THE HARVEY VOLCANIC SUITE, NEW BRUNSWICK. II. POSTMAGMATIC ADJUSTMENTS IN THE MINERALOGY AND BULK COMPOSITION OF A HIGH-FLUORINE RHYOLITE

CHRISTINE PAYETTE AND ROBERT F. MARTIN

Department of Geological Sciences, McGill University, 3450 University Street, Montreal, Quebec H3A 2A7

ABSTRACT

The Harvey volcanic suite, New Brunswick, of Early Carboniferous age, consists of three units: 1) York Mills (base): volcanogenic sediments, minor ash-flow and laminated rhyolite; 2) Cherry Hill: ash-flow and ash-fall tuffs, quartz-feldspar porphyry, and 3) Harvey Mountain, rhyolitic lava flows. Quartz paramorphic after tridymite is present throughout the flow, and may indicate a high temperature assemblage that failed to equilibrate structurally. Intermediate microcline is only very locally developed. The chemical composition suggests highly evolved rhyolites: high Si (>76% SiO2), low Fe (<2% Fe2O3), Mg (<0.05% MgO), Ti (<0.15% TiO2), and Ca (<2% CaO), high Rb, Nb, Y, Th, and low Ba, Sr and Zr. The composition of the glass trapped in the quartz phenocrysts indicates a fluorine-rich (up to 2% F) potassic peraluminous rhyolitic magma (71% SiO2, 6.5% K2O, 14.9% Al2O3). Comparison of the glass and bulk-rock compositions shows a net dilution of all elements by SiO2 added after devitrification. The mineralogy, chemical composition, peraluminous character and F-enrichment of the Harvey rocks reflect the characteristics of the F-rich magma. The Harvey rocks were probably derived by partial melting of continental crust in an extensional environment, in response to an influx of basaltic magmas derived from the mantle.

Mots-clés: suite volcanique de Harvey, Carbonifère, ignimbrites, tridymite, rhyolites évoluées, fluor, rhyolites à topaze, feldspar alcalin, Nouveau-Brunswick.

INTRODUCTION

The Early Mississippian Harvey volcanic suite occurs on the northern edge and stratigraphically at the base of the Central Carboniferous basin, 55 km southwest of Fredericton, New Brunswick (Fig. 1). Felsic volcanic to volcanogenic rocks outcrop in a N-NE-trending homoclinal lens-shaped body 16 km in length and 2 km in width. The village of York Mills and Harvey Mountain mark the southwestern and northeastern extremities of the lens, respectively. Although the study area has been examined by Robb (1870), Bailey & Matthew (1873, 1905), Freeze (1936), Laughlin (1960), Clark (1961), Kuan (1970) and Beaudin et al. (1980), still relatively little is known about the mineralogy, chemistry and origin of these rocks. This study contains information on the petrography, chemical composition, origin and tectonic setting of these rocks. Because the existing data on this suite is mostly contained in theses and unpublished company reports, a brief summary of the stratigraphy is provided in the following paragraphs.

The first subdivision of the Harvey volcanic rocks was made by Kuan (1970), who named and subdivided the Harvey volcanic rocks into the York Mills (lower) and Harvey Mountain (upper) units (Fig. 1, units 2 and 4). Kuan included in the York Mills unit red siltstones, sedimentary and volcanogenic sedimentary rocks; the Harvey Mountain unit consisted of two ash-flow sheets, agglomerates, ash-fall tuffs and lava flows.

Beaudin et al. (1980) redefined the stratigraphic sequence in light of more detailed mapping and distinguished a third unit, the Cherry Hill unit (Fig. 1, unit 3), between the other two. In their view, the
York Mills unit includes sedimentary rocks, lithic tuffs and laminated rhyolites; the Cherry Hill unit comprises volcaniclastic and volcanogenic sedimentary rocks, ash-flow and ash-fall tuffs and a quartz-feldspar porphyry; the Harvey Mountain unit contains a pyroclastic breccia and laminated rhyolites with intercalated ash-fall tuffs. Beaudin et al. (1980) subdivided the Cherry Hill unit into five members: A) volcanogenic sediments (estimated maximum thickness of 10 m), B) the two sheets of ash-flow tuff (ignimbrite), C) volcaniclastic sediments (maximum 20 m), D) quartz-feldspar porphyry and E) ash-fall tuff (about 40 m). They further separated this unit into a proximal volcanic facies, of small lateral extent, consisting of the two ash-flow sheets (3B, Fig. 1) and the quartz-feldspar porphyry (3C, Fig. 1), for an overall thickness of 60 to 150 m at Grieve Lake and Cherry Hill, and a distal volcanic facies (3A, 3D, Fig. 1), the lateral equivalent to the proximal facies, made up of ash-fall tuff (3D, Fig. 1) and volcanogenic sediments (3A, Fig. 1), with an approximate thickness of 45–60 m. The two facies show important and rapid lateral variations.

The subdivision used here has been slightly modified after that of Beaudin et al. (1980). Four of the original five members of Beaudin et al. are retained...
(Fig. 1). The original unit 3C is abandoned, as we found those rocks to be petrographically and chemically very similar to those of the Harvey Mountain unit (map unit 4). The original units 3D and 3E of Beaudin et al. (1980) have been renumbered 3C and 3D in Figure 1. Felsic volcanic rocks are dominant, but related detrital, volcanogenic sediments occur in the basal York Mills unit. The three units define a 200-m-thick succession of tuffaceous sediments, felsic tuffs and intrusive and extrusive rhyolites (Beaudin et al. 1980). Stratigraphic and petrological data suggest that the Harvey volcanic rocks can be correlated with those of the Piskawegan Group, within the Mount Pleasant caldera (Fig. 1; van de Poll 1967, Kuan 1970, Pajari 1973, Gemmell 1975, Beaudin et al. 1980, Ruitenberg & McCutcheon 1985).

The Harvey volcanic suite is underlain by Silurian metasediments (unit 1, Fig. 1) and overlain successively by red beds (unit 5, Fig. 1) that can be traced laterally into the Mississippian-Pennsylvanian Shin Formation southwest of the map area and grey sandstone of the Pennsylvania “Pictou Group” (unit 6, Fig. 1) (van de Poll 1972, Kuan 1970, Pajari 1973, Beaudin et al. 1980). The contacts between the units are commonly not exposed, and the quality of exposure in the area is generally poor.

During Carboniferous times, the basin underwent regional extension that resulted in large-scale normal and, later, strike-slip faults, and numerous associated small grabens. The Harvey volcanic unit forms part of the Fredericton sub-basin (Fig. 1); it includes rounded conglomerates and shales. These rocks outcrop only locally and are usually poorly exposed. Detrital grains in the sandstone consist of fragments of rhyolite and phenocrysts of feldspar and quartz.

This unit also contains a minor but significant volcanic component. Centimetre-thick beds of lapilli tuff are present throughout this unit. A lithic tuff with dark green and red rhyolitic fragments is exposed at York Mills (Fig. 1); it includes rounded to angular metasedimentary and granitic boulders up to 15 cm across. This tuff is recognized in a “mylonitized” zone related to the Fredericton–Norumbega fault zone (Beaudin et al. 1980). A slightly welded to nonwelded ash-flow tuff outcrops on the western side of York Mills Lake (Fig. 1). It contains fragments of volcanic rocks and isolated feldspar phenocrysts in a devitrified groundmass. A laminated rhyolite and a flow breccia(?) that overlie the tuff are exposed on the eastern side of the Magaguadavic River. Small angular cavities lined with quartz, albite and fluorite crystals are common in the interstices. Chemical analyses were carried out on representative samples of the ash-flow tuff (2 samples) and the laminated rhyolite (4 samples). Their composition is listed below.

**Cherry Hill unit**

The best exposures of the Cherry Hill unit are along the southern tip of Big Cranberry Lake (unit 3, Fig. 1). This unit is mainly composed of two ash-flow subunits with associated layers of ash-fall tuff, and a quartz–feldspar porphyry.

The base of the Cherry Hill unit is composed of volcanogenic sediments (unit 3A, Fig. 1) and of a lithic tuff. The volcanogenic sediments show faint laminations in thin section, and are composed of devitrified, lithified material (Beaudin et al. 1980). The lithic tuff contains broken fragments of rare quartz, K-feldspar and plagioclase phenocrysts, angular to subrounded fragments of siltstone, rhyolite (up to 6 mm across) and presumed basaltic material in a fine-grained pinkish matrix. Four samples of the volcanogenic sediments were analyzed.

Two superposed ash-flow sheets were recognized by both Kuan (1970) and Beaudin et al. (1980): an older sheet 5–6 m thick is covered by one 100 m thick. Both have a soft lithic base and a densely welded porphyritic portion. Poorly to well-developed columnar joints (dip 20° SE) were noted at the top of the second sheet. Locally, this unit has the appearance of a massive quartz-feldspar porphyry (3C). The average composition of seven samples of the upper ash-flow is presented below.

A moderately welded tuff (3B), part of the lower sheet, has also been recognized along the shore of Harvey Lake. The shards are of large size, somewhat flattened, devitrified, and show a clear axiolitic texture. The glass in these shards has been replaced by a mica-rich material common in all rocks of the Harvey volcanic unit (illite and quartz; Kuan 1970, Pajari 1973). Numerous fragments of volcanic and metasedimentary origin, pumice fragments, broken spherulites, quartz, K-feldspar and plagioclase phenocrysts are characteristic of the unit. Many fragments and feldspar(?) phenocrysts have been replaced by an aggregate of fine green needles.
Samples of the ash-flow sheets (3B, Fig. 1) show a eutaxitic texture (Ross & Smith 1961) that is defined by parallel, flattened, devitrified shards and pumice fragments molded against phenocrysts and lithic fragments. Lapilli-sized clasts of flattened, devitrified pumice are common. Small spherulites line the periphery of the lapilli, and well-developed quartz and albite crystals are concentrated along their axis, the axiolitic "seam". The area between the axis and the periphery is filled either by a mica-rich cryptocrystalline material interpreted to be illite and quartz (Pajari 1973), a vapor-phase deposit of quartz or, in the largest fragments, colorless to purple fluorite and rare calcite. A few fragments of metasedimentary or volcanic (basaltic?) origin are found. Rare broken phenocrysts of quartz and feldspar and small isolated patches of fluorite grains also occur in the matrix. The feldspar phenocrysts are commonly altered to green micaceous aggregates locally associated with fluorite.

The quartz-feldspar porphyry (QFP, unit 3C) may correspond to the most densely welded portion of an ash-flow tuff. It contains between 15 and 25% phenocrysts of euhedral quartz (paramorphic after β-quartz) and feldspar phenocrysts (up to 2 mm across) set in purplish matrix of devitrified welded shards molded around the phenocrysts. Also typical of the porphyry are pumice fragments and rare lithic fragments. A few fragments of previously welded tuff and rhyolite occur throughout the matrix. Pumice lapilli are also common, similar to those described in the ash-flow unit; fluorite, quartz and albite crystals also fill in the cavities. Rare fragments of basaltic (?) origin are scattered in the matrix. The quartz phenocrysts commonly contain melt (glass) inclusions (Payette & Martin 1986). The mineralogy of the feldspars is discussed below. Zircon occurs as an accessory mineral. Twelve samples of the porphyry were analyzed.

Unit 3D (Fig. 1) is composed of massive, devitrified and recrystallized ash-fall tuff of pale violet to pinkish red color, with a spherulitic texture and rare quartz phenocrysts. This unit also includes a local breccia (?) (southernmost part of 3D, Fig 1), with fragments of devitrified laminated rhyolite. The interstices are filled by locally alternating colorless to brownish yellow layers of microcrystalline quartz (chalcedony ?) arranged in a botryoidal texture. The average composition of five samples is discussed in a later section.

Harvey Mountain unit

The Harvey Mountain unit outcrops best at Harvey Mountain, east and south of Holland Lake (unit 4, Fig. 1). There, a high cliff is dominated by laminated rhyolite and minor intercalated ash-fall tuffs, with an estimated aggregate thickness of 75–150 m (Beaudin et al. 1980). The rhyolite flows exhibit a well-developed, continuous laminated texture, defined by an alternation of well-defined greenish grey layers of coarse spherulites (up to 3–4 mm across, spherulitic textures; Lofgren 1971) and aphanitic devitrified layers (axiolitic texture, Ross & Smith 1961) (Fig. 2A) with rare lithic fragments. Layers of relatively coarse vapor-phase-deposited albite (?) and K-feldspar appear at the interface between spherulitic and aphanitic layers, and are typical of this unit. The formation of interstitial cavities and the growth of second-generation feldspars and tridymite reflect the volume reduction associated with devitrification (Lofgren 1971).

Typical textural features common to all examples of this unit include distinctive flow-banding, a striking development of coarse K-feldspar at the interface of aphanitic and spherulitic layers (Fig. 2A), an abundance of fluorite lining the cavities and the presence of tablets of quartz paramorphic after tridy-
mite. The presence of all these characteristics in the original unit 3C of Beaudin et al. (1980) led to our reassignment of this member of the Harvey Mountain unit. The average chemical composition of twenty-five samples is presented in a later section.

**THE INVERTED TRIDYMITE**

Quartz paramorphic after tridymite (Fig. 2B) in the lava flow of the Harvey Mountain unit resembles that described by Wager et al. (1953), Stevenson (1963) and Pouliot (1968). The characteristic acicular habit of tridymite and alkali feldspar intergrown in spherulites was retained during cooling, as was the tabular habit of the crystals of tridymite (Fig. 2B) that are randomly oriented in and among laths of alkali feldspar in interstices between spherulites. The occurrence of tridymite, if formed in its stability field, indicates crystallization (devitrification) and, implicitly, emplacement at a high temperature, at least 870 to 900°C (Fenner 1913, Pouliot 1968, Deer et al. 1980).

**FELDSPAR MINERALOGY**

The Harvey rocks are dominated by quartz, sodium- and potassium-rich feldspar, accessory zircon and rare altered biotite (?), with a few granitic and basaltic (?) fragments set in a matrix of devitrified glass shards and pumice fragments or spherulites and aphanitic layers. The porphyritic unit is dominated by quartz and alkali feldspar phenocrysts. The rocks contain no primary ferromagnesian minerals. Quartz, albite, orthoclase (commonly less abundant than albite), fluorite and opal also occur as vapor-phase deposits.

As the Harvey volcanic rocks have a high-temperature origin, they should contain a disordered and compositionally intermediate (Na-K)-feldspar as a phenocryst phase. The groundmass feldspar in the Harvey Mountain rhyolites should be similar because devitrification in this unit probably occurred at a high subsolidus temperature. The detailed feldspar mineralogy of twenty-one samples was determined to evaluate just how close the Harvey volcanic rocks conform to this prediction, and to what extent they have re-equilibrated during the subsolidus events.

To evaluate the degree of Al-Si order, powder X-ray-diffraction patterns were run on hand-picked phenocryst fragments (or the whole rock, where the grain size is aphanitic). Selected sets of cell dimensions have been listed in Table 1. Compositional and structural variables (Table 2) were inferred from the cell constants (Guinier–Hägg focusing camera, synthetic spinel internal standard, \( a = 8.0833 \) Å at room temperature, CuK\( \alpha \) radiation).

The use of a focusing camera normally ensures that the diffraction maxima are sharp and well resolved, and sufficiently numerous that a least-squares refinement of the cell parameters can be obtained. In the case of the Harvey suite, however, problems were encountered; less than half of the sets of refined cell-dimensions are included in Table 1.

**TABLE 1. CELL PARAMETERS OF NA-RICH AND K-RICH FELDSPARS FROM THE HARRVY RHYOLITIC SUITE, NEBRASKA**

<table>
<thead>
<tr>
<th>Description</th>
<th>( a(\text{Å}) )</th>
<th>( b(\text{Å}) )</th>
<th>( c(\text{Å}) )</th>
<th>( \beta(\text{°}) )</th>
<th>( V(\text{Å}^3) )</th>
<th>( \alpha(\text{°}) )</th>
<th>( \beta(\text{°}) )</th>
<th>( \gamma(\text{°}) )</th>
<th>( \rho(\text{g/cm}^3) )</th>
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<td>12.8072</td>
<td>7.1529</td>
<td>94.1777</td>
<td>116.6515</td>
<td>88.1000</td>
<td>664.522</td>
<td>0.013</td>
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<tr>
<td>20 vapor Ab</td>
<td>8.1313</td>
<td>12.7985</td>
<td>7.1494</td>
<td>94.2144</td>
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<td>0.137526</td>
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<td>2 pheno-</td>
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<td>88.6456</td>
<td>664.650</td>
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<td>crys-</td>
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<td>12.7968</td>
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<td>0.029</td>
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<td>7.2070</td>
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**Legend:** Ab albite, Or orthoclase, IM Intermicroclastic. In the sample description, "vapor" refers to a vapor-phase deposit, "interstices" refers to relatively coarse crystals, probably deposited from the vapor phase, found between spherulites. Samples represent units 3A (37), 3B (20), 3C (2, 22, 43) and 4 (12, 14). \( \rho = 29.13 \) - 28.13, in degrees. \( \Delta \alpha \) average standard error associated with diffraction maxima, in degrees. Refinement carried out with program of Appleman & Evans (1973). CuK\( \alpha \) radiation.
Other refinements are not presented because too few diffraction peaks could be unambiguously indexed, leading to unacceptably large errors. This problem can be explained by a combination of the following factors: 1) as silicification is an important process in many specimens, the volume of feldspar in a 1-mm³ sample of a rock is reduced. 2) The presence of disseminated hematite leads to a high background on the powder pattern, such that many faint lines become illegible. 3) Products of devitrification are probably metastable structurally if not compositionally, and most likely are heterogeneous on a small scale. This leads to broadened, lower-intensity peaks. 4) Albitization is widespread, and the removal of some K by ion exchange means that the volume of the K-feldspar is reduced over that of albite. Note that the heterogeneities mentioned in point 3 are bound to affect the K-feldspar more than the albite, because the K-feldspar departs more importantly from its equilibrium degree of Al–Si order than the albite.

The entire set of results can certainly be used qualitatively if not quantitatively. The specific association of feldspar minerals in each specimen is recorded in Table 2, along with an indicator of degree of Al–Si order of the K-feldspar where this is allowed positionally, the sodic phase is virtually free of potassium and calcium. Microprobe data are available to confirm this XRD finding in the case of albite in specimens 2 and 13 (mean of 15 compositions Ab₀.₉₉₀Or₀.₃An₀.₃). The K-feldspar contains some sodium, as expected, but probably less than 5 mole % Ab. The only microprobe determination (sample 2) gives Or₉₈.₂Ab₁₈.₂. There is certainly no trace remaining of the original high-temperature sanidine, inferred to have had a composition in the range Or₆₅ to Or₇₀. In terms of composition of the coexisting phases, the Harvey rocks contain a low-temperature (<300°C) assemblage (e.g., Martin 1974).

In almost all cases where the two feldspars coexist, the volume occupied by albite exceeds that of the K-feldspar. This is an indication that many of the Harvey volcanic rocks have undergone mild readjustments in the relative proportion of Na and K. This is well reflected in the bulk composition of the rhyolites (see Discussion).

Structurally, both sodic and potassic feldspars show clear evidence of metastability. In the time available during the cooling of this near-surface volcanic edifice, the feldspars did order partly, but failed to reach the equilibrium state, low microcline and low albite. In almost all cases, the K-rich feldspar is orthoclase (nomenclature of Ribbe 1983). It is relatively well ordered; 2t₁ is close to 0.88 (maximum disorder: 2t₁ = 0.50). A proportion of Al in the two T₁ sites of orthoclase of 0.88 is close to the limit normally encountered in monoclinic K-feldspar, and implies that the K-feldspar has gone to the limit short of a transformation to a triclinic structure, which is a major reconstructive step. The inversion to microcline, expected near 400°C, failed to occur except in the vicinity of specimens 13 and 43 near Harvey Mountain (Fig. 1).

Specimens 13 and 43 of the quartz-feldspar porphyry both contain intermediate microcline. In specimens 13, both phenocryst and matrix contain intermediate microcline (t₁O 0.87 and 0.55, respectively; t₂O is 1 in low microcline). In specimen 43, the phenocryst is intermediate microcline (t₁O 0.83), but the matrix still contains well-ordered orthoclase (t₁O 0.44, Table 2). Samples 13 and 43 both seem to violate a rule of thumb that applies to subsolidus assemblages containing K-feldspar: the finer the grain size, the more evolved is the degree of Al–Si order. One way to explain the anomaly is to propose that because of silicification, the porosity and permeability of the matrix were greatly reduced, thus impeding the interaction of feldspar with fluid that must proceed to transform a disordered feldspar into an ordered one. The same reason may apply to the Harvey suite as a whole, as an explanation of the scarcity of microcline.

Similarly, the sodic feldspar is "stranded" in a metastable, transitional state. This can be illustrated in a β* – γ* plot (Fig. 3), the best diagram to separate the effects of composition and degree of Al–Si order in sodic plagioclase (Smith 1974). The points should
Chemical Composition of the Harvey Rhyolites

In order to better characterize the Harvey rocks, the chemical composition of 59 representative samples of the various units was obtained by X-ray fluorescence. Only the volcanic rocks were considered in this study (Table 3). Complete chemical data are available at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario KIA 0S2.

The Harvey rocks are rich in silica and potassium (76–83% SiO₂, 3–7% K₂O, respectively) and poor in titanium (<0.2% TiO₂), magnesium (<0.5% MgO), calcium (<2% CaO) and phosphorus (<0.03% P₂O₅) (Table 3). Their average composition indicates a peraluminous character (A/CNK between 1.19 and 1.53). The trace-element data indicate enrichment in Nb, Y, Rb and Th and a strong depletion in Ba, Sr and Zr (Table 3), typical of highly evolved rhyolites (Miller & Mittlefehldt 1984, Pichavant & Manning 1984).
The SiO₂ values of the laminated rhyolite of the York Mills unit range from 80 to 83.7%. The SiO₂ values of the ash-flow subunit in the York Mills (>76.5%) are more similar to those of the Cherry Hill (ash-flow tuff 76%, porphyry 79%), and Harvey Mountain units (lava flow 77.5%). The Al₂O₃ values are more uniform, except for those units where SiO₂ is close to or exceeds 80% (units 2, 3C, 3D); Al₂O₃ content ranges from 12 to 12.8% in the Cherry Hill unit, except for the porphyry subunit, which contains 10 to 11%, and the Harvey Mountain unit (11.6 to 12.6%). The Al₂O₃ content is more variable, from 6 to 10%, in the York Mills unit and unit 3D of the Cherry Hill sequence, all cases where the SiO₂ content is high. All three divisions of the Harvey volcanic suite have low contents of iron (0.2–2% Fe₂O₃), magnesium (0–0.5% MgO), manganese (0–0.05% MnO), titanium (0.04–0.15% TiO₂) and calcium (0–2% CaO). Sodium and potassium are more variable, and range from 0 to 4.4% Na₂O and 3 to 7.2% K₂O. Ba, Sr and Zr are generally found in low concentrations: 0–185 ppm Ba, average less than 50, 15–400 ppm Sr, average less than 70, 78 to 174 ppm Zr, average 130, respectively; in contrast, Nb, Rb, Y and Th are present in relatively high concentrations: Nb 26–107, average 50 ppm, Rb 400–691, average 500, with a few exceptions with less than 400 ppm, Y 40–243, average 110, Th 21–47, average 35 ppm. F, Cl and REE contents were not determined on the whole rocks. The trace-element content is variable within each map unit and subunit. Each subunit of the Cherry Hill unit displays a well-defined range of concentration for each element, but neither the major units nor the subunits may be distinguished on this basis, owing to overlap (e.g., unit 4 covers the whole range of all other units or subunits). The variable Ca content is explained by the presence or absence of fluorite (a secondary mineral) in the vugs and in the matrix.

As with all ignimbritic rocks, various postmagmatic processes such as devitrification and deposition from the vapor phase have played an important role in modifying the chemical composition of those originally glassy volcanic rocks, and this is especially the case with the major elements. The SiO₂ values observed for many samples in units 2, 3C and 3D are unusually high (80 to 84%), and not representative of magmatic values. The net effect of adding Si to a rhyolite will be to dilute all other elements, as has been found in uranium-enriched ignimbrites (which become albitites; e.g., White & Martin 1980).

The mildness of the metasomatic adjustments is consistent with the lack of economic grades of uranium mineralization at Harvey.

The reactions recorded in the feldspar assemblage were caused by hot aqueous fluids that had the ability to transport silica. The SiO₂ values observed in the rocks of York Mills unit (up to 84 wt.%) and in some other units, such as 3D, suggest extensive silicification. Petrographically, this is illustrated by the presence of microcrystalline quartz in the groundmass of some rocks (chalcedony in unit 3D).

Experimental studies have shown that the alteration of silicic glass proceeds first by hydration of the glass, followed by the development of spherulites and, possibly, granophyric textures (Lofgren 1971). Devitrification is accomplished by diffusion of the alkali ions (Jezek & Noble 1978), usually with minor overall chemical changes of the bulk-rock compositions (Ewart 1971, Fisher & Schmincke 1984). However, loss of Na, Si, Al (Lofgren 1970, Ziehn-ritter 1980) and halogens (Noble et al. 1967, Lipman et al. 1969) have been reported in some instances. Major- and trace-element variation diagrams (Fig. 4) may be used to demonstrate the consequences of silicification on the bulk composition of the rhyolites at Harvey. In the case of Na and K, a much bet-

**DISCUSSION**

Although the Harvey volcanic rocks have a high-temperature origin, their feldspar mineralogy is not primary. In fact, the alkali feldspar(s) found in phenocrysts, in products of devitrification of glass, and in vapor-phase deposits have all interacted with a fluid phase at a low temperature, and have become better ordered to some extent. Both sodic and potassic feldspars still fall short of the fully ordered configurations, however, suggesting that the length of time available for ordering was relatively short (hundreds of years?). Unfortunately, this aspect cannot be quantified with the information available. More work needs to be done on the sodic feldspar phase, which seems unusually far from pure, ordered albite for a product of crystallization of such an evolved, low-calcium granitic liquid (Payette & Martin 1986).

It is known that the ordering reaction does become very sluggish below 300°C (e.g., Martin 1974), even that in sodic feldspar, which is more reactive than the K-rich feldspar. Mobilization of alkalis in the Harvey rocks resulted in the replacement of K-feldspar by albite, but, with one exception, this process was not sufficiently intense or did not last long enough to lead to the elimination of K-feldspar, as has been found in uranium-enriched ignimbrites (which become albitites; e.g., White & Martin 1980).
ter negative correlation exists between the SiO₂ content and the sum (Na + K) than with either Na or K taken individually. Whereas the main consequence of depositing silica in pore spaces is to decrease the relative proportion of all other elements present, the alkalis have been further disturbed by an ion-exchange reaction, possibly taking place at the same time as the addition of silica. All this silica must have been selectively dissolved from rhyolitic material deeper in the section upon its devitrification (Ross & Smith 1961), presumably at a higher temperature than that at the site of SiO₂ deposition. If the composition of the Harvey suite did correspond, on average, to the composition of glass in the inclusions in quartz (Payette & Martin 1986), then the deeper parts of the section must contain quartz-poor, relatively feldspathic tuffs. An important finding is that at Harvey, the bulk compositions are not primary, and in most cases are quite far from being so.

**Comparison with topaz rhyolites**

The mineralogy, chemical composition (Table 3), enrichment in F and Rb, depletion in Ba, Sr, Ca and Mg, the peraluminous character of both the glass in the melt inclusions and the whole suite of Harvey rocks, the presence of high concentrations of F (up to 2%) in the glass and the abundant fluorite in both the matrix and open vugs as a vapor-phase deposit, all point to the similarity of the Harvey group to topaz rhyolites (see Burt et al. 1982, Christiansen et al. 1983, 1984, Naumov et al. 1984, Payette & Martin 1986). It is true that topaz has yet to be found, but other F-rich phases have been identified in the melt inclusions (Payette & Martin 1986).

A comparison of the major- and trace-element compositions of the Harvey glass and rhyolites to those of topaz rhyolite, ongonite, calc-alkaline and peralkaline rhyolites (Christiansen et al. 1983) is illustrated in Figure 6 of Payette & Martin (1986). F-rich (topaz) rhyolites differ from peralkaline rhyolites by their higher F, Rb, U and Th contents, and lower Sr, Ba, Eu, CΙ, Zr, Nb, Fe, Mg, Ti, Zn and LREE (Hildreth 1981, Christiansen et al. 1983). Topaz rhyolites are usually high in SiO₂ (>74%), Na₂O (~3.6%), K₂O/Na₂O ratio (>1) and fluorine (0.1–1%) and low in TiO₂ (<0.2%), CaO (<0.9%), MgO (<0.2%) and P₂O₅ (<0.01%) (Christiansen et al. 1983). Devitrification and hydrothermal alteration of the originally glassy rocks of Harvey most probably caused the observed discrepancies in Al, Na, Ca, Rb and Sr (cf. significant loss of alkalis, Rb and Al: Lipman et al. 1969, Lofgren 1971, Zielinski 1982) when compared to the average composition of topaz rhyolites, obtained using fresh rhyolitic glass and felsites (Christiansen et al. 1983). Y is more concentrated at Harvey (up to 250 ppm) than expected for a topaz (F-rich) rhyolite, but this might

**FIG. 4. Dilution effect of increasing Si on Al, Na and K (cation %). All other elements show the same effect. Shaded pattern and the open circles represent glass compositions (Payette & Martin 1986; see also Table 3). Filled circles: bulk compositions of the Harvey rocks. a. Al versus Si, b. Na versus Si, c. K versus Si, d. (Na + K) versus Si.**
be related to the presence of accessory Y-bearing phases such as zircon, as a solid solution toward xenotime, and britholite (Payette & Martin 1986). The high concentrations of K, Rb, Th and the low concentrations of Ba and Zr are especially well defined in Figure 5a. All three groups shown in Figure 5 show a K, Rb, Th enrichment and a depletion in Zr. Unfortunately, as the dashed lines indicate, there are still some elements for which the data base is fragmentary in one suite or another.

Yet another way of comparing these rocks to other types of rhyolite is to plot the Rb and Zr concentrations in all units and formations of the Harvey Group (Fig. 6). The Harvey rocks define a cluster of points that overlaps the population of F-rich rhyolites (topaz rhyolites) of Christiansen et al. (1983). Note, however, that some topaz rhyolites are more evolved than the Harvey rhyolites, on the basis of their Rb content.

That the parent magma was fluorine-rich is supported by the concentration of F in the glass (up to 2%), the presence of crystals and patches of fluorite in the devitrified rocks and of a F-bearing liquidus mineral in the melt inclusions (Payette & Martin 1986). Separation of a F-rich fluid phase and its rise to the upper parts of the magma chamber may provide an efficient means of concentrating fluorophile trace-elements (Be, Li, U, Th, Sn, etc.) by volatile-complexing with F (Bailey 1977, Mahood 1981, Burt et al. 1982, Christiansen et al. 1983, 1984, Pichavant & Manning 1984). The fluorine may have become concentrated in the top part of a magma reservoir either by "thermogravitational diffusion" (Hildreth 1981) or crystal fractionation (Christiansen et al. 1983, 1984).

**Comparison with Mount Pleasant**

Petrographically, the Harvey volcanic suite is quite similar to a typical nonproductive (i.e., unmineralized in Sn–W) topaz rhyolites vent-complex (Burt et al. 1982). For example, some rhyolites are strongly flow-banded (unit 4) and have a crystal-poor spherulitic groundmass. Fluorite is common to locally abundant, both in the lava flow and in the underlying ash-flow unit, and local anomalies in uranium have been reported (Kuan 1970, Beaudin et al. 1980). The Mount Pleasant caldera and the associated Sn–W–Mo deposit (Fig. 1) could represent a productive vent-complex (Pouliot et al. 1978, Burt et al. 1982, Samson et al. 1985). The Harvey Group and the Mount Pleasant rocks occur at the same stratigraphic level and are considered of the same age (early Mississippian, 340–330 Ma); their genetic relationship has been suggested repeatedly (Kuan 1970, Pajari 1973, Gemmell 1975, Beaudin et al. 1980), though not documented. The ash-flow tuffs of the Mount Pleasant caldera are petrographically and geochemically very similar to the Harvey rocks (Gemmell 1975, S.R. McCutcheon, pers. comm.), but there must be subtle differences that determine whether a rhyolitic vent-complex becomes productive or non-productive. A search for these indicators will form the basis of a future study.
Origin and tectonic setting

The geochemical data reported here allow some interpretations to be made concerning the tectonic setting of magmatism. In particular, the Rb versus (Y + Nb) and Nb versus Y discriminants (Fig. 7) effectively attribute the Harvey rocks to the Within-Plate-Granite (WPG) category of Pearce et al. (1984). This approach assumes that these elements at Harvey have not been seriously affected by the subsolidus processes described in this paper. Also considered typical of WPG-type rhyolites are the high contents of K, Rb and Th and depletions in Ba and Sr. WPG-type rhyolites may be considered extrusive members of anorogenic plutonic suites (Martin & Piwinskii 1972, Loiselle & Wones 1979).

Although there is no question concerning the tectonic setting of the Harvey suite, the ultimate origin of the volcanic rocks is more contentious, in view of our lack of information on isotopic systems. The Harvey suite contains small xenoliths of basic rocks, and basalt flows have been mapped at the same stratigraphic level as the Harvey volcanic rocks to the northeast and southwest. Burt et al. (1982) and Christiansen et al. (1983) proposed an origin for topaz rhyolites linked to the emplacement of basaltic magma in the crust at an early stage of lithospheric extension. Was the role of the mantle-derived basaltic magma simply that of a heat source, which initiated anatexitic reactions on a sufficiently large scale to account for the volume of rhyolite produced (Burt et al. 1982, Christiansen et al. 1983, 1984)? Or did the basaltic magma differentiate very efficiently near the surface to give a suite of derivative magmas (Martin & Piwinskii 1972, Higgins 1978)? We have favored the first hypothesis for the Harvey suite (Payette & Martin 1986) in view of the peraluminous nature of the melt, preserved as glass in quartz phenocrysts. Also considered relevant is the potassic composition of the melt. Both criteria are usually considered earmarks of an anatexitic granitic liquid formed at the expense of a sedimentary succession containing metapelites (e.g., Miller 1985). A weaker criterion would be the clear bimodality between the suite and the basaltic flows that could be related to it. The Mount Pleasant suite has an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.713 (Kooiman et al., in press). Such a high value is consistent with the direct involvement of metasedimentary crustal material in the genesis of those rhyolites. Note that the metasedimentary material may have been metasomatized by mantle-derived, F-bearing fluids (Bailey 1978) prior to anatexitis.

In the reservoir of rhyolitic magma, important zonation of F and lithophile elements such as the heavy rare-earths, uranium and thorium could have occurred through crystal–liquid equilibrium involving monazite, titanite, zircon and britholite, and through volatile complexing and other poorly understood processes (Hildreth 1981, Mahood 1981, Christiansen et al. 1983, 1984, Pichavant & Manning 1984). Documentation of such zonation would be difficult to obtain at Harvey in view of the analytical problems in determining concentrations of such trace elements in the glass inclusions, and the disturbances in trace-element distributions in the whole rocks expected as a result of the postmagmatic reactions.
ACKNOWLEDGEMENTS

The authors thank Messrs. L.R. Fyffe and S.R. McCutcheon, of the New Brunswick Department of Natural Resources, for critical comments on an earlier version of this paper. Research costs and field expenses were covered by an operating grant (A7721) from the Natural Sciences and Engineering Research Council to R.F. Martin.

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Received July 25, 1985, revised manuscript accepted February 25, 1986.