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THE PHOSPHORUS-ENRICHED, S-TYPE MIDDLE RIVER RHYOLITE, TETAGOUCHE GROUP, NORTHEASTERN NEW BRUNSWICK

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ABSTRACT

In the Middle River area of the Bathurst Mining Camp, northern New Brunswick, lenses of flow-banded rhyolite are underlain by middle Ordovician sedimentary rocks of the Miramichi Group, and overlain by shales and wackes of the Tetagouche Group. The least-altered rhyolites have microscopic spherulites in which the alkali feldspar contains up to 0.32 wt.% P_2O_5 (berlinite substitution). These high-silica rhyolites are peraluminous ($1.1 < ASI < 1.4$) with very low TiO_2 (0.043 to 0.053 wt.%), Zr (36 to 42 ppm), Th (1.5 to 2.4 ppm), Y (9 to 14 ppm), Nb (12 to 14 ppm), V (<1 to 3 ppm), Sc (2 to 3 ppm), and rare-earth elements (ΣREE between 16 and 19 ppm), but have elevated P_2O_5 contents (0.2 and 0.3 wt.%). Their high Nb/Y (>0.7), Ta/Yb (>4.3), Nb/Ta (<6) and Rb (>200 ppm) values indicate an S-type parentage, which is consistent with the high $\delta^{18}O$ value (13.4 to 15.4‰) for three least-altered samples of rhyolite. The felsic magma is interpreted as a product of fusion of supracrustal rocks, associated with heat advection from intruding continental backarc mafic magmas; the magma then underwent low-temperature fractionation of Fe–Ti oxides, zircon and apatite.

Keywords: S-type rhyolite, high-silica rhyolite, phosphorus enrichment, Tetagouche Group, Bathurst Mining Camp, New Brunswick.

SOMMAIRE

Des lentilles of rhyolite à texture due à l'épanchement ont été découvertes dans la région de Middle River, dans le camp minier de Bathurst, dans le nord du Nouveau-Brunswick; ces coulées recouvrent un socle de roches sédimentaires d'âge ordovicien moyen du Groupe de Miramichi, et sont recouvertes de shales et de wackes du Groupe de Tetagouche. Les rhyolites les moins altérées contiennent des sphérulites microscopiques riches en feldspath alcalin contenant jusqu'à 0.32% de P_2O_5 par poids, le phosphore y étant incorporé selon la substitution dite "berlinite". Ces roches à teneur élevée en silice sont hyperalumineuses ($1.1 < ASI < 1.4$), avec des teneurs très faibles en Ti (0.043 à 0.053% par poids de TiO_2), Zr (36 à 42 ppm), Th (1.5 à 2.4 ppm), Y (9 à 14 ppm), Nb (12 à 14 ppm), V (<1 à 3 ppm), Sc (2 à 3 ppm), et en terres rares (ΣTR entre 16 et 19 ppm), mais elles montrent une teneur élevée en P (P_2O_5 entre 0.2 et 0.3% par poids). La valeur élevée des rapports Nb/Y (>0.7), Ta/Yb (>4.3), et Nb/Ta (<6), et la teneur élevée en Rb (>200 ppm), font penser à un antécédant métasédimentaire, ce qui concorde avec les valeurs élevées en $\delta^{18}O$ (entre 13.4 et 15.4‰) de trois échantillons relativement frais. Ces rhyolites représenteraient les produits de la fusion partielle de roches supracrustales, cette fusion étant attribuable à l'apport de chaleur associé avec la mise en place de magmas mafiques dans un milieu d'arrière-arc; le magma semble avoir ensuite évolué par fractionnement d'oxydes de Fe–Ti, zircon et apatite à faible température.

(Traduit par la Rédaction)

Mots-clés: rhyolite de type S, rhyolite siliceuse, enrichissement en phosphore, Groupe de Tetagouche, camp minier de Bathurst, Nouveau-Brunswick.

INTRODUCTION

Lenses of rhyolite occur at three places at the contact between middle Ordovician mature carbonaceous sedimentary rocks of the Patrick Brook Formation (Miramichi Group) and the immature carbonaceous sedimentary rocks of the Boucher Brook Formation (Tetagouche Group), along the autochthonous eastern margin of the Bathurst Mining Camp, northern New Brunswick (Figs. 1, 2; Lentz *et al.* 1996). The host sedimentary sequence, interpreted as distal turbidites (Patrick Brook Formation), is transitional upward into a starved ocean-basin environment with minor volcanic input (Boucher Brook Formation; Lentz *et al.* 1996). This submarine bimodal volcanosedimentary sequence (Tetagouche Group) formed along the rifted eastern

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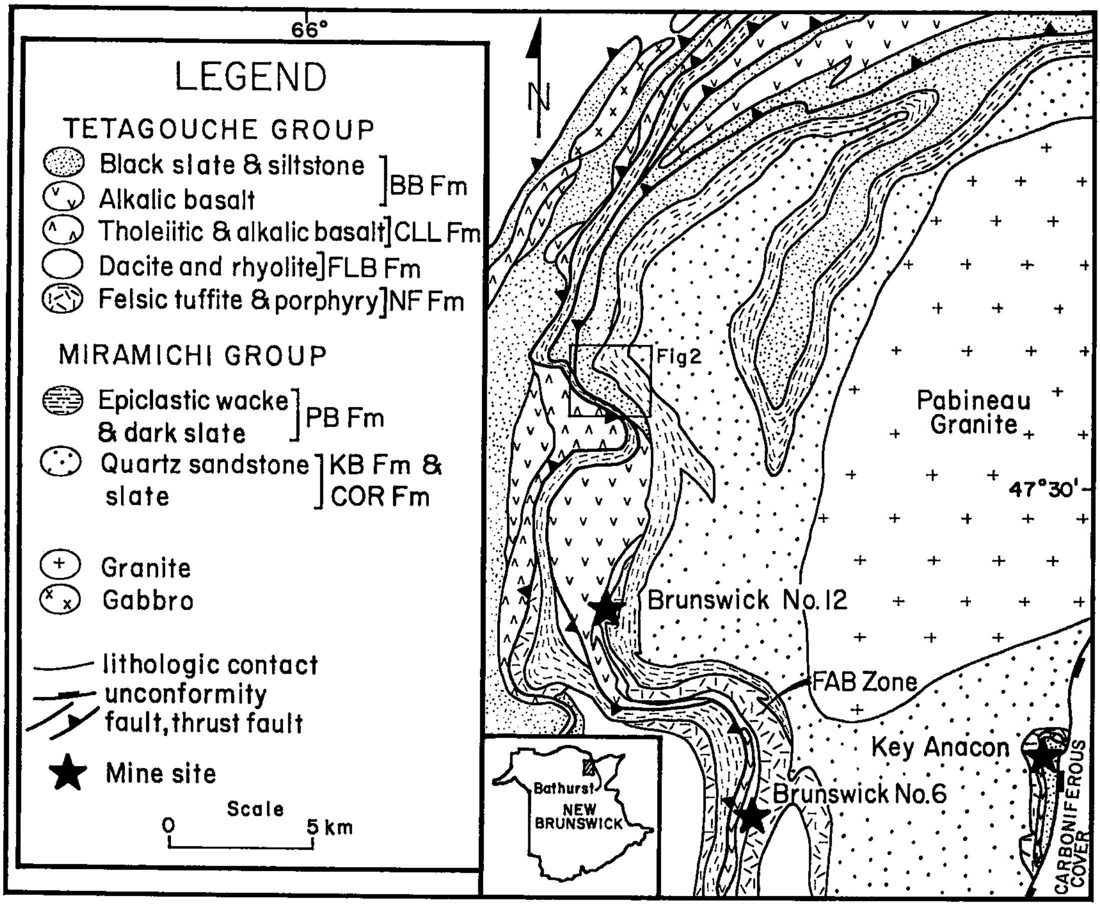


FIG. 1. Geology of the northeastern part of the Bathurst Mining Camp (after van Staal *et al.* 1991). This study area (inset Fig. 2) is shown with respect to the Brunswick No. 6 and 12 and Key Anacon massive sulfide deposits, New Brunswick.

continental margin of an evolving backarc-basin system (Iapetus II: van Staal 1987, van Staal *et al.* 1991, van Staal & Fyffe 1995). Interestingly, the rhyolite in these lenses has a preliminary U–Pb zircon age (≈ 480 Ma; Lentz & McNicoll, in prep.) that seems to be slightly older than the oldest known felsic volcanic rocks (472 to 476 Ma) in the Tetagouche Group (Sullivan & van Staal 1996, Rogers *et al.* 1997). Therefore, this rhyolite may represent the first episode of magmatism in the inner protoarc–backarc system. Although considerable deformation occurred during the early stages of the Acadian Orogeny, with coincident middle-greenschist-facies metamorphism in this part of the camp, there are low-strain windows that permit interpretation of primary volcanic and sedimentary features. These distinctive lenses of rhyolites were re-examined and re-analyzed to enhance stratigraphic correlations along the Brunswick Belt, examine the limitations of some trace-element discrimination techniques, and determine their petrogenetic significance.

Description of Rhyolite Lenses and Their Stratigraphic Setting

In all three lenses, the rhyolite has a prominent flow-foliation (Figs. 3, 4a) oriented perpendicular to the inferred contacts and cut by several synvolcanic dikes. Pebble to cobble conglomerate of the Patrick Brook Formation occurs discontinuously along its base. Coarse rhyolitic breccia and finer-grained fragmental rhyolite (Fig. 4b), along with minor clasts of massive sulfide, are interlayered with shale above the rhyolite (Lentz *et al.* 1996).

The regional geological map of van Staal (1995) indicates the presence of two different and parallel rhyolite units in this area: 1) rhyolite interpreted as part of the Flat Landing Brook Formation to the east, and 2) rhyolite interpreted as part of the Boucher Brook Formation to the west. However, remapping of this area by the staff of Teck Exploration Limited (Moore 1993) indicates that (1) the two rhyolite units are, in fact, lenses of the same unit, and

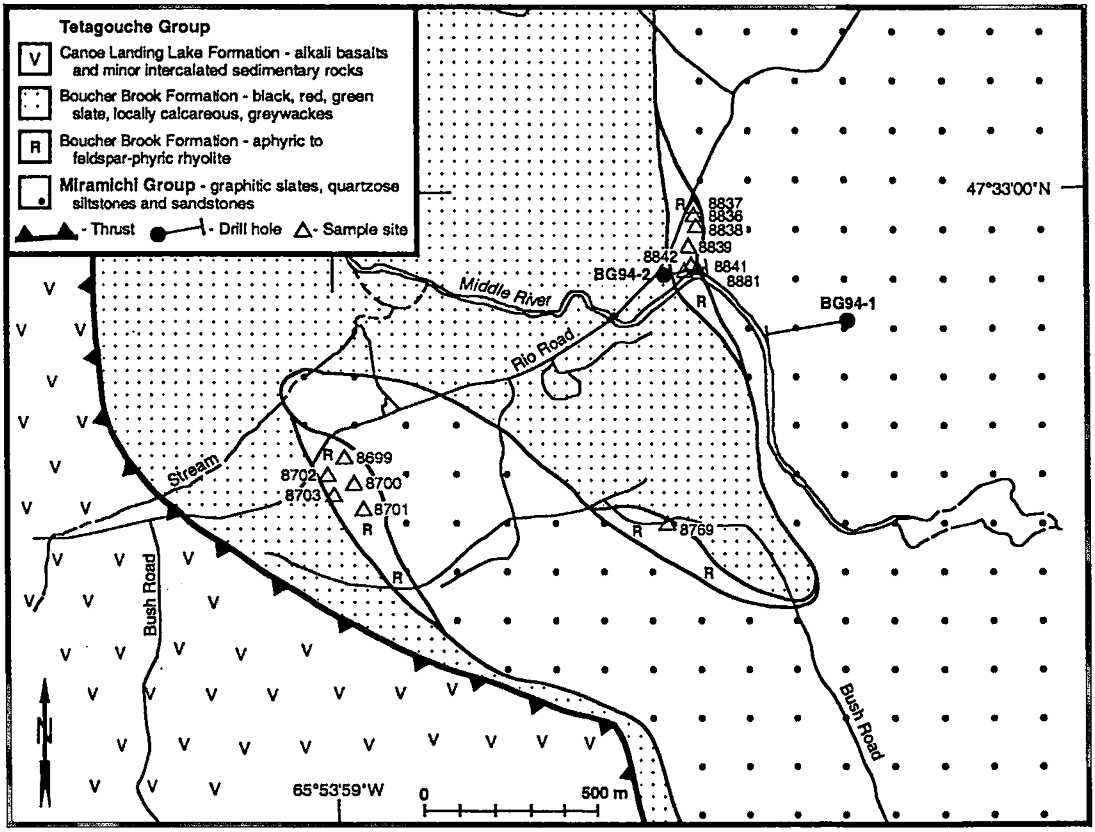


FIG. 2. Local geology of the study area (after Moore 1993), with the location of two drill holes (BG94-1 and 2). Also shown are Teck's original sample numbers (see Table 1).

(2) a third lens occurs between the two, which indicates that it is probably folded by F_2 (Fig. 2). Chemical data presented by Moore (1993) indicate that these felsic rocks are unique in the Bathurst Mining Camp, owing to their extremely low contents of high-field-strength elements (*HFSE*) and moderately high P content.

PETROGRAPHY

Like many other felsic volcanic rocks in the Tetagouche Group, the Middle River rhyolite lenses exhibit variable degrees of seawater-induced alteration and development of a tectonic fabric, which are both evident in the eastern and central lenses. However, the western lens is, for the most part, very minimally altered, with negligible development of a fabric on the basis of mesoscopic and petrographic observations. Very small alkali feldspar spherulites (<0.5 mm, Table 1) form most of the rhyolite, with only minor sericitic and possibly chloritic alteration evident in the groundmass, whereas the flow layers are marked by partially to completely recrystallized spherulites forming a mottled quartz–feldspar intergrowth (Figs. 5, 6a, b). Some of the spherulites have nucleated on pre-existing feldspar phenocrysts (Fig. 6b, Table 1), whereas others formed on other spherulites. The small size of the spherulites reflects devitrification-induced crystallization at very high degrees of undercooling (Lofgren 1971).

The compositions of spherulitic intergrowths of feldspar were determined by electron-microprobe analysis (Table 1). The nuclei to some spherulites are albite phenocrysts (or xenocrysts), and in some cases, the spherulitic alkali feldspar has a notable enrichment in phosphorus. Table 1 presents a compositional profile of one of the well-developed examples (sample points 1 to 10, Fig. 6b). The P contents generally increase from the core to the margin of the spherulite (0.03 to 0.32 wt.% P_2O_5), whereas the albite core contains no detectable phosphorus; the levels of phosphorus are generally lower than those present from other moderate- to high-P rhyolites and granites (London *et al.* 1990, London 1992a, Kontak *et al.* 1996).

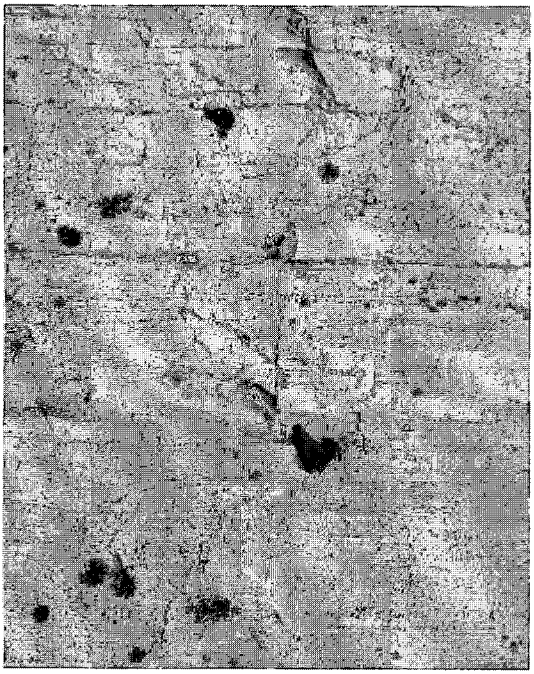


FIG. 3. Pronounced flow-induced foliation (differential weathered surface) in rhyolite, western lens, Middle River. Width of field of view: 7 cm.

GEOCHEMICAL CHARACTERIZATION

Sampling and analytical considerations

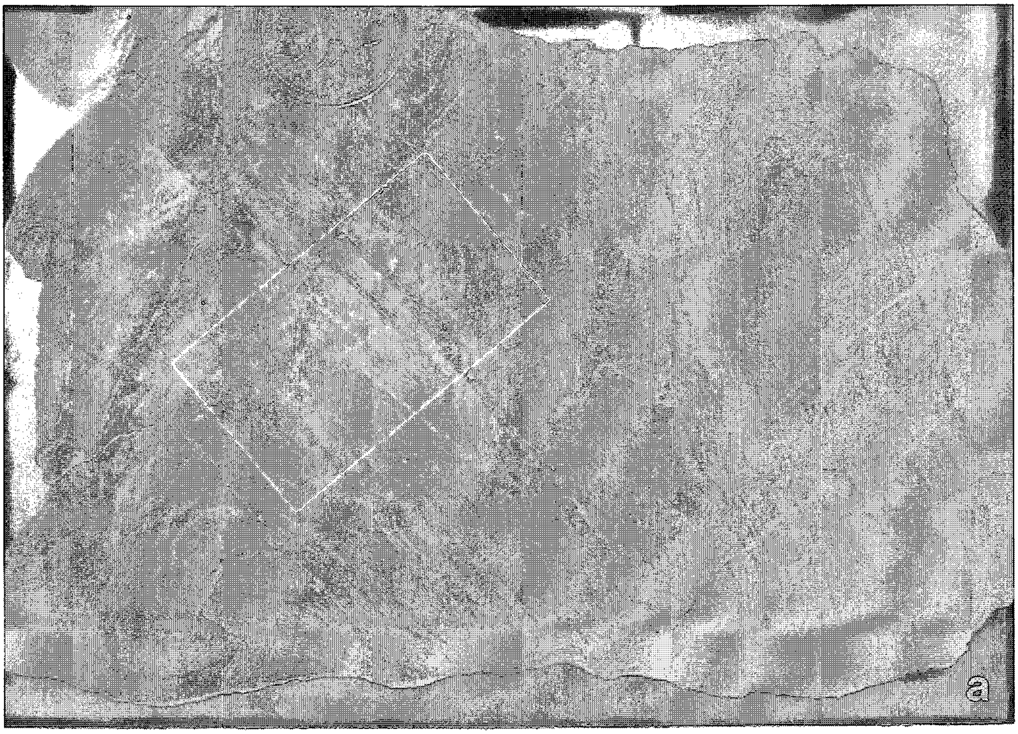
Thirteen samples from the three rhyolite lenses, which are inferred to represent a folded single horizon (Fig. 2), were crushed and then pulverized in a chrome steel swing mill. These samples were analyzed with a Philips 2400 X-Ray Fluorescence (XRF) Spectrometer using fused disks at the geochemical laboratory of the University of Ottawa (major elements and selected trace elements; Table 2). All samples also were analyzed by neutron activation at X-Ray Assay Laboratories, Don Mills, Ontario. Based on the 94–RHY–1 in-house standard (Lentz 1995), concentrations of major elements are quoted with less than a 2% error; with most trace elements, the error is less than 10%, although several very-low-abundance trace elements have slightly higher errors. The rare-earth elements (*REE*) are close to their practical limits of detection (6σ times analytical detection limit). Neutron-activation-derived trace-element data were used in preference to the equivalent XRF data.

The oxygen isotope values were determined on the three least-altered samples of rhyolite from the west lens using an Optima mass spectrometer at the University of Western Ontario. Precision and accuracy are judged to be approximately ±0.2‰.

TABLE 1. FELDSPAR COMPOSITIONS FROM A SPHERULITE IN THE WEST LENS OF THE MIDDLE RIVER RHYOLITE, BATHURST, NEW BRUNSWICK

	Center									Edge
Spot	1	2	3	4	5	6	7	8	9	10
SiO_2	69.12	66.33	65.62	65.57	65.96	66.03	65.40	65.26	65.02	65.61
Al_2O_3	19.53	18.63	18.83	18.58	18.54	18.46	18.44	18.40	18.34	18.53
Fe_2O_3	0.04	0.04	0.04	0.00	0.04	0.14	0.01	0.01	0.00	0.00
BaO	0.00	0.06	0.07	0.08	0.16	0.08	0.04	0.11	0.05	0.00
CaO	0.04	0.01	0.00	0.00	0.03	0.11	0.28	0.36	0.32	0.10
SrO	0.00	0.00	0.01	0.02	0.03	0.00	0.13	0.04	0.01	0.00
Na_2O	11.32	2.48	1.02	0.21	0.24	0.22	0.22	0.20	0.21	0.23
K_2O	1.14	12.93	15.07	16.14	16.08	15.97	16.06	16.06	16.12	16.10
P_2O_5	0.00	0.03	0.12	0.04	0.09	0.11	0.20	0.32	0.31	0.12
SUM	101.2	100.5	100.8	100.6	101.2	101.1	100.78	100.8	100.4	100.7
Si	2.996	3.008	2.992	3.004	3.006	3.008	2.995	2.990	2.990	3.002
Al	0.998	0.996	1.012	1.004	0.996	0.991	0.995	0.994	0.994	0.999
Fe3+	0.001	0.001	0.001	0.000	0.001	0.004	0.000	0.000	0.000	0.000
Ba	0.000	0.001	0.001	0.001	0.003	0.002	0.002	0.002	0.001	0.000
Ca	0.002	0.001	0.000	0.000	0.002	0.005	0.014	0.018	0.016	0.004
Sr	0.000	0.000	0.000	0.000	0.001	0.000	0.003	0.001	0.000	0.000
Na	0.951	0.217	0.090	0.019	0.022	0.020	0.020	0.018	0.018	0.062
K	0.063	0.748	0.877	0.944	0.935	0.928	0.938	0.938	0.946	0.940
P	0.000	0.001	0.004	0.001	0.003	0.004	0.008	0.012	0.012	0.005
O	8	8	8	8	8	8	8	8	8	8

NOTES: See figure 6B for microprobe traverse (sample 96-DL-14A). Chemical analyses were obtained by Dr. Douglas Hall using the JEOL 733 microprobe at the University of New Brunswick with an accelerating voltage of 15 kV and 5 nA current and a beam diameter of 5 μm. The analytical limits (3.3 * √ background counts) for the low abundance elements are: CaO - 0.03 wt.%, Fe - 0.06 wt.%, Sr - 0.06 wt.%, Ba - 0.03 wt.%, and P - 0.03 wt.%.



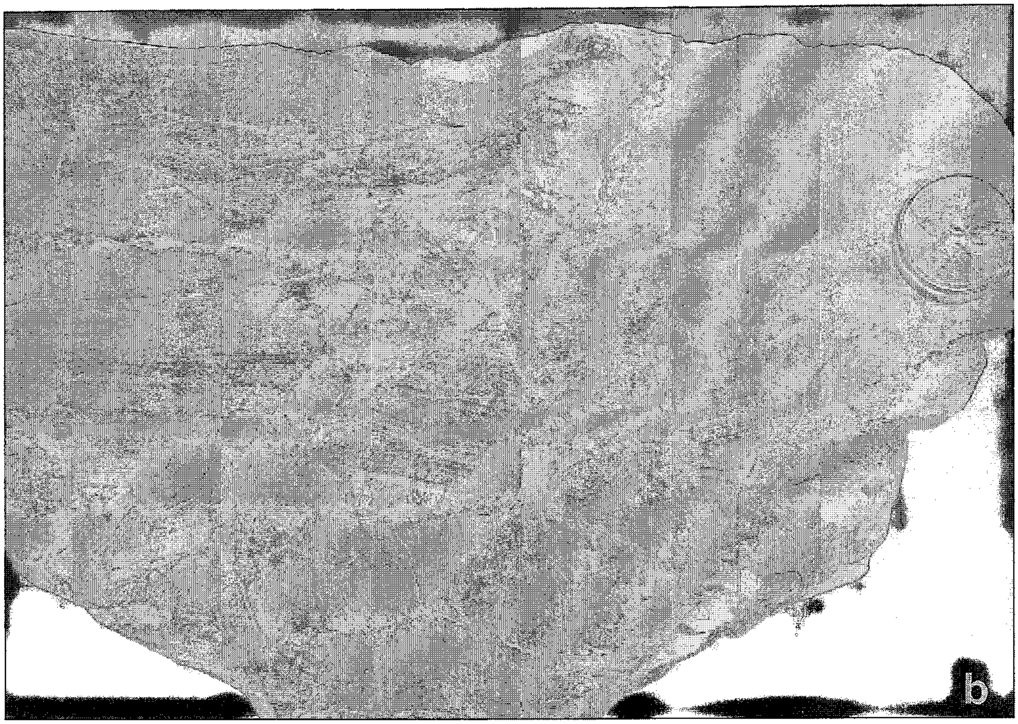


FIG. 4. a) Refolded folds in flow-banded rhyolite, west lens, Middle River (sample 96–DL–14A). The location of the thin section is outlined. b) Brecciated flow-banded rhyolite, west lens, Middle River (sample 96–DL–14B).

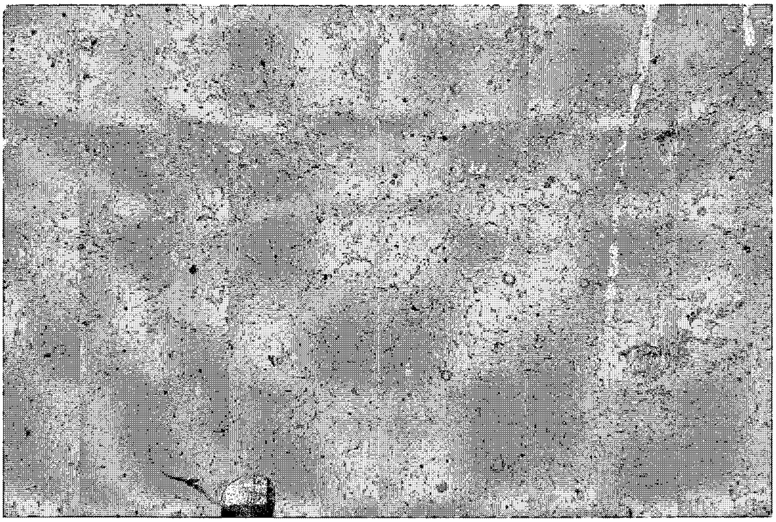


FIG. 5. Photomicrograph of flow-banded rhyolite (sample 96–DL–14) with alternating light yellow (spherulitic) and medium beige layers (recrystallized spherulites and mottled feldspar, *i.e.*, no micas) from left margin (Fig. 4) of thin section, western lens, Middle River. Plane-polarized light; the field of view is 5 mm.

Geochemical data

As previously indicated, the rhyolite from the east and central lenses is moderately altered, whereas that in the western lens is only very weakly altered; therefore, data from the western rhyolite lens are emphasized. Data on the other lenses will also be used, to enhance the overall geochemical interpretation, with the effects of alteration being taken into account.

The least-altered samples of rhyolite typically have high silica and alkali contents and a low Ca content (Fig. 7, Table 1), although considerable mobility of alkalis and silica is associated with sericitization and albitization, particularly in the eastern exposure (Lentz *et al.* 1996). The aluminum saturation index [ASI = $Al_2O_3/(CaO + Na_2O + K_2O)$] of the least-altered samples of Middle River rhyolite ranges between 1.1 and 1.4 (Fig. 8), with the higher values enhanced by weak sericitic alteration. The antipathetic variations between Al_2O_3 and SiO_2 (Fig. 9a) are too large to be related to magma fractionation, but instead reflect mass changes owing to hydrothermal alteration in the form of sericitization, albitization and silicification (Al dilution) (Leitch & Lentz 1994). This is accompanied by considerable Na–K exchange, probably due to seawater-induced alteration and devitrification reactions. The least-altered rocks have 13 to 15 wt.% Al_2O_3 and approximately equal concentrations of Na_2O and K_2O, as do other least-altered felsic volcanic rocks in the Bathurst Camp. Sericitization is particularly evident in rocks rich in Al (Fig. 9b), whereas high levels of Ca reflects carbonatization that is associated with silicification. The Fe_2O_3 (total), MgO, and MnO contents are typically less than 1.0, 0.5, and 0.05 wt.%, respectively, although higher values relating to alteration also occur (Table 2).

The minor- and trace-element contents of the rhyolite are particularly noteworthy; Cs, Rb and Sr contents are higher, and Ba content is lower, in the least-altered Middle River rhyolite than in other felsic volcanic rocks in the Bathurst Camp, although these elements were certainly somewhat mobile during seawater-induced alteration. Levels of TiO_2 (0.03 to 0.06 wt.%), Zr (30 to 52 ppm), Y (9 to 14 ppm), Nb (9 to 16 ppm), and V (1 to 8 ppm) are low, but P_2O_5 content (0.16 and 0.34 wt.%) is high compared to the other felsic volcanic rocks in the camp (0.03 to 0.18 wt.%; Lentz 1996b). The strong covariation between Al_2O_3 and TiO_2, Zr, Nb, and Ga (Figs. 9c, d, e, f) indicates that they also were relatively immobile during alteration. Though yttrium generally is considered an immobile element, its concentration is variable.

Immobile-element ratios are not sensitive to mass-change effects and, therefore, are most effective in determining compositional affinity and evolution in altered rocks. The Zr/TiO_2 values (0.5 to 0.9) are typical of felsic volcanic rocks of the Bathurst Camp (Fig. 10a), whereas high Nb/Y values (>0.7) cause these rhyolite samples to fall erroneously within the trachyandesite field (Fig. 10b). The low *HFSE* contents of these rhyolites are not typical of alkaline igneous

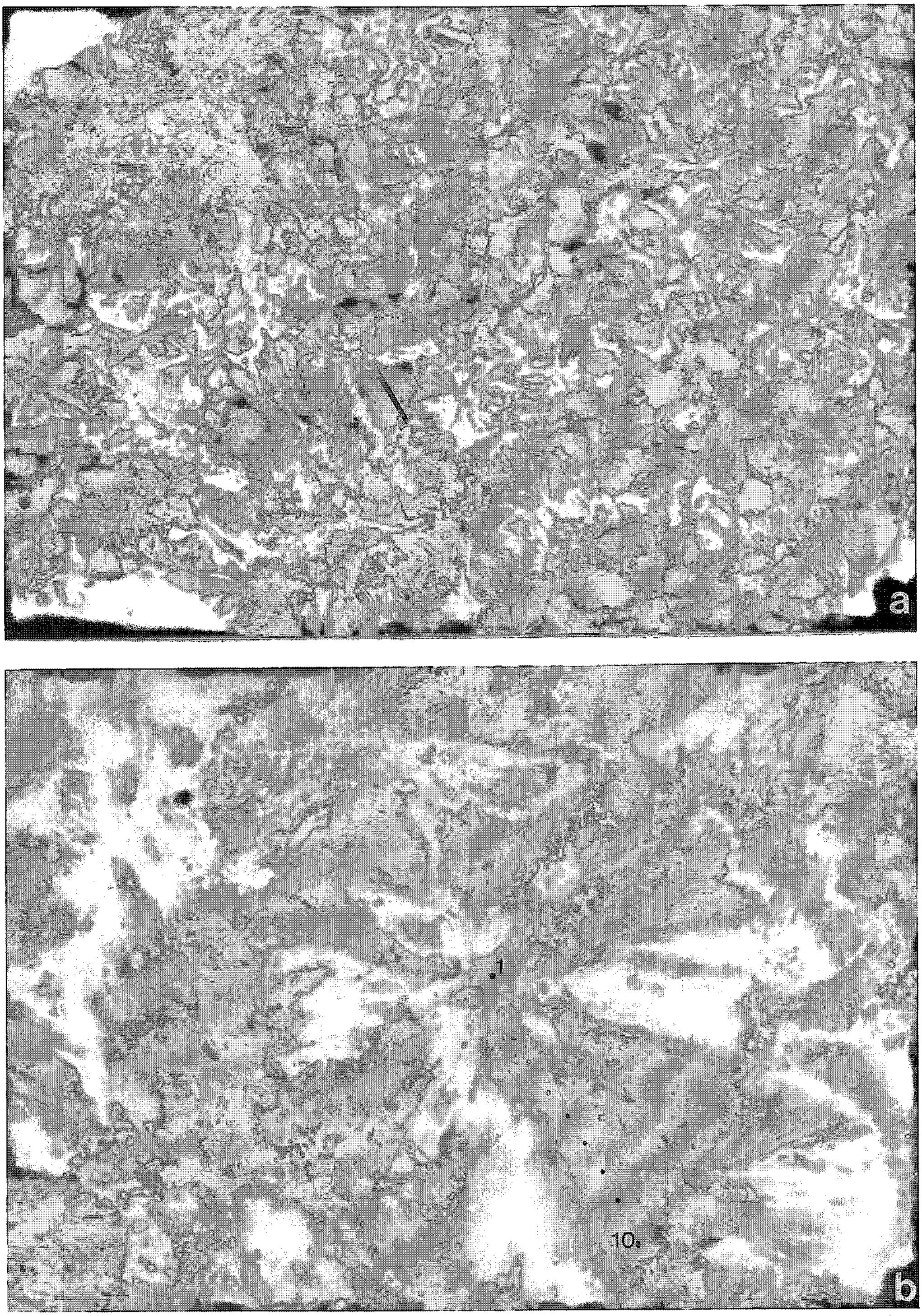


FIG. 6. a) Intergrown spherulites (80 vol.%) from the Middle River rhyolite (sample 96–DL–14A). The line is the microprobe profile of the spherulitic feldspar (Fig. 6b). Crossed-polarized light, field of view is 1.2 mm. b) Spherulitic alkali feldspar with albite nucleus. The points 1 to 10 locate the feldspar compositions presented in Table 1. Crossed-polarized light; field of view is 0.3 mm.

TABLE 2. WHOLE-ROCK GEOCHEMICAL DATA ON THE MIDDLE RIVER RHYOLITE AND A RHYOLITE FROM THE BOUCHER BROOK FORMATION

Sample	8699	8700	8701	8702	8703	8769	8836	8837	8838	8839	8841	8842	8881	BBrhy
Lens	West	West	West	West	West	Mid	East	East	East	East	East	East	East	
wt.%														
SiO_2	76.95	75.19	75.28	74.98	73.39	78.92	70.09	78.63	74.65	69.45	78.89	74.16	78.67	74.00
TiO_2	0.046	0.050	0.048	0.045	0.047	0.044	0.064	0.039	0.051	0.060	0.039	0.039	0.050	0.05
Al_2O_3	12.85	14.19	13.87	13.61	14.21	11.77	18.45	11.20	14.90	18.17	10.10	11.39	9.92	14.24
Fe_2O_3(T)	1.11	0.97	0.96	0.91	0.91	0.51	1.13	0.61	1.44	0.67	0.84	1.84	2.05	0.42
MnO	0.01	0.03	0.01	0.01	0.01	0.01	0.02	0.05	0.09	0.00	0.12	0.14	0.11	0.00
MgO	0.27	0.27	0.34	0.28	0.21	0.37	0.67	0.17	0.61	0.34	0.49	0.56	0.76	0.22
CaO	0.33	0.54	0.36	0.34	0.27	0.50	0.15	1.34	0.40	0.46	2.11	3.39	1.81	0.28
Na_2O	3.86	3.61	4.45	2.21	3.14	4.23	0.13	4.70	0.11	5.19	2.44	0.05	0.02	2.40
K_2O	2.39	2.66	2.26	5.38	5.70	1.58	5.27	0.59	4.11	2.39	1.25	2.58	2.41	7.18
P_2O_5	0.21	0.29	0.26	0.25	0.19	0.26	0.16	0.29	0.30	0.34	0.29	0.23	0.24	0.22
LOI	0.80	1.20	1.10	1.10	0.80	0.70	3.00	1.30	2.60	1.70	2.60	4.70	3.10	0.72
SUM	98.8	99.0	98.9	99.1	98.9	98.9	99.1	98.9	99.3	98.8	99.2	99.1	99.1	99.7
ppm														
Sc*	2.5	2.3	2.5	2.1	2.2	2.0	3.1	1.5	2.7	3.6	1.6	2.0	2.1	4.0
V	4	<1	1	2	1	8	3	2	7	3	1	3	1	18
Pb	43	19	0	0	15	51	13	9	8	69	13	12	0	9
Zn	43	111	31	26	103	81	29	76	119	56	87	104	70	22
As*	33	20	4	2	19	36	11	7	6	52	8	4	6	-
Sb*	1.4	2.6	0.9	1.4	2.6	2.6	3.7	1.8	3.0	5.8	2.9	7.2	3.3	-
Rb	130	150	142	273	272	101	342	39	267	173	82	150	145	290
Cs*	3.2	2.1	2.8	2.7	3.2	4.6	16.5	2.0	12.7	6.3	5.7	8.6	9.7	3.3
Ba	299	240	323	227	246	37	412	64	323	162	65	207	117	309
Sr	112	88	130	60	76	104	37	162	43	136	98	31	31	77
Ta*	2.3	2.5	2.5	2.3	2.3	1.7	3.6	1.5	2.9	3.2	1.6	2.2	1.9	1.7
Nb	15	15	15	16	15	12	19	14	16	19	10	14	12	16
Hf*	1.7	1.6	1.6	1.8	1.8	1.1	2.6	1.5	2.3	2.4	1.2	1.7	1.5	1.7
Zr	37	39	39	37	37	31	52	32	41	48	29	32	30	55
Y	9	12	9	11	9	11	8	11	11	14	12	11	12	14
Ga	22	23	22	20	21	18	30	12	24	35	14	16	15	16
Th*	1.7	2.1	2.1	1.8	2.1	1.4	2.2	1.5	2.3	2.7	1.3	2.0	1.6	2.1
U	6.0	5.9	5.8	5.1	5.9	6.0	7.0	5.8	7.4	10.5	4.3	6.6	6.4	4.0
La*	2.4	4.4	3.6	3.6	3.6	3.1	2.9	3.1	3.0	3.6	3.8	3.2	4.1	4.2
Ce*	5	10	7	8	7	7	7	6	7	7	8	8	9	8.8
Nd*	3	6	5	5	5	4	3	5	5	5	5	5	5	3.2
Sm*	1.08	1.85	1.32	1.41	1.35	1.40	0.96	1.56	1.68	1.82	1.24	1.70	1.67	1.08
Eu*	0.26	0.08	0.29	0.16	<0.05	0.18	0.14	0.18	0.10	0.29	0.03	0.14	0.12	0.05
Gd*	-	-	-	-	-	-	-	-	-	-	-	-	-	1.4
Tb*	0.2	0.3	0.2	0.2	0.2	0.3	0.2	0.3	0.3	0.4	0.2	0.3	0.4	-
Yb*	0.39	0.42	0.40	0.45	0.41	0.39	0.48	0.38	0.52	0.47	0.36	0.50	0.48	0.45
Lu*	0.04	0.05	0.06	0.06	0.06	0.05	0.07	0.05	0.07	0.05	0.05	0.06	0.06	0.08
Zr/TiO_2	0.080	0.078	0.078	0.077	0.082	0.070	0.081	0.082	0.080	0.080	0.074	0.082	0.060	0.110
Zr/Hf	22	24	24	21	21	28	20	21	18	20	24	19	20	32
Zr/Y	4.1	3.3	4.3	3.4	4.1	2.8	6.5	2.9	3.7	3.4	2.4	2.9	2.5	3.9
La/Yb_{CN}	3.9	6.8	5.8	5.2	5.7	5.1	3.9	8.2	3.7	5.0	6.8	4.1	5.5	6.0
Nb/Ta	6.5	6.0	6.0	7.0	6.5	7.1	5.3	9.3	5.5	5.9	6.3	6.4	6.3	9.4
Nb/Y	1.67	1.25	1.67	1.46	1.67	1.10	2.38	1.27	1.46	1.36	0.83	1.27	1.00	1.14

NOTES: Sample denotes Teck Exploration Limited's (TK) sample numbers. * denotes results obtained by instrumental neutron activation analysis, BB rhy denotes "trachy-andesite" sample WS76 (van Staal et al. 1991, data file). Fe_2O_3(T) denotes total Fe as Fe_2O_3. - denotes no analysis.

suites (*e.g.*, comenditic rhyolites), but rather are more typical of S-, I-, or M-type felsic rocks on the basis of Nb–Y systematics (Fig. 10c). The high Ta/Yb value (Fig. 10d) indicates an S-type (syncollisional, Pearce *et al.* 1984) parentage for the rhyolites. Although Rb can be mobile, the Rb content in the least-altered samples is greater than 200 ppm, which also supports an S-type parentage (see Fig. 10d).

The high concentration of Ta results in Nb/Ta values (6.5 ± 1.0, Fig. 11) lower than mantle (ave. 17.5) and most crustal (ave. 11.5) magmatic rocks (Green 1994), but within the range typical of S-type igneous rocks (Taylor 1992). The low Nb relative to Ta may result from compositional inheritance from the source region, presumably sedimentary rocks, or fractionation of Fe–Ti phases or amphibole.

There are fairly well-developed trends evident between TiO_2 and several trace elements (Fig. 12) that were enhanced by metasomatism, but they are also evident in the least-altered material (shaded). Covariation of Zr and Th with TiO_2 (Figs. 12a, b) indicates similar behavior of zircon and the Fe–Ti silicate and oxide phases. Although V usually covaries with TiO_2, its low abundance and possible analytical imprecision

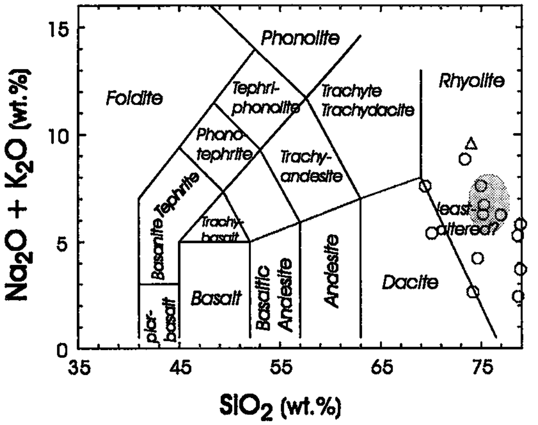


FIG. 7. $Na_2O + K_2O$ *versus* SiO_2 discrimination diagram (Le Maitre *et al.* 1989) illustrating the compositional spectrum of the Middle River rhyolite samples (circle) and the Boucher Brook Formation rhyolite (triangle). Shaded area is field of least-altered samples.

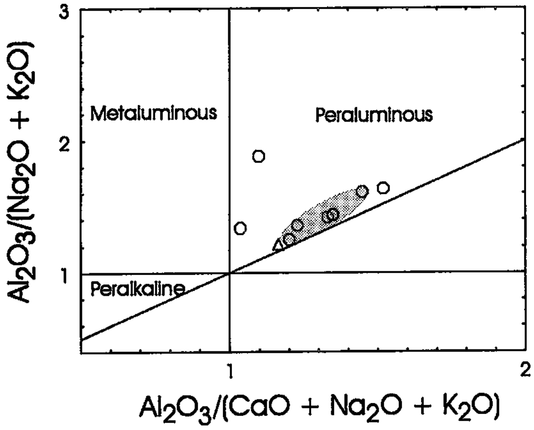


FIG. 8. $Al_2O_3/(CaO + Na_2O + K_2O)$ *versus* $Al_2O_3/(Na_2O + K_2O)$ diagram (Maniar & Piccoli 1989) illustrating the peraluminous compositional spectrum (Table 2) of the Middle River rhyolite samples (circle) and the Boucher Brook Formation rhyolite (triangle). Shaded area is field of least-altered samples.

probably account for the scatter in Figure 12c. Like V, Sc typically substitutes into Fe–Ti oxide and mafic silicate phases, also accounting for the strong covariation with TiO_2 (Fig. 12d). The strong covariation of Nb and Ta with TiO_2 also indicates substitution into Fe–Ti oxide and silicate phases (Green 1994). Trends in the least-altered parts of the arrays could reflect either fractional crystallization or partial fusion.

Compared to the average continental crust (Wedepohl 1995) and relative to other felsic volcanic rocks in the Bathurst Camp, the Middle River rhyolite is depleted in Ba, Th, La, Ce, Sr, Nd, Hf, Zr, Sm, Eu, Ti, Sc, Tb, Y, Yb, and Lu, and enriched in Rb, Ta, and P (Fig. 13). The low levels of Ba and Sr, and high levels of Rb, indicate that the rhyolite is compositionally evolved. Concentrations of the light rare-earth elements (*LREE*) are approximately ten times chondrite, whereas those of the heavy *REE* (*HREE*) are between one and two times chondrite, yielding a *LREE*/*HREE* slope of approximately 5 (Σ*REE* in the range 16 to 19 ppm). The negative Eu anomaly is pronounced, but variable, even in the least-altered samples, which indicates either fractionation of feldspar or very selective partial melting. The *REE* abundances are *ca.* 10 times lower than in typical aphyric rhyolitic rocks of the Bathurst Camp (Lentz 1996b).

The P content of the rhyolite is unusually high (0.16 to 0.34 wt.%, Fig. 14) compared to the felsic volcanic rocks of the Tetagouche Group. The Ca–P trend of the least-altered samples is consistent with fractionation of apatite, although it is evident that some P also is tied up in alkali feldspar (Table 1). The concentration of P is variable relative to Al (Fig. 15a) which, if immobile, indicates preferential removal of P relative to other *HFSE*. The weak anticorrelation of P and K (Fig. 15b) might indicate leaching of P during devitrification and alteration. However, the moderate correlation between P and Y (Fig. 15c) and a weaker correlation between P and La (Fig. 15d) suggest coupled removal of these elements, whose concentration seems to be largely primary.

OXYGEN ISOTOPE SYSTEMATICS

Whole-rock oxygen isotopic values ($\delta^{18}O$) are 14.9‰ (TK8699), 13.4‰ (TK8701), and 15.4‰ (TK8703), all three samples being from the least-altered western lens. Although the fluid–rock reactions seem to be minimal there, the variation in the alkalis could reflect very low-temperature alkali-exchange reactions in feldspars, which can produce large shifts in the oxygen isotopes (Taylor & Sheppard 1986). The preservation of alkali feldspar spherulites and albite nuclei, however, indicates that such exchange was minimal in the samples analyzed. Considering the least-altered nature of these samples, the $\delta^{18}O_{SMOW}$ values are interpreted to reflect primary signatures, with very minor changes due to alteration.

The ^{18}O-enriched signature of these samples is consistent with a derivation by anatectic reactions involving shale (Taylor & Sheppard 1986). The felsic volcanic rocks of the Nepisiguit Falls and Flat Landing Brook formations (Fig. 1) also show an enrichment in ^{18}O (Lentz & Goodfellow 1993, Lentz *et al.* 1997) that is interpreted to originate from partial melting of upper crust sources (Avalonian margin) during backarc rifting (van Staal 1987, van Staal *et al.* 1991, Lentz 1996a, b).

DISCUSSION

Chemostratigraphic significance

The compositional similarities of the three lenses of strikingly flow-banded, aphyric rhyolite at Middle River suggest that they can be correlated. This view contrasts with the interpretation of van Staal (1995). The three lenses occur at the contact between the carbonaceous sedimentary rocks of the Miramichi Group and the Boucher Brook Formation (Tetagouche Group), which is consistent with the position interpreted for the

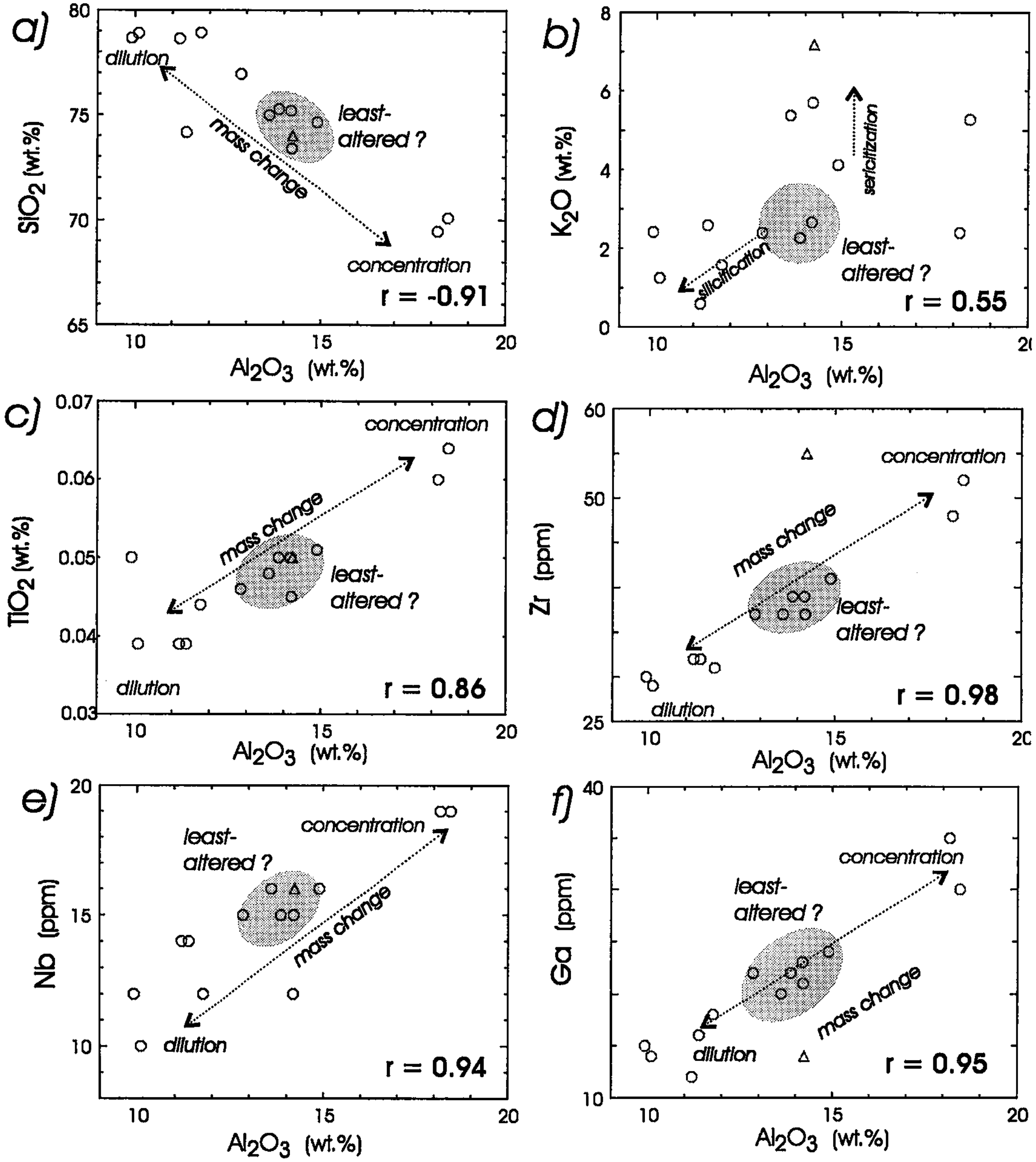


FIG. 9. Al_2O_3 *versus* a) SiO_2, b) K_2O, c) TiO_2, d) Zr, e) Nb, and f) Ga for the Middle River rhyolite (circle) and the Boucher Brook Formation rhyolite (triangle) (Table 2) illustrating the changes in mass associated with the weak to moderate alteration. r: Pearson Product correlation coefficient; r values greater than 0.53 (n = 13) are significant above the 95% confidence level (Le Maitre 1982).

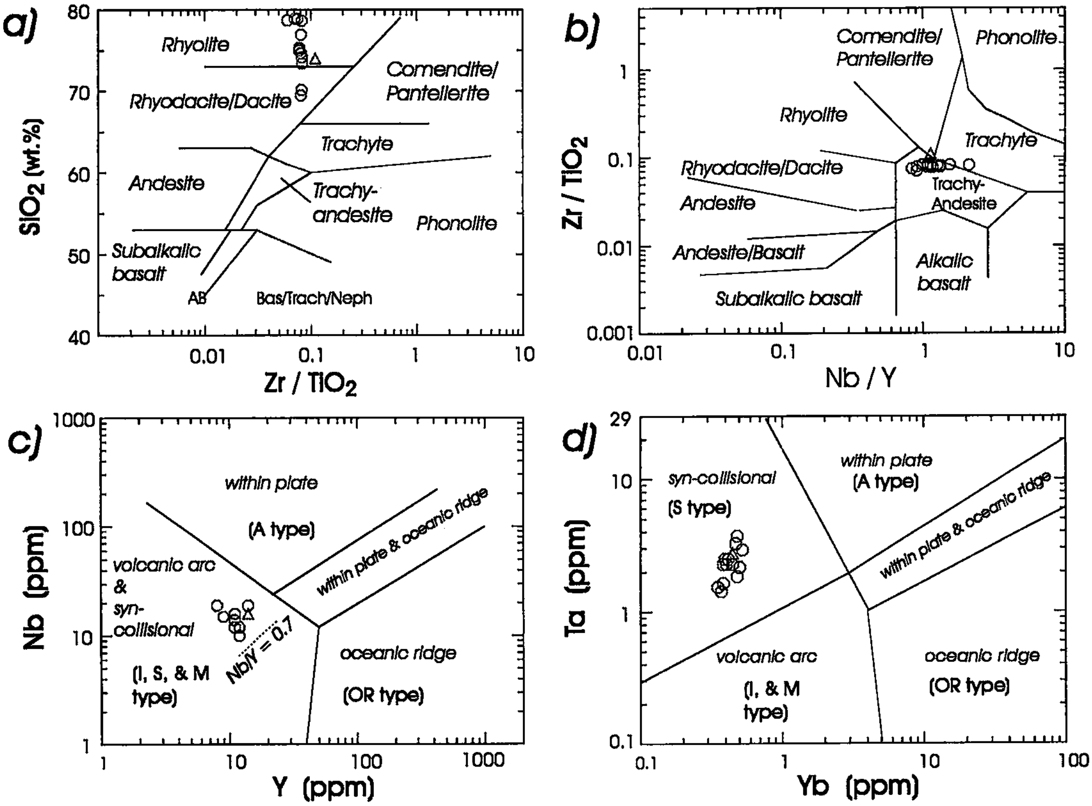


FIG. 10. a) SiO_2 *versus* Zr/TiO_2 and b) Zr/TiO_2 *versus* Nb/Y discrimination diagrams (Winchester & Floyd 1977); c) Nb *versus* Y and d) Ta *versus* Yb tectonic discrimination diagram [after Pearce *et al.* (1984) and modified by Christiansen & Keith (1996)] illustrating the compositional variation (Table 2) and tectonic affinities of the Middle River rhyolite (circles) and Boucher Brook Formation rhyolite (triangles).

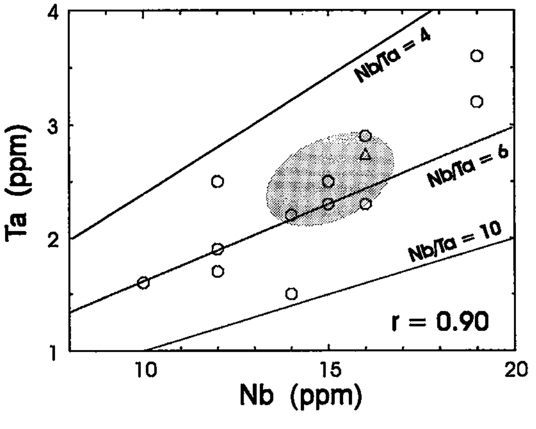


FIG. 11. Nb *versus* Ta diagram illustrating the range in compositions of the Middle River rhyolite and data for the least-altered samples (shaded).

rhyolite on Middle River (Fig. 2, see Lentz *et al.* 1996). However, the Middle River rhyolite is chemically distinct from and possible older than flow-banded aphyric rhyolite of the Flat Landing Brook Formation (Tetagouche Group). Instead, it is compositionally very similar to a rhyolite mistakenly referred to as a comendite on the basis of trace-element compositional discrimination techniques (sample WS76, van Staal *et al.* 1991), located within an alkali basalt sequence (Boucher Brook Formation?) in the Lovalls Lake Antiform, a few kilometers to the west of the area covered by Figure 2 (see Lentz & van Staal 1995), and two porphyritic dikes at the top of the Flat Landing Brook Formation, to the north of Brunswick No. 12. (Lentz 1996a). The very low Y content of sample WS76 (Lentz & van Staal 1995) results in a Nb/Y value greater than 1, thus an "apparent" alkaline affinity in Figure 10c. However, neither this sample (WS76) nor the Middle River suite have characteristics expected of an alkaline felsic rock; on the contrary, they are

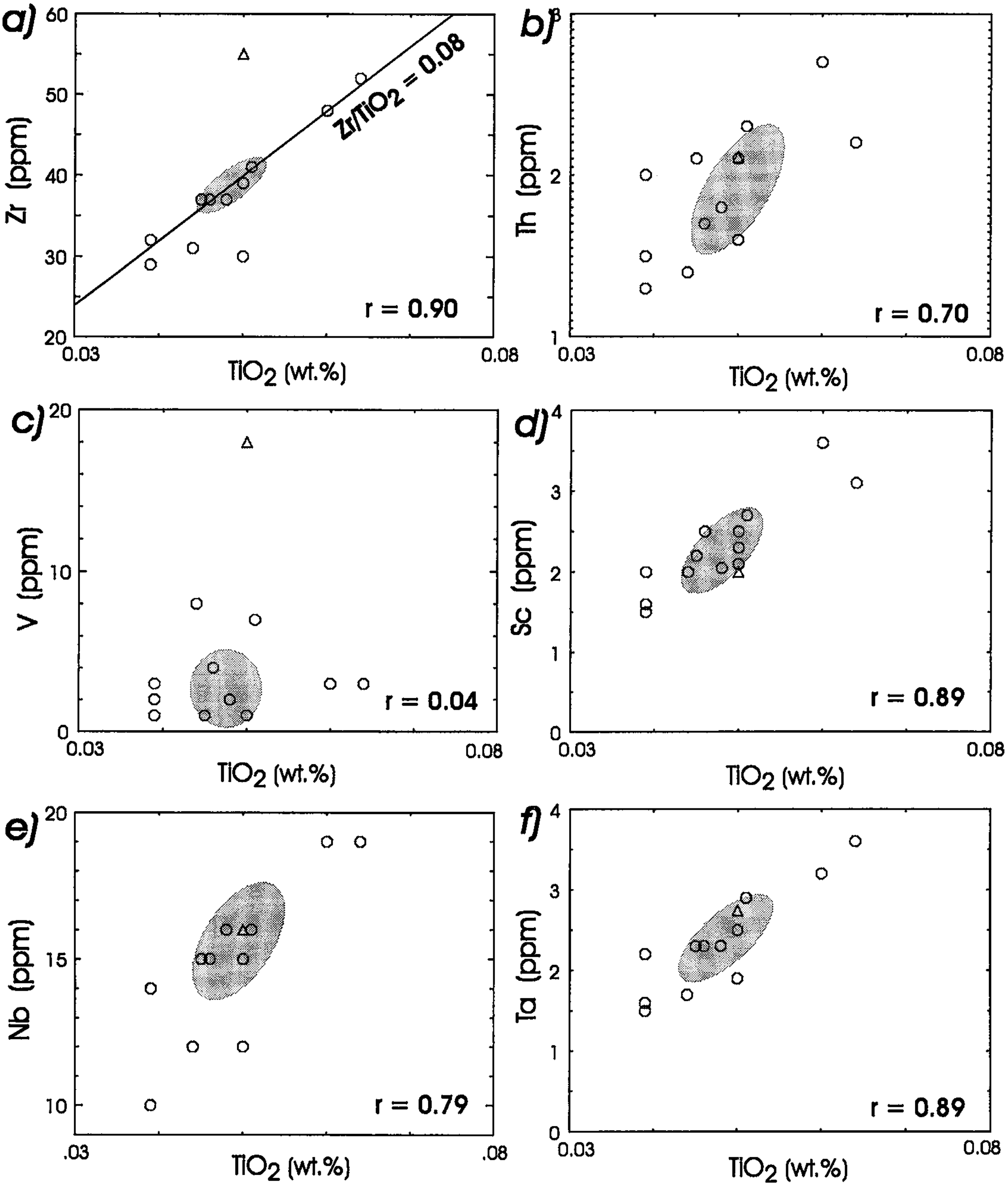


FIG. 12. TiO_2 *versus* a) Zr, b) Th, c) V, d) Sc, e) Nb, and f) Ta diagrams illustrating the range of compositions of the Middle River rhyolite and data for the least-altered samples (shaded).

subalkaline, peraluminous, phosphorus-enriched, high-silica alkali rhyolites with anomalously low levels of Y and *HREE*. To the south, however, these low-*HFSE*, P-enriched, high-silica rhyolites have not been identified in the Brunswick alkali basalt – comendite suite (J. Carroll, Noranda Exploration and Mining Limited, pers. comm.). The low-*HFSE* and moderate-P contents of the Middle River rhyolite and related Lovall's Lake rhyolite are, at present, unique geochemical features in the Bathurst Camp.

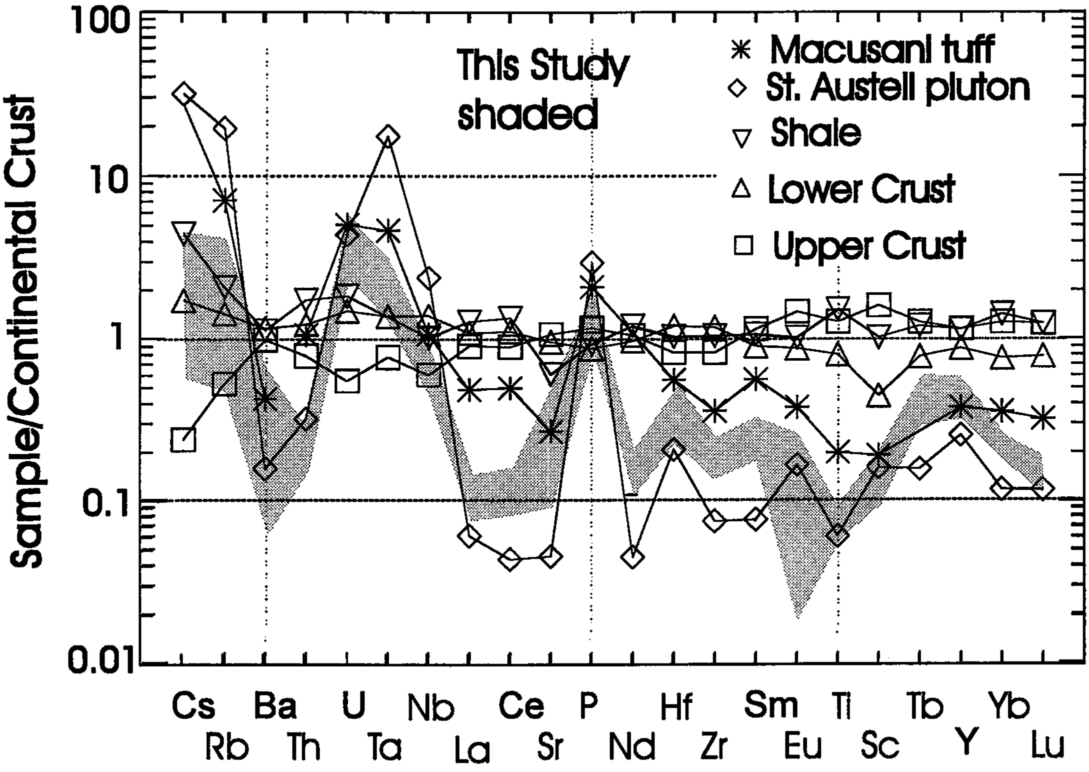


FIG. 13. Continental-crust-normalized (Wedepohl 1995) extended trace-element spider diagram illustrating the compositional similarities between the Middle River rhyolite (Table 2), a rhyolite sample from the Boucher Brook Formation (BB; this study) with the two other high-P felsic rocks, the Macusani tuff (Pichavant *et al.* 1987) and the St. Austell granite (Manning & Hill 1990, Taylor 1992), and an average shale composition (Taylor & McLennan 1985).

Crystal-chemical considerations

In many cases examined (London *et al.* 1990, London 1992a, Kontak *et al.* 1996), it is probable that the coupled P + Al for 2Si substitution in feldspar (berlinite substitution, Simpson 1977) represents a primary feature. Here, the P contents increase in the spherulitic alkali feldspar from core to rim. Considering that spherulites form by diffusion-limited growth at high degrees of undercooling (Lofgren 1971, Fenn 1977, MacLellan & Trembath 1991), the P + Al = 2Si substitution in the spherulitic feldspar may simply represent metastable or disequilibrium partitioning (*cf.* Fowler *et al.* 1987) resulting from very slow diffusion of these highly charged cations or complex polymers at the crystal–glass interface during devitrification.

Petrogenetic considerations

It is generally accepted that extreme fractional crystallization of a subalkaline felsic magma can profoundly change the compatibility of both large-ion – lithophile elements (*LILE*) and *HFSE* elements (Mahood & Hildreth 1983, Michael 1983, Miller & Mittlefehldt 1984, Nash & Crecraft 1985). The low abundance of *HFSE* in the Middle River rhyolite indicates that it was highly fractionated or a low-temperature partial melt. The absence of related felsic volcanic rocks here precludes a detailed petrogenetic evaluation of the origin of this rhyolite. Instead, comparison will be made to other felsic igneous rocks with similar geochemical characteristics (Fig. 13).

The Macusani glass-bearing tuff in southeastern Peru, one of the few known extrusive high-P magmas, geochemically resembles, in part, the Middle River rhyolite. It is interpreted to be a highly fractionated product of a peraluminous magma (Pichavant *et al.* 1987, 1988, London *et al.* 1989; Fig. 13), which is consistent with the isotopic evidence. S-type peraluminous felsic rocks typically have higher average P_2O_5 (0.15 ± 0.1 wt.%) than other types of granite (Whalen *et al.* 1987, Christiansen & Keith 1996). The highly peraluminous nature ($1.1 < \text{ASI} < 1.4$) of the least-altered rhyolite is consistent with these observations.

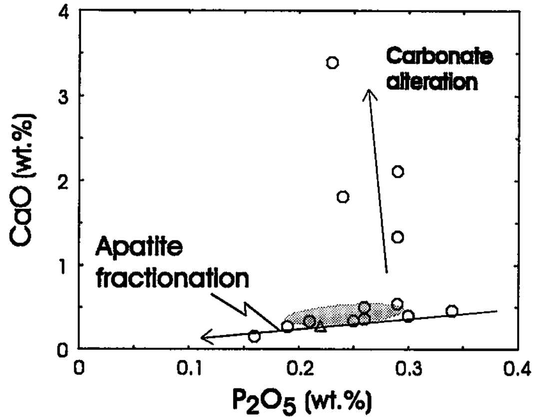


FIG. 14. P_2O_5 *versus* CaO diagram illustrating the range of compositions of the Middle River rhyolite and data for the least-altered samples (shaded). Note the trend expected for fractionation of apatite and carbonate-alteration trend.

The covariation between TiO_2 and Zr, Hf, Sc, Nb, and Ta is either indicative of variable degrees of solution of restite phases during partial melting, xenocryst incorporation or fractional crystallization. The covariation in P_2O_5 and Y and, to a lesser degree, La and Yb, also may indicate low-temperature fractionation or variations in degrees of partial melting. Although retention of the original heterogeneities associated with disequilibrium partial melting is possible, it is not probable within this small flow-banded rhyolite unit. Therefore, very minor degrees of fractional crystallization of zircon, Fe–Ti oxides and apatite may have occurred in the subvolcanic magma-chamber before eruption.

In subalkaline igneous systems, the low Zr and Hf contents (29 to 52 ppm and 1.1 to 1.8 ppm, respectively), which are mostly inherited (Lentz & V. McNicoll, in prep.), indicate that these very-low-temperature magmas (<700°C; see Watson & Harrison 1983) are derived by selective low-degree melting, because of the xenocrystic nature of most of the zircon crystals (Watson 1996).

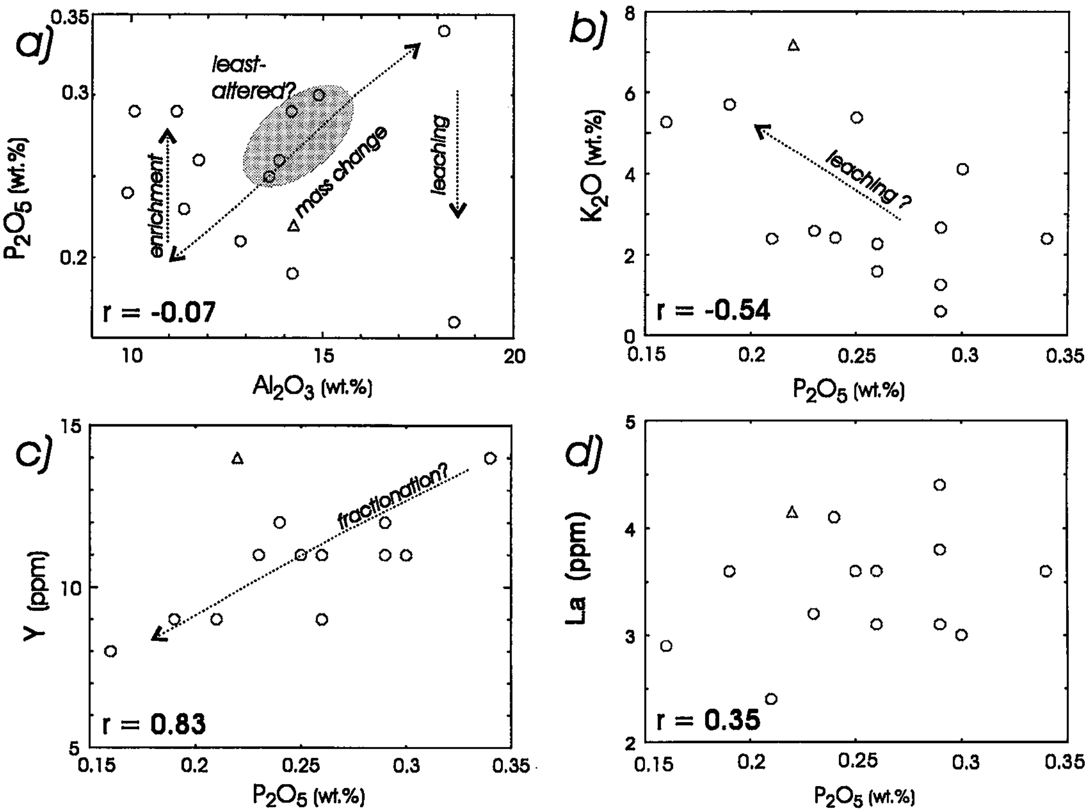


FIG. 15. P_2O_5 *versus* a) Al_2O_3, b) K_2O, c) Y and d) La, illustrating the compositional variation and tectonic affinities of the Middle River rhyolite (circles) and rhyolite in the Boucher Brook Formation (triangle) (Table 2). r: Pearson Product correlation coefficient; r values greater than 0.53 (n = 13) are significant above the 95% confidence level (Le Maitre 1982).

Strong compatibility of Hf in zircon in felsic magmas (Mahood & Hildreth 1983) results in Hf depletion by fractionation of zircon. However, Hf is generally slightly more incompatible than Zr (see Chyi 1986), such that the Zr/Hf decreases to low values in these rhyolites (21 to 28) *via* fractionation(?), which contrasts with the Zr/Hf ratio for various crustal rocks, including shale, which ranges from 33 to 41 (Taylor & McLennan 1985, Wedepohl 1995). The Nb/Ta value of the Middle River rhyolite also is low (6.5 ± 1.0), in contrast with the value for various crustal rocks, which ranges between 10 and 17 (Taylor & McLennan 1985, Wedepohl 1995). Pearce *et al.* (1984) indicated that collision-zone magmas commonly have low Nb/Ta values. Green (1994) has shown that many felsic suites can have low Nb/Ta values with variable Nb and Ta abundances. Topaz granites and ongonites typically have Nb/Ta values less than 10 (Christiansen *et al.* 1986, Taylor 1992). Ta is usually more compatible than Nb in various minerals, except pargasitic amphibole (Green 1994) and biotite (Nash & Crecraft 1985). Thus, to decrease the Nb/Ta ratio, amphibole or biotite may be involved in fractionation or selective partial melting. The low Th content (1.3 to 1.8 ppm) is attributed to removal of zircon (*cf.* Mahood & Hildreth 1983) and possibly apatite (*cf.* Rapp & Watson 1986) as fractionating liquidus phases or phases remaining in restite.

The geochemical feature of particular importance here is the enriched P content (>0.14 wt.% P_2O_5). This suggests that the peraluminous composition of the melt increased the solubility of apatite (Bea *et al.* 1992, London 1992a, Pichavant *et al.* 1992, Taylor 1992). High P contents are typical of highly fractionated, S-type felsic magmas derived from low-Ca, aluminous sedimentary protoliths (London 1992a, Bea *et al.* 1992, Christiansen & Keith 1996), but the latter generally have high *HFSE* contents. Typically, high-P topaz leucogranite and rhyolite have low levels of the *HFSE* and high concentrations of Rb, Li, Nb, Ta, and F (Manning & Hill 1990, Taylor 1992, Christiansen & Keith 1996), consistent with an S-type affinity. Also, evolved, high-P felsic magmas commonly are depleted in *REE*, as are the Middle River rhyolites, whereas otherwise similar low-P type felsic magmas remain enriched in *REE* (Taylor 1992), which suggests a relationship with high activity of P. The partition coefficient (K_d) for the *REE* in apatite is high (>10) in rhyolitic magmas (Watson & Capobianco 1981, Watson & Green 1981). The correlation among Y, La and P_2O_5 in the Middle River rhyolite could indicate apatite fractionation from even higher P contents. The good correlation between CaO and P_2O_5 in the least-altered rhyolites (Fig. 14) supports a relationship with apatite fractionation.

The very low *REE* content of the high-P rhyolites may result from the stability of residual apatite or other residual or refractory P-bearing phase, or a silicate or oxide phase (garnet, zircon, titanite, *etc.*) in the source protolith that hosts the *REE*. Alternatively, very early fractionation of apatite (*LREE*-bearing), monazite (*LREE*-rich), xenotime (*HREE*-rich), and zircon (*HREE*-bearing) (Watson 1980, Watson & Capobianco 1981) resulting from the high activity of P may also reduce the *REE* and Th contents.

Extreme compositional zoning in felsic magmas chambers (Hildreth 1981) is commonly interpreted as the product of extensive crystal fractionation in the magma chamber (Mahood & Hildreth 1983, Michael 1983, Miller & Mittlefehldt 1984) as opposed to volatile-related, liquid-state diffusion processes (Hildreth 1981). Concentration of network modifiers (H_2O, HF, *etc.*) in the uppermost parts of chambers reduce extent of crystallization and allow fractionation to very low temperatures (London *et al.* 1989, London 1992b), which is consistent with the inferred zircon-saturation temperatures of less than 700°C for the Middle River rhyolite. The aphyric, flow-banded nature of the Middle River rhyolite and lack of vesicles are consistent with the contention that these magmas were undersaturated in volatiles and highly viscous during emplacement, although the confining pressure exerted by seawater may have impeded vesiculation.

The Middle River rhyolite may be related to the partial melting of Avalon supracrustal sedimentary rocks that underlie the Gander Zone passive margin sequence (Miramichi Group). Interestingly, the environment and magmatic association are not unlike the early ^{18}O-enriched Torre Alfina lavas of the Roman igneous Province (Taylor & Sheppard 1986). Typically, the most contaminated magmas are the first through the magmatic conduits; the smallest volumes interacted with hottest country-rocks. This is somewhat similar to the processes that are envisaged for the episodes of protorift backarc felsic volcanism in the area (Lentz 1996b). Also, the macusanite occurrences (Peru) form within three basins situated within a continental inner arc environment in the Western Cordillera (Kontak *et al.* 1984, Pichavant *et al.* 1987). Therefore, small-volume, evolved peraluminous S-type magmas may be associated with early orogenic, continental subduction environments (*cf.* Pearce *et al.* 1984, Harris *et al.* 1986). Advection of heat related to upwelling asthenospheric mantle and resultant later subalkaline felsic then alkaline mafic volcanism were probably responsible for the early selective crustal melting.

CONCLUSIONS

Three flow-banded rhyolite lenses define the base of the Tetagouche Group in the Middle River area along the eastern flank of the Bathurst Mining Camp. They are spherulitic, with some evidence of Al + P = 2Si substitution in alkali feldspar. Overall, the least-altered rhyolite samples have high silica contents and are peraluminous, with very low levels of Ca and *HFSE*, but they have high P contents (0.16 and 0.34 wt.% P_2O_5) relative to other subalkaline felsic volcanic rocks in the Bathurst

Mining Camp. These features, together with the high Nb/Y (>0.7), Ta/Yb (>4.3), Rb contents (>200 ppm) and high $\delta^{18}O$ (13.4 to 15.4‰) and low Nb/Ta (<6), are consistent with an S-type affinity. These P-enriched, high-silica, S-type rhyolites represent evolved, low-temperature magmas. The variations in *HFSE* and their ratios are consistent with low-temperature fractionation processes of phases with high specific gravity, although their low abundances may, in part, be inherited by low-temperature partial melting processes of a sedimentary protolith. These S-type rhyolites erupted in a continentally situated, proto-arc to backarc-rift setting, which is atypical of the normal tectonic interpretation for S-type magmatic systems.

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