41	
TiO ₂	0.37	0.37	0.29	0.26	0.29	0.37	0.32	0.30	0.15	0.16	0.17	0.30	0.25	0.25	0.25	0.38	2.42	1.36	1.70	
Al ₂ O ₃	13.27	13.77	13.48	13.09	13.36	13.00	11.58	12.92	13.06	12.31	12.50	11.80	13.64	13.25	13.03	13.07	15.30	16.26	16.10	
Fe ₂ O ₃	2.48	3.39	2.82	3.99	2.13	3.28	2.50	3.70	2.46	1.16	2.14	2.71	1.39	2.75	3.29	3.49	11.58	12.71	10.52	
MnO	0.06	0.06	0.09	0.05	0.02	0.07	0.04	0.06	0.07	0.01	0.05	0.05	0.02	0.03	0.01	0.12	0.19	0.21	0.19	
MgO	0.34	0.43	0.70	0.61	0.19	0.81	0.46	0.19	0.19	0.13	0.10	0.76	0.19	1.02	0.36	0.60	3.86	8.79	6.53	
CaO	1.12	0.39	0.21	0.11	0.43	0.72	0.92	0.07	0.07	0.09	1.16	0.47	0.71	0.60	0.28	1.77	6.40	6.91	9.25	
Na ₂ O	3.07	5.50	3.75	3.37	4.53	5.03	1.76	2.12	4.37	2.73	3.35	1.74	4.05	4.33	0.86	2.78	3.80	2.38	3.39	
K ₂ O	5.13	3.23	5.32	5.32	4.41	2.94	5.10	7.03	4.06	5.97	5.04	6.50	5.37	3.73	10.15	4.50	2.30	1.80	0.87	
P ₂ O ₅	0.08	0.07	0.04	0.04	0.04	0.06	0.08	0.06	0.02	0.03	0.01	0.03	0.04	0.04	0.04	0.08	0.53	0.13	0.20	
LOI	1.87	0.54	0.81	0.83	0.72	1.07	2.13	1.85	0.99	0.77	1.05	1.00	0.37	1.23	0.54	3.13	1.51	4.41	2.18	
Total	99.74	99.71	99.85	99.99	99.16	99.71	99.88	98.74	98.96	99.49	98.77	100.06	100.09	99.83	99.77	99.42	100.08	99.77	99.34	
ppm																				
Cr	6	0	8	64	0	18	8	15	49	9	19	10	45	39	11	12	53	220	118	
Ni	3	5	3	2	3	2	3	2	1	1	3	1	3	3	4	2	19	79	28	
Co	1	3	2	5	1	4	2	1	1	1	1	0	1	3	1	3	0	37	36	
Sc	8	6	5	6	5	7	7	8	1	3	3	3	5	6	12	9	33	32	32	
V	14	14	8	2	6	26	15	2	2	5	1	1	8	6	3	15	216	225	251	
Rb	193	140	181	145	90	90	188	242	142	223	168	146	131	87	232	187	43	75	20	
Cs	2.2	0.6	0.6	0.5	0.3	0.5	3.7	5.9	0.8	1.5	0.1	2.3	0.5	0.5	0.4	1.3	0.00	0.00	0.00	
Ba	651	244	591	661	580	490	634	594	139	641	442	614	636	524	1214	464	537	265	197	
Sr	85	58	97	55	109	76	53	38	24	59	78	79	90	87	107	50	350	162	308	
Ga	18	27	22	23	18	21	16	20	22	16	20	20	18	17	21	20	22	15	19	
Ta	1.50	1.66	1.56	1.73	1.49	1.55	1.28	1.85	2.07	1.41	3.50	2.20	1.68	1.55	1.87	1.49	0.72	0.14	0.33	
Nb	16.3	21.3	18.2	21.6	17.1	19.7	13.6	20.9	22.7	11.4	36.0	28.0	19.6	19.4	26.0	17.0	12.6	2.5	5.3	
Hf	8.1	10.8	10.4	11.5	10.1	10.2	6.4	11.9	10.7	4.9	13.0	14.2	8.8	8.2	11.2	8.2	6.3	2.1	3.5	
Zr	276	362	371	421	360	373	240	482	368	150	528	500	295	286	441	296	218	68	124	
Y	62	69	70	83	105	96	52	83	88	38	96	90	64	58	62	74	49	26	35	
Th	23.2	26.6	26.9	25.1	26.6	23.1	19.6	22.0	26.0	29.0	27.1	26.8	21.4	19.8	17.5	21.9	5.46	2.10	1.73	
U	6.26	7.33	7.89	6.97	7.01	6.60	4.84	3.93	5.45	4.95	8.60	6.40	5.54	5.24	3.11	6.44	1.74	0.32	0.56	

(Continued)

Table 1. *Continued.*

Sample No.	Rhyolite																Basalt		
	238	173	5	f-34	56	20	195	141	59	6	107	201	207	263	278	67	99	1	34
	CMF	CMF	CMF	CMF	CMF	CMF	CMF	CMF	CMF	CMF	CMF	CMF	PBF	PBF	PBF	PBF			
La	46.1	53.8	54.3	65.4	109.0	84.7	42.6	56.2	39.5	43.5	80.1	64.4	58.1	37.7	26.7	66.2	27.52	6.61	9.80
Ce	96.5	108.0	96.9	127.0	198.8	161.0	77.5	125.0	95.9	90.7	187.0	137.0	106.0	82.2	65.0	97.2	64.5	18.3	24.8
Pr	11.60	14.20	12.50	16.00	22.20	19.20	10.60	15.50	10.60	9.87		15.70	13.90	9.47	8.01	14.80	8.15	2.65	3.54
Nd	43.1	51.2	44.2	58.0	79.1	70.6	38.7	58.6	40.1	33.6		62.1	48.0	33.7	31.7	53.7	35.90	12.20	16.20
Sm	9.15	10.90	9.00	12.00	15.50	14.60	8.23	13.80	9.77	6.91		13.60	9.78	7.07	7.35	10.70	9.43	3.46	4.39
Eu	1.55	1.18	1.09	1.40	2.04	2.01	1.34	2.74	0.59	0.71		1.75	0.78	0.57	1.46	2.04	2.55	1.19	1.63
Gd	9.12	9.58	8.40	10.80	16.60	15.00	7.76	13.30	10.60	6.09		14.40	9.72	6.93	7.46	10.30	9.64	4.01	5.09
Tb	1.53	1.83	1.65	2.06	2.71	2.56	1.35	2.41	2.26	1.02		2.50	1.63	1.27	1.45	1.78	1.70	0.72	0.91
Dy	9.26	11.30	9.99	12.20	15.30	14.10	7.63	14.40	14.60	5.98		15.40	9.90	8.12	9.49	10.30	10.46	4.44	5.59
Ho	1.89	2.24	2.06	2.44	2.95	2.61	1.46	3.00	3.13	1.22		3.20	2.02	1.70	2.10	2.03	2.07	0.91	1.10
Er	5.69	7.17	6.28	7.57	8.54	7.40	4.37	8.75	9.34	3.69		9.80	5.96	5.53	6.68	5.95	5.98	2.70	3.19
Tm	0.87	1.13	0.97	1.15	1.26	1.09	0.67	1.32	1.39	0.57		1.49	0.90	0.90	1.10	0.89	0.88	0.39	0.47
Yb	5.50	7.33	6.19	7.34	7.59	6.73	4.14	8.19	8.68	3.65		9.40	5.93	5.80	7.34	5.45	5.35	2.41	3.02
Lu	0.79	1.10	0.91	1.07	1.08	0.95	0.60	1.26	1.25	0.54		1.42	0.87	0.83	1.09	0.79	0.74	0.34	0.44

Fe_2O_3^+ , total Fe as Fe_2O_3 ; CMF, Costigan Mountain Formation; PBF, Pentland Brook Formation; LOI, loss on ignition.

Table 2. Nd isotopic composition of volcanic rocks of the Tobique Group

Sample	Age (Ma)	Rock	Formation	Nd (ppm)	Sm (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}_{(m)}$	2σ	$^{143}\text{Nd}/^{144}\text{Nd}_{(i)}$	$\epsilon_{\text{Nd}}(t)$	T_{DM} (Ma)
207	415	Rhyolite	Pentland	49.62	9.94	0.1212	0.512490	6	0.512161	1.12	917
278	415	Rhyolite	Pentland	33.61	7.41	0.1334	0.512495	6	0.512132	0.57	1043
238	415	Rhyolite	Costigan	42.28	8.99	0.1286	0.512370	5	0.512020	-1.62	1204
173	415	Rhyolite	Costigan	46.00	9.98	0.1312	0.512456	8	0.512099	-0.08	1086
202*	415	Basalt		11.87	3.78	0.1923	0.512864	7	0.512341	4.65	1260
71*	415	Basalt		24.20	6.50	0.1623	0.512726	6	0.512285	3.54	948
117*	415	Basalt		15.89	4.98	0.1610	0.512754	7	0.512316	4.16	849

T_{DM} , depleted mantle model age calculated using the model of DePaolo (1988); $\epsilon_{\text{Nd}}(t)$, age-corrected values ($t = 415$ Ma); $^{143}\text{Nd}/^{144}\text{Nd}_{(m)}$, measured value; $^{143}\text{Nd}/^{144}\text{Nd}_{(i)}$, initial (corrected to 415 Ma).
*Data from Dostal *et al.* (2016).

University of Newfoundland (St John's, Newfoundland, Canada) using a multi-collector Finnigan MAT 262 mass spectrometer (Pollock *et al.* 2015). Replicate analyses of JNdi-1 yield a mean $^{143}\text{Nd}/^{144}\text{Nd} = 0.512100 \pm 6$. The 2σ values are given in Table 2. $\epsilon_{\text{Nd}}(t)$ values were calculated with respect to CHUR (chondritic uniform reservoir) using a present-day $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512638 and a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.196593, and were subsequently age-corrected. A T_{DM} model age (Table 2) was calculated according to the model of DePaolo (1988).

Alteration

Rocks of the Tobique Group were metamorphosed to the lower greenschist facies (Wilson 1992), which may result in the mobility of some elements, particularly Na, K, Cs and Rb. In contrast, high field strength elements such as Ti, Zr, Nb, Y and rare earths are considered relatively immobile during alteration processes. The concentrations of K and Na show some scatter in Harker diagrams (Fig. 4a), suggesting some mobility of these elements. However, most samples exhibit generally consistent variations of immobile- and mobile-element patterns on primitive-mantle- and chondrite-normalized diagrams. This suggests that trace elements have not been noticeably remobilized and that most of their variations are likely to relate to magmatic processes. In addition, we used the more immobile elements for most of the interpretations on the petrogenesis and tectonic settings.

Geochemistry

Volcanic rocks of the Tobique Group range from basalt to rhyolite, with very rare intermediate rocks, thus making the suite bimodal with a silica gap (Fig. 4). The mafic rocks were described by Dostal *et al.* (1989, 2016) and correspond to continental tholeiites. The felsic rocks of the Tobique Group have SiO_2 levels ranging from *c.* 70 to 78 wt% (loss on ignition (LOI)-free basis) accompanied by ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) ranging between 8 and 10 wt%. A total alkali v. silica classification diagram shows that the felsic rocks are rhyolites (Fig. 4a). On diagrams involving relatively stable elements, the rocks plot in the fields of rhyodacite and rhyolite (Fig. 4b). The rocks typically have an agpaitic index/peralkaline index (mol. $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} + \text{K}_2\text{O}$) and aluminum saturation index (mol $\text{Al}_2\text{O}_3/\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$) > 1, implying that they are mainly peraluminous. However, they do not contain characteristic minerals of S-type granites, such as muscovite or Al-rich minerals. The rocks have low abundances of CaO, MgO and FeO^{T} , characteristics that are typical of A-type granites.

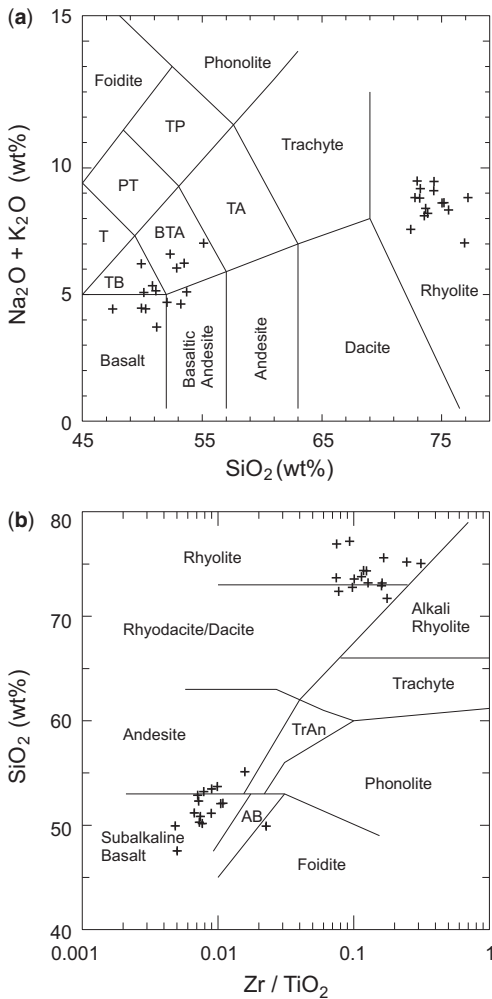


Fig. 4. (a) Total alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) v. SiO_2 (wt%) diagram (LOI-free) for rocks of the Tobique Group (+). Fields: TB, alkali basalt, trachybasalt; BTA, basaltic trachyandesite; TA, trachyandesite; T, tephrite, basanite; PT, phonotephrite; TP, tephritphonolite. (b) Zr/TiO_2 v. SiO_2 discrimination diagram (LOI-free) for the Tobique Group (+). AB, alkali basalt; TrAn, trachyandesite. Mafic rocks include data from Dostal *et al.* (2016).

The chondrite-normalized REE patterns display a distinct light REE (LREE) enrichment but relatively flat heavy REE (HREE) segments, common of crustal melts (Fig. 5). The patterns are generally sub-parallel and accompanied by negative Eu anomalies. $(\text{La}/\text{Yb})_n$ and $(\text{La}/\text{Sm})_n$ ratios are typically 4–7 and 2.5–4, respectively, whereas the $(\text{Tb}/\text{Yb})_n$ ratios are usually c. 1–1.6; the flat HREE segments reflect an absence of garnet at the source of these rocks. The

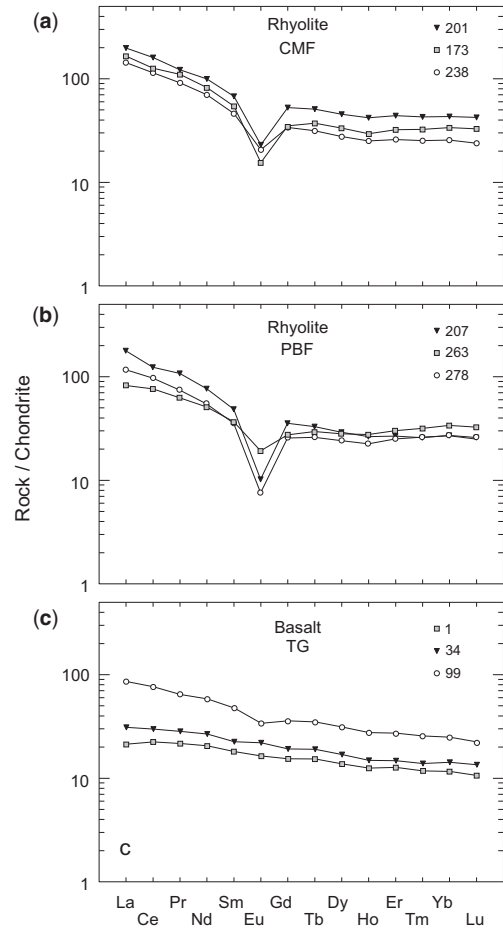


Fig. 5. Chondrite-normalized REE diagrams for: (a) felsic volcanic rocks of the Costigan Mountain Formation (CMF); (b) felsic volcanic rocks of the Pentland Brook Formation (PBF); and (c) mafic volcanic rocks of the Tobique Group (TG). Normalizing values are after Sun and McDonough (1989).

chondrite-normalized REE patterns of the associated basalts show a negative slope with $(\text{La}/\text{Yb})_n$ c. 1–6, without noticeable negative Eu anomalies. In the primitive-mantle-normalized multi-element plots, the felsic rocks are enriched in some large ion lithophile elements, including Rb and Th, but the patterns show distinct negative anomalies of Nb, Ta, Ba, Sr, Eu and Ti (Fig. 6). Based on mantle-normalized plots, the basaltic rocks are slightly enriched in Th and light REE, and show a slight relative depletion of Nb and Ta (Fig. 6).

$\varepsilon_{\text{Nd}}(t)$ values in the felsic volcanic rocks are close to chondritic values (–1.6 to +1.1), indicating that they were derived from a reservoir with a long-term history of near-chondritic Sm–Nd values, and

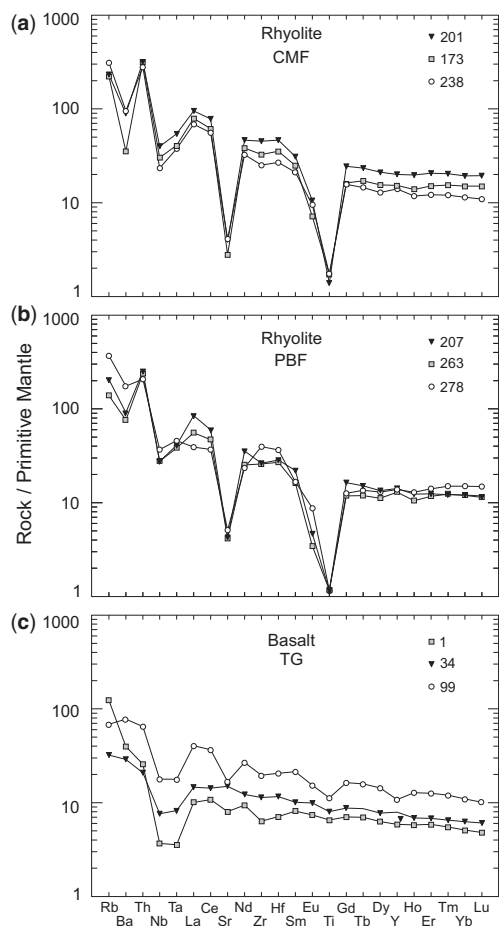


Fig. 6. Primitive-mantle-normalized incompatible element abundances for: (a) felsic rocks of the Costigan Mountain Formation (CMF); (b) felsic rocks of the Pentland Brook Formation (PBF); and (c) mafic rocks of the Tobique Group (TG). Elements are arranged in the order of decreasing incompatibility from left to right. Normalizing values are after Sun and McDonough (1989).

suggesting a crustal source, or a mantle source with crustal admixture. The values differ from those of associated basalts (Table 2) (Dostal *et al.* 2016) but resemble those of Siluro-Devonian granites in northern New Brunswick (Whalen *et al.* 1996). They are also similar to the granitic rocks of Ganderia in Newfoundland (e.g. Kerr *et al.* 1995; Whalen *et al.* 2006).

Discussion

Chemical characteristics and tectonic setting

Compositionally, the felsic volcanic rocks correspond to A-type granites (Fig. 7a, b). Their 10 000

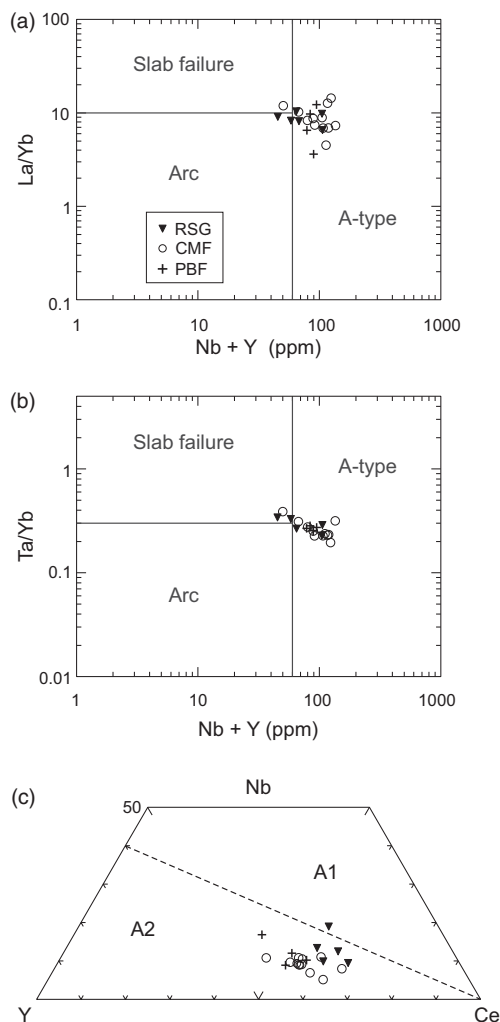


Fig. 7. (a) La/Yb v. Nb + Y (ppm) and (b) Ta/Yb v. Nb + Y (ppm) discrimination diagrams of Whalen and Hildebrand (2019) showing the A-type characteristics of the Tobique felsic volcanic rocks, as well as the Redstone Mountain granitic rocks. CMF, Costigan Mountain Formation (○); PBF, Pentland Brook Formation (+); RMG, Redstone Mountain granite (▼). (c) Nb–Y–Ce discrimination diagram for the subdivision of A-type granites (after Eby 1992). Symbols are the same as in (a).

× Ga/Al ratios are also high, typically >2.6, which are values that are characteristic of A-type granites (Whalen *et al.* 1987). The rocks belong to the A2 subdivision of A-type granites (*sensu* Eby 1992), which typically represents magmas derived from lower to middle continental crust or underplated crust (Fig. 7c). The relationship between

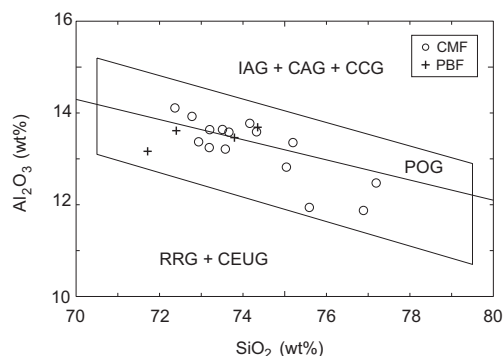


Fig. 8. Al₂O₃ v. SiO₂ (wt%; LOI-free) tectonic discrimination diagram of Manier and Picolli (1989) for the Tobique felsic volcanic rocks. Abbreviations: IAG, island arc granitoids; CAG, continental arc granitoids; CCG, continental collision granitoids; POG, post-orogenic granitoids; RRG, rift-related granitoids; CEUG, continental epirogenic uplift granitoids. Symbols: CMF, Costigan Mountain Formation (○); PBF, Pentland Brook Formation (+).

major elements is indicative of a post-orogenic setting for these felsic rocks (Fig. 8), which are also ferroan (Frost *et al.* 2001).

Petrogenesis of the felsic rocks

The abundant Upper Silurian (Pridolian)–Lower Devonian (lower Emsian) volcanic rocks of the northern mainland Appalachians occur predominantly as bimodal suites. The mafic members of the suites are typically within-plate types ranging from continental tholeiites, mostly, to transitional basalts and rare alkaline types (Keppie and Dostal 1994). These mafic rocks were derived from the sub-continental lithospheric mantle (SCLM), which was modified by subduction processes (Dostal *et al.* 2016). They differ from regional Early–Late Silurian volcanic rocks (Llandoverly–lower Pridolian) of the Coastal volcanic belt in southern New Brunswick and Maine, which are typical of continental arcs and which display an almost continuous range of compositions from basalt to rhyolite, with mafic rocks having a calc-alkaline character (Llamas and Hepburn 2013).

The bimodal mafic–felsic suites of the Tobique Group are compositionally similar to many bimodal suites worldwide. Such bimodal volcanic suites include those from both large igneous provinces such as the Panjal traps of India (Shellnutt *et al.* 2012) and some other Late Silurian–Early Devonian volcanic complexes of the northern Appalachians (e.g. Dostal *et al.* 1989, 1993; Hon *et al.* 1992; Keppie and Dostal 1994; Keppie *et al.* 1997).

A scarcity of rocks of intermediate composition in some basalt–rhyolite suites was probably first noted by Bunsen (1851) and subsequently confirmed by Daly (1925). The reason for this so-called ‘Daly gap’ (Chayes 1977) has remained controversial and is still under debate. Contrasting hypotheses discussing both the evolution of felsic rocks and the existence of bimodal suites produced a century-long debate (e.g. Bowen 1928; Melekhova *et al.* 2013). The traditional process invoked for the genesis of felsic rocks is extensive fractional crystallization of mantle-derived basaltic magma (e.g. Bowen 1928; Lacasse *et al.* 2007). However, this process alone has been considered in many cases to be insufficient to account for the large volume of felsic rocks relative to associated mafic magmas (e.g. Musselwhite *et al.* 1989; Wanless *et al.* 2010). In addition, geochemical data suggest that felsic rocks may contain a crustal component, which can be explained by fractional crystallization combined with the assimilation of continental crust (e.g. DePaolo 1988). However, these models do not explain the lack of intermediate types. Thus, the gap has been also attributed to differing origins for mafic and felsic rocks. The formation of felsic rocks can result from partial melting of the crust by heat generated from underplated basalts (e.g. Huppert and Sparks 1988; Wanless *et al.* 2010), whereas mafic rocks are assumed to be derived from melting of the mantle.

Alternatively, other models for the gap suggest the immiscibility of different magma types (e.g. Charlier *et al.* 2011) and the crystallization of specific mineral phases (e.g. Grove and Donnelly-Nolan 1986), as well as processes occurring within magma chambers (Brophy 1991; Freundt-Malecha *et al.* 2001; Lakhssassi *et al.* 2010; Dostal *et al.* 2017), among others. Thus, the question remains regarding how large volumes of felsic magmas are produced, and to what extent they evolve by fractional crystallization in crustal, sub-volcanic magma chambers.

Despite some scatter, felsic rocks of the Tobique Group show a negative correlation of Al (Fig. 8), Ti, Fe, Mg and Ca with SiO₂, which is broadly consistent with the fractionation of ferromagnesian minerals, Fe–Ti oxides and calcic plagioclase. The distinct depletion of Ba, Sr and Eu on the mantle-normalized multi-element and chondrite-normalized REE patterns may result from the fractional crystallization of feldspars during magma evolution. In addition, Rb/Sr v. Sr and Ba v. Eu/Eu* relationships (Fig. 9a, b) suggest that the fractionation of plagioclase played a major role (assuming that these elements were not mobile during the secondary processes). Variations of (La/Yb)_n v. La (Fig. 9c) show that fractionation of REE, the bulk of which is hosted by accessory phases, was dominated by the crystallization of monazite or allanite. The Nb/Ta ratio decreases from 15 to 10 with an increase of SiO₂

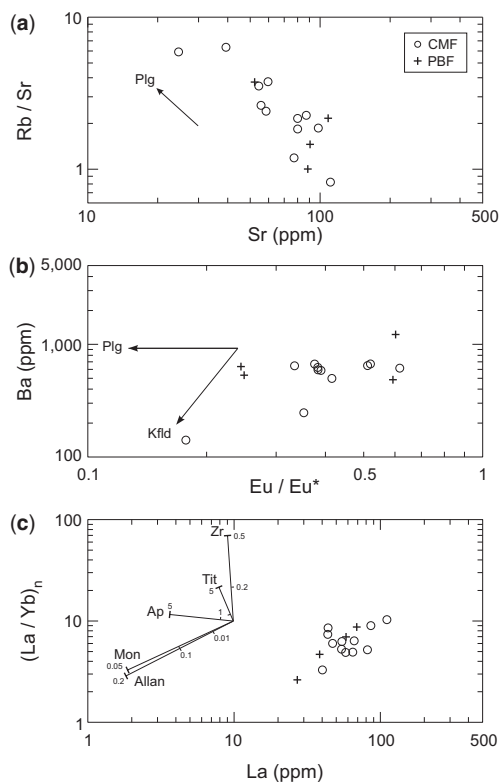


Fig. 9. (a) Rb/Sr v. Sr (ppm) and (b) Ba (ppm) v. Eu/Eu* diagrams for the Tobique felsic volcanic rocks. Vectors depict the fractionation trends of the compositional changes in the residual liquid when the specified phase is progressively removed from the magma during fractional crystallization; Plg, plagioclase; Kfhd, K-feldspar. (c) Chondrite-normalized La/Yb ratio v. La (ppm) diagram for the felsic rocks of the Tobique Group. Fractionation vectors for accessory minerals are after *Wu et al. (2003)*. Mineral vectors are based on fractionation of monazite (Mon), allanite (Allan), apatite (Ap), titanite (Tit) and zircon (Zr). The percentages of fraction are shown for each mineral. Symbols: CMF, Costigan Mountain Formation (○); PBF, Pentland Brook Formation (+).

and Ta, a feature that is typical of peraluminous granites (*Dostal and Chatterjee 2000*). This variation is probably related to the crystallization of columbite–tantalite. However, the Tobique felsic rocks only underwent limited fractional crystallization. The geochemical characteristics of the mafic and felsic rocks indicate that fractional crystallization of the mafic magma that sourced the tholeiitic basalts of the Tobique Group could not have produced the felsic magma that sourced its rhyolites. This is also supported by differences in $\epsilon_{\text{Nd}}(t)$ isotopic values between the two rock types (*Table 2; Fig. 10*). The

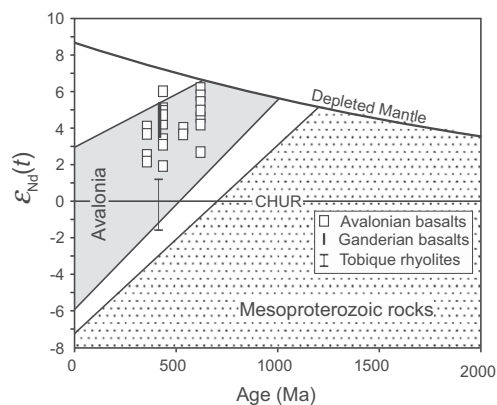


Fig. 10. $\epsilon_{\text{Nd}}(t)$ v. time plot comparing new Sm–Nd isotopic data of the Tobique rhyolitic rocks with basaltic rocks of Avalonia (*Keppie et al. 1997; Murphy et al. 2011*) and Ganderia (*Dostal et al. 2016*) of the Canadian Maritimes. The shaded area is the Avalonian basement and SCLM (after *Murphy et al. 2011; Keppie et al. 2012*). The field for Mesoproterozoic rocks is from *Murphy et al. (2008)*. CHUR, chondritic uniform reservoir.

compositional contrasts in whole-rock geochemical and Nd isotopic compositions, the lack of intermediate rock types (Daly gap), and the large volume of felsic volcanic rocks relative to mafic rocks together imply that the mafic and felsic suites were derived from different sources. The felsic volcanic rocks were likely to have been derived from the melting of a crustal source triggered by heat derived from a rising mafic magma. More specifically, peraluminous A2-type felsic rocks are typically considered to be derived from partial melting of dehydrated, granulite-facies lower crust (*King et al. 1997*).

According to *Collins et al. (1982)* and *Clements et al. (1986)*, A-type granites could be generated by partial melting of a granulitic residue from which an I-type granitic melt had been previously extracted. However, experimental investigation (e.g. *Creaser et al. 1991*) showed that such a residue cannot readily generate A-type melts containing high SiO_2 and alkalis contents, and argued that only crustal rocks that have not undergone any previous partial melting can be involved in the formation of A-type granites. *Creaser et al. (1991)* and *Patiño Douce (1997)* suggested that dehydration melting of I-type tonalitic or granodioritic rocks in the crust may generate magma with A-type affinities. As shown in *Figure 11*, partial melts of granodioritic, tonalitic and charnockitic rocks have major element compositions similar to the peraluminous A-type Tobique felsic rocks, including an enrichment in alkalis and a depletion in iron.

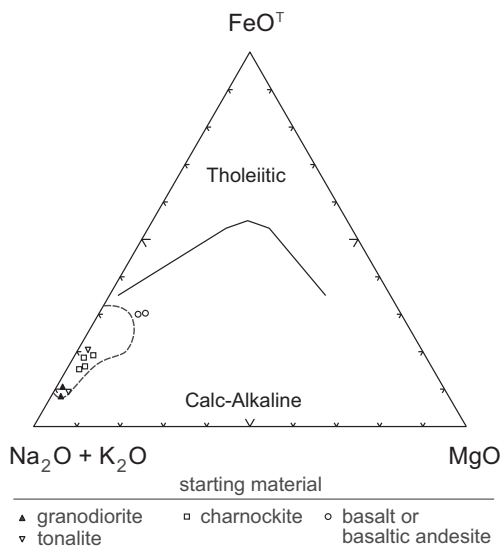


Fig. 11. AFM ($\text{Na}_2\text{O} + \text{K}_2\text{O}-\text{FeO}^{\text{T}}-\text{MgO}$) plot of felsic volcanic rocks of the Tobique Group, with a solid line separating tholeiitic and calc-alkaline fields. The field outlined by the dashed line represents the range of composition observed for the felsic volcanic rocks of the Tobique Group. Experimental melts derived from a variety of crustal rocks in water-undersaturated conditions are shown for comparison (modified after Su *et al.* 2007). Experimental data for granodiorite, tonalite, charnockite, basalt and basaltic andesite are from Patiño Douce (1997), Beard *et al.* (1994) and Beard and Lofgren (1991), respectively.

The high temperatures that are necessary to melt this relatively anhydrous protolith requires underplating of the lithosphere by mantle-derived mafic magma. Magma that sourced the coeval continental tholeiitic basalts, which were derived from spinel-bearing SCLM material (Dostal *et al.* 2016), could have provided the necessary heat. This process is common during lithospheric extension (e.g. Huppert and Sparks 1988).

Distinct depletions of Nb, Ta, Ti, Ba and Sr in felsic rocks compared to the primitive mantle (Fig. 6) also support derivation of the felsic rocks from the melting of continental crust. Nd model ages suggest that this crustal source was composed of late Precambrian rocks (Table 2). A late Precambrian basement was also invoked as the source of Late Silurian–Early Devonian plutons in the Gander Zone of Newfoundland (Kerr *et al.* 1995; Whalen *et al.* 1996), which also have near chondritic Nd isotopic values. A similar origin can be proposed for some Siluro-Devonian granitic plutons in neighbouring areas of central and northern New Brunswick (in the Miramichi Highlands or the Miramichi subzone of Ganderia). These granites have comparable chemical

compositions and are approximately coeval (Whalen *et al.* 2006; Pilote *et al.* 2013; Wilson and Kamo 2016).

Tectonic implications

By the Late Ordovician (Taconic phase 3 of van Staal *et al.* 2009), the main tract of the Iapetus Ocean had closed, and the leading edge of the peri-Gondwanan microcontinent of Ganderia had joined the composite Laurentian margin (Zagorevski *et al.* 2010). Between *c.* 450 and 425 Ma, the leading and trailing edges of Ganderia converged through the NW-dipping subduction of the Tetagouche–Exploits back-arc oceanic crust (Fig. 12a), generating sparse arc magmatic rocks from Maine to Newfoundland (David and Gariépy 1990; Moench and Aleinikoff 2002; Whalen *et al.* 2006; Wilson *et al.* 2008). Final closure of this back-arc basin is responsible for the *c.* 425 Ma Salinic orogenesis (Fig. 12b), which is marked by a widespread unconformity in the northern Appalachians (Wilson and Kamo 2012; Wilson *et al.* 2017). Breakoff of the Tetagouche–Exploits slab is interpreted to have occurred by the early Pridolian, and is recorded by evidence of rapid uplift and extensional collapse (Fig. 12c) which produced S3 extensional deformation in the Brunswick subduction complex (van Staal 1994; van Staal *et al.* 2009; Wilson *et al.* 2017).

Pridolian–lowermost Devonian bimodal volcanic rocks of the Tobique Group (and Dickie Cove Group north of the Rocky Brook–Millstream Fault: Fig. 2) were emplaced in an extensional setting within a post-Salinic successor basin, which forms the upper part of the MCS (Fig. 12d). The age and geographical distribution of these rocks supports an origin that is linked to the breakoff of the Tetagouche–Exploits back-arc slab (van Staal and de Roo 1995; van Staal *et al.* 2009, 2014; Wilson *et al.* 2017), which would have allowed the rise of hot asthenospheric mantle, and which would have triggered melting of the SCLM and lower crust (Fig. 12d). A post-orogenic extensional setting linked to slab breakoff is also consistent with associated felsic melts that plot as A2-types with some minor overlap into the slab failure field (Fig. 7).

The $\epsilon_{\text{Nd}}(t)$ values of the Tobique basalts (Table 2) imply that the source of the mafic rocks was Neoproterozoic SCLM material (Dostal *et al.* 2016) that was enriched between 1.0 and 0.6 Ga, probably during ancient Neoproterozoic subduction. There are no indications of the presence of juvenile asthenospheric mantle material at the source of the uppermost Silurian–Lower Devonian basalts in northern New Brunswick, suggesting that extensional rifting did not produce replacement of the old SCLM by juvenile asthenospheric material and that the rifting

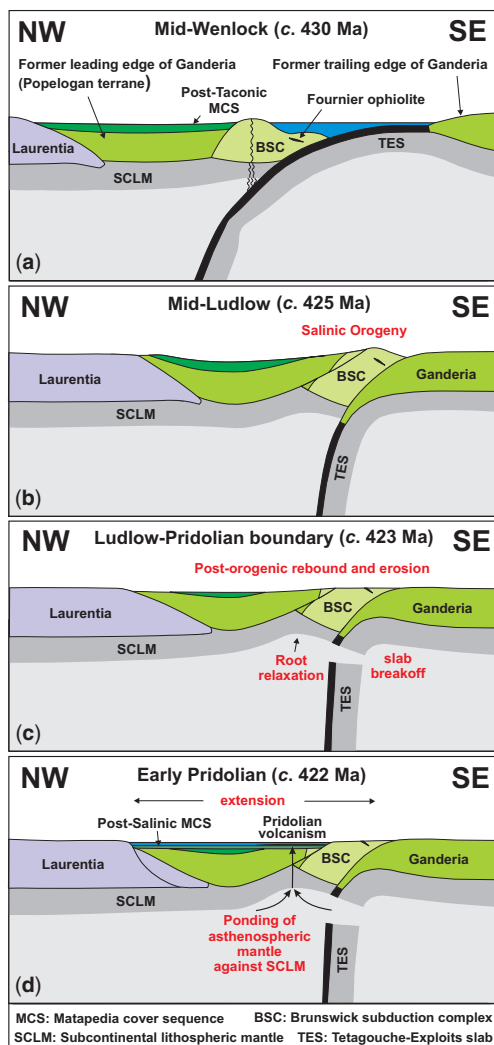


Fig. 12. Tectonic model for the Silurian evolution of Ganderia. (a) Gradual closure of the Tetagouche–Exploits back-arc basin and formation of the Brunswick subduction complex. (b) Final closure of the Tetagouche–Exploits back-arc basin and peak Salinic deformation. (c) Slab breakoff and post-orogenic uplift and erosion. (d) Initiation of extensional volcanism in the post-Salinic upper part of the Matapedia cover sequence by asthenospheric ponding below the uplifted root of the Salinic Orogen.

was of limited extent. The range of $\varepsilon_{\text{Nd}}(t)$ in the Tobique basaltic rocks (Table 2) overlaps that of the uppermost Silurian–Lower Devonian mafic lavas in Avalonia (Fig. 10), suggesting that both Ganderia and Avalonia are underlain by a similar Neoproterozoic SCLM. Likewise, Nd isotopic data for some Late Silurian–Early Devonian granitic

and felsic volcanic rocks from other parts of Ganderia (e.g. Whalen *et al.* 1994, 1996) are similar to comparable rocks of Avalonia (Fig. 10), implying that even the lower crust was similar in these two terranes. This is consistent with models in which Avalonia and Ganderia share a similar Neoproterozoic history and an origin as continental blocks subsequently rifted off from the same region of Gondwana (Amazonia) (e.g. van Staal *et al.* 2012; Waldron *et al.* 2014).

Conclusions

The felsic volcanic rocks of the uppermost Silurian–Lower Devonian bimodal suite of the Tobique Group in northern New Brunswick are part of the Matapedia overstep sequence deposited across accreted vestiges of the Iapetus Ocean on Laurentia. The felsic rocks are peraluminous and possess geochemical characteristics of A2-type granites. They have high contents of alkalis but low abundances of CaO, MgO and FeO^{T} . Their primitive-mantle-normalized patterns show an enrichment in some large ion lithophile elements, and a strong depletion in Ba, Sr, Eu, Ti, Nb and Ta. The rocks were produced by dehydration melting of older felsic rocks of the lower or middle crust, triggered by heat from a rising mafic magma. The geological and geochemical characteristics of these rocks are consistent with their emplacement in a post-collisional extensional setting. The rapid transition from compressional to extensional magmatism in uppermost Silurian–Lower Devonian times in this part of Ganderia is probably due to Late Silurian Ganderia–Laurentia collision followed by slab breakoff. Based on their Sm–Nd isotopic characteristics and the similarity of their felsic rocks, it appears that both Ganderia and Avalonia are underlain by similar lower crust and Neoproterozoic SCLM.

Acknowledgements We thank Drs. Chris Hepburn, Joe Whalen and Brendan Murphy for constructive reviews that significantly improved the manuscript.

Funding This research was supported by NSERC (Canada) Discovery grants to J. Dostal and P. Jutras, and by the New Brunswick Department of Energy and Resource Development, Geological Surveys Branch.

Author contributions JD: investigation (equal), writing – original draft (lead); RAW: investigation (equal), writing – review & editing (equal); PJ: investigation (equal), writing – review & editing (equal).

Data availability statement All data generated or analysed during this study are included in this published article.

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