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THE HARVEY VOLCANIC SUITE, NEW BRUNSWICK. I. INCLUSIONS OF MAGMA IN QUARTZ PHENOCRYSTS

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ABSTRACT

The quartz phenocrysts of the quartz–feldspar porphyry member of the Cherry Hill unit, Harvey volcanic suite, New Brunswick, contain melt inclusions preserved as glass since the emplacement of this early Carboniferous ignimbritic sequence. Most of the small- and medium-sized inclusions were spared of any alteration or devitrification and yield a composition representative of the parent fluorine-rich (up to 2%), potassic, peraluminous rhyolitic magma (6.5% K_2O, 14.9% Al_2O_3, 71% SiO_2). Two types of minerals are found in the inclusions: trapped minerals (liquidus phases) and daughter minerals formed by incipient devitrification in some inclusions. Britholite $(Ce,Y)_3Ca_2(Si,P)_3O_{12}(OH,F)$, which is a fluorine- and rare-earth-rich (3.5–7.5% F, 48–50 wt.% *REE*,Y, U, Th) silicate–phosphate apatite-group mineral, magnetite and a Na-, Fe-rich fassaitic pyroxene are the common liquidus phases. High concentrations of Al, F, Rb and Th and low concentrations of Ba and Sr in the melt emphasize the similarity of the Harvey rocks with topaz (F-rich) rhyolites and ongonites.

Keywords: Carboniferous, rhyolite, melt inclusions, britholite, magnetite, fassaitic pyroxene, topaz rhyolites, Harvey volcanic suite, New Brunswick, ongonites.

SOMMAIRE

Les phénocristaux de quartz du porphyre à quartz et feldspath de l'unité Cherry Hill, de la suite volcanique de Harvey, Nouveau-Brunswick, contiennent des inclusions vitreuses conservées depuis la mise en place de cette suite d'ignimbrites, au début du Carbonifère. Ces inclusions, complètement isolées, ont été préservées de toute altération ou dévitrification, et indiquent un magma parent de composition rhyolitique, hyperalumineuse et potassique (6.5% K_2O, 14.9% Al_2O_3, 71% SiO_2), riche en fluor (jusqu'à 2% F). On trouve deux types de minéraux dans ces inclusions: minéraux piégés (sur le liquidus) et minéraux néoformés, qui représentent un début de dévitrification dans quelques inclusions. Britholite $(Ce,Y)_3Ca_2(Si,P)_3O_{12}(OH,F)$, silicate–phosphate du groupe de l'apatite riche en fluor et en terres rares (3.5–7.5% F, 48–50% terres rares, Y, U, Th), magnétite et un pyroxène fassaïtique riche en Na et Fe sont les minéraux piégés communs. Les fortes concentrations en Al, F, Rb et Th, et les faibles concentrations en Ba et Sr, font penser que les roches de Harvey auraient un lien avec les rhyolites à topaze (riches en F) et les ongonites.

Mots-clés: Carbonifère, rhyolite, inclusions vitreuses, britholite, magnétite, pyroxène fassaïtique, rhyolite à topaze, suite volcanique de Harvey, Nouveau-Brunswick, ongonites.

INTRODUCTION

The Harvey volcanic suite, exposed 55 km southwest of Fredericton, New Brunswick, is a 200-m-thick ignimbritic sequence of Lower Mississipian age. It is composed of volcanogenic sediments, ash-flow and ash-fall tuffs and rhyolite flows collectively referred to as the Harvey Group (Kuan 1970, Beaudin *et al.* 1980). Rocks of the Harvey volcanic suite outcrop over a 32-km^2 area along the northern edge of the Central Carboniferous basin, at the base of the Fredericton sub-basin (Fig. 1). The Harvey volcanic suite occurs at the same stratigraphic position as the Mount Pleasant rhyolitic centre, site of a W–Mo–Sn porphyry deposit, located on the southeastern limb of the basin (Ruitenberg & McCutcheon 1985).

This paper provides information on the nature of melt inclusions that are trapped in the quartz phenocrysts of the quartz–feldspar porphyry member of the Cherry Hill unit (Fig. 1; Beaudin *et al.* 1980, Payette & Martin 1986). These inclusions, preserved as glass, appear to have behaved as small closed systems since Carboniferous times, and may hold the key to the ultimate origin of the rhyolitic magma.

DESCRIPTION OF THE SPECIMENS

The porphyry is massive and does not display any obvious eutaxitic texture in hand specimen. However, thin-section studies clearly define the pyroclastic origin of this unit. Fragmented euhedral to subhedral phenocrysts of quartz (paramorphic after β-quartz) and K-feldspar are set in a purplish aphanitic matrix that contains flattened glass shards and pumice fragments, now devitrified. Small scattered greenish xenoliths are presumed to represent remnant altered basaltic material.

The melt inclusions are found in most of the quartz phenocrysts of the porphyry. This study deals with results from samples 2 and 13 (Fig. 1; Payette & Martin 1986), which were subjected to a detailed investigation. The inclusions are relatively abundant;

up to 35 were noted in a thick section (~200 μm) of a single phenocryst. They are usually randomly distributed about the crystal. In a few crystals the inclusions define growth zones about the *c* axis. Their shape varies from spherical to bipyramidal. They range in size from one to 275 μm, but in most cases are on the order of 10 to 50 μm across. The majority of the largest inclusions are devitrified and consequently have become opaque, owing either to internal crystallization or to hydrothermally induced devitrification as a consequence of cracks developed in the host phenocryst. The phenomena have been described in studies by Clocchiatti (1975), Takenouchi & Imai (1975), Roedder (1979) and Petrov & Marchev (1981).

The inclusions can be assigned to one of five groups on the basis of the phases observed: 1) single-phase transparent glass (Fig. 2A), 2) glass + bubble (Fig. 2B), 3) glass + bubble + daughter minerals (Fig. 2C), 4) glass + bubble + trapped minerals (Fig. 2D) and 5) devitrified glass (Fig. 2E).

All types of inclusions are common, with the exception of type 1, which is rare. Upon cooling of the melt phase, a contraction bubble commonly forms since the thermal contraction of the melt exceeds that of the enclosing crystal (Clocchiatti

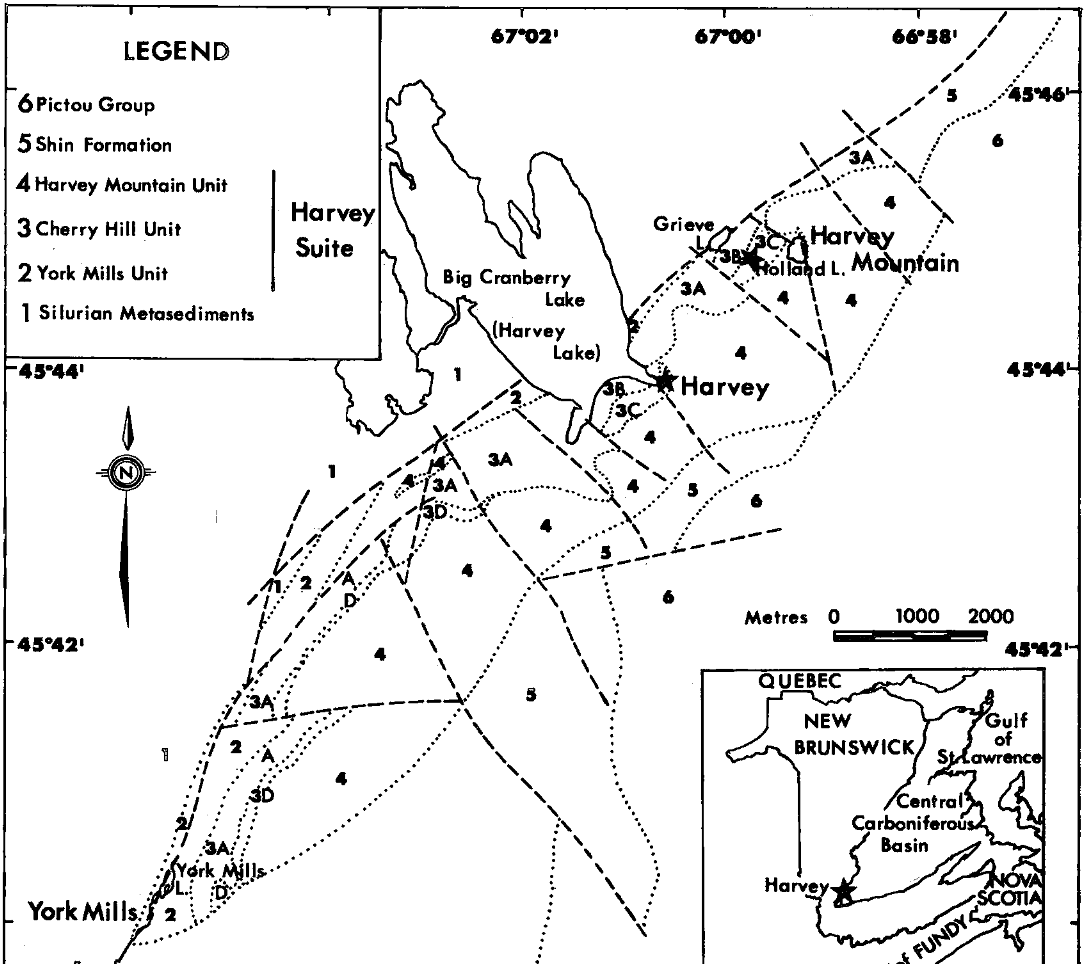

FIG. 1. Location map of the Harvey volcanic suite [2: York Mills unit, 3: Cherry Hill unit (A: volcanogenic sediments, B: ash-flow tuff, C: quartz–feldspar porphyry, D: ash-fall tuff)]. 4: Harvey Mountain unit. The contacts between the units are dotted; the faults are dashed. ★: Sample location (2, located beside Harvey Lake, and 13, located near Harvey Mountain). (Modified after Beaudin *et al.* 1980).

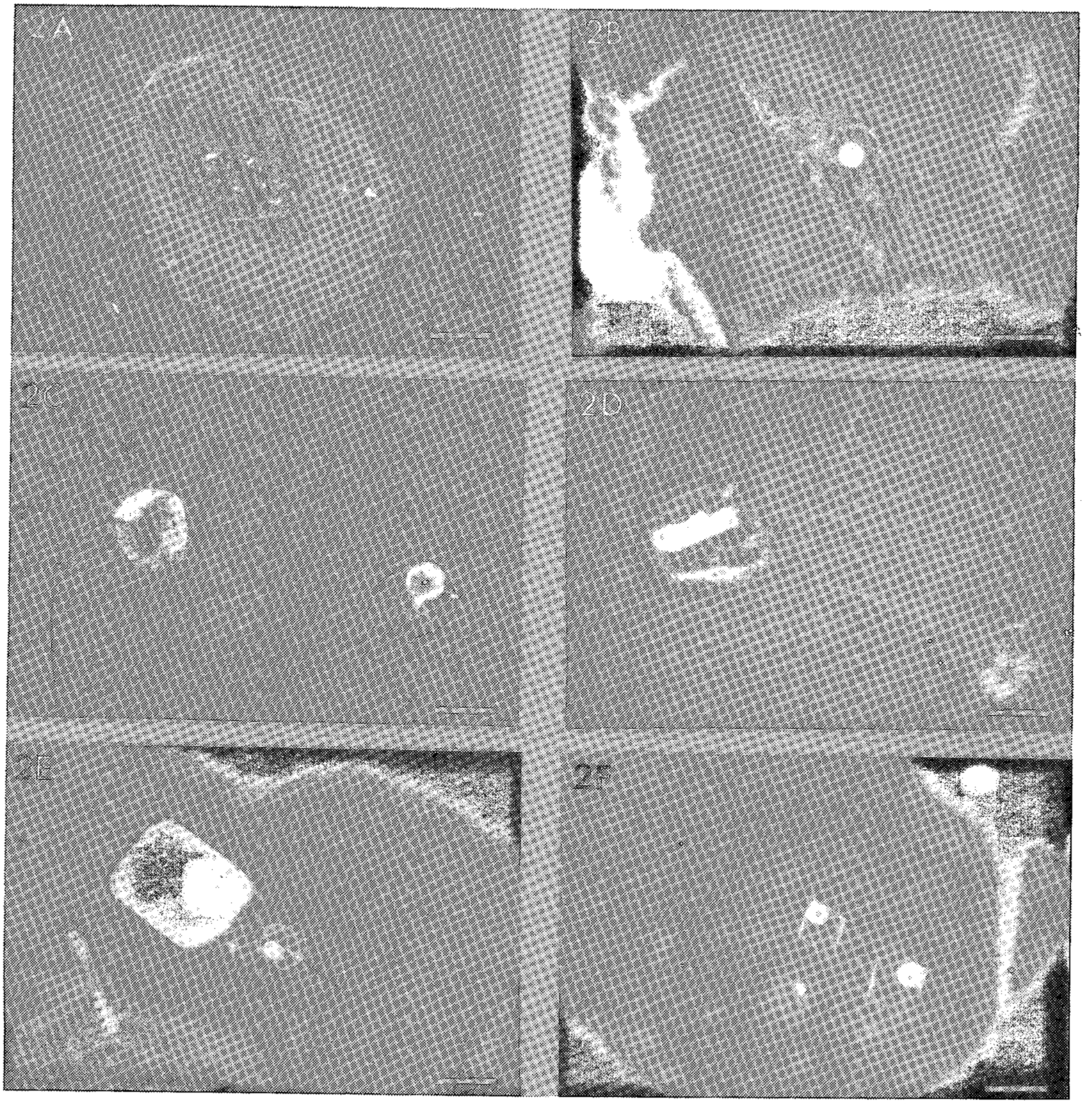

FIG. 2. Types of melt inclusions. A. single phase, transparent glass (scale bar 20 μm). B. Glass + bubble (scale bar 35 μm). C. Glass + bubble + daughter minerals (scale bar 30 μm). D. Glass + bubble + trapped minerals (pyroxene; scale bar 40 μm). E. Devitrified glass inclusion (black) with a smaller inclusion containing a trapped acicular mineral (scale bar 40 μm). F. Melt inclusions with a negative crystal-shape. The acicular mineral below the fibrous minerals inside the inclusions is unidentified (scale bar 75 μm).

1975). In the case of a melt undersaturated in water at the time of trapping, and thus characterized by a low vapor-pressure, the bubble in fact may essentially be under a vacuum (Roedder 1979). The size of the bubble provides an indication of the degree of shrinkage that occurred in the inclusion following entrapment and before solidification. If the volume of the bubble V_b is large relative to the volume of the cavity V_c for the collection of inclusions, a vapor phase may have been trapped along with the melt. The relative volume of the bubble may also be increased through the growth of daughter phases within the inclusion (Roedder 1979) and through the deposition of SiO_2 on the walls (Anderson 1973, Clocchiatti 1975). The volume V_b observed in this study is approximately 10 to 15% of the volume of the cavity.

The presence of a contraction bubble or of

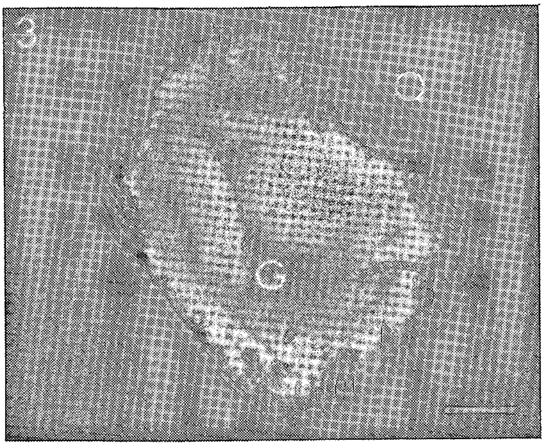

FIG. 3. Platelets of quartz on the walls of the inclusion. This type of epitactic deposition is unusual; the quartz is usually added as a continuous layer on the wall. The long fibre to the right is unidentified. The cavity is still partly filled with glass (G). Q: quartz host-crystal.

daughter minerals is largely a function of the cooling rate, the viscosity of the melt, and the overall size of the inclusion (Clocchiatti 1975, Takenouchi & Imai 1975, Roedder 1979). The nucleation and growth of daughter phases are restricted to a relatively narrow range of temperature (700–800°C is the optimum range: Clocchiatti 1975, Roedder 1979) and are favored in large inclusions. A slow rate of cooling is probably the main factor favoring the appearance of a contraction bubble and daughter crystals.

Following entrapment, quartz may deposit on the walls of the inclusion (Fig. 3), if temperature and cooling rate are favorable (Clocchiatti *et al.* 1978, Roedder 1979, Naumov *et al.* 1984, Clocchiatti & Massare 1985). Through this process of anisotropic growth (or, in some cases, perhaps through dissolution), the cavity gradually evolves from an initial round shape to that of a negative crystal (Fig. 2F; Clocchiatti 1975, Vincent 1982). The initial outline of the cavity (Fig. 3) can sometimes be traced by a diffuse contact between the original wall and the overgrowth or by a trapped or daughter mineral partly embedded in the new growth and abutting against the original host-crystal (Clocchiatti 1975, Roedder 1979, Laridhi 1981).

Most of the inclusions of the Harvey porphyry display a euhedral shape; some have reached the negative-crystal stage (Fig. 2F). Rare examples have reached a further stage, such that the faces of the negative crystal are now slightly concave, a habit characteristic of very slowly cooled systems (Clocchiatti 1975).

TABLE 1. CHEMICAL COMPOSITION OF THE TRAPPED MINERALS

	brith	brith	mag	mag	fas	fas	fas	fas
SiO_2 %	21.46	20.96	1.04	1.78	45.13	41.85	43.74	41.95
TiO_2	-	-	0.82	0.16	0.82	0.84	0.11	0.16
Al_2O_3	-	-	0.72	0.66	4.37	6.78	4.95	5.30
FeO	1.0	0.75	88.18	89.77	22.71	25.81	25.15	27.73
MnO	0.14	0.14	0.51	0.44	-	0.96	1.29	1.28
MgO	-	-	0.00	0.01	3.31	0.68	2.26	0.60
CaO	18.70	17.47	0.12	0.14	20.26	18.58	20.06	17.77
Na_2O	-	-	0.08	0.33	1.09	1.44	1.57	1.98
K_2O	-	-	0.06	0.29	0.07	0.36	0.05	0.06
P_2O_5	5.91	4.14	0.00	0.03	0.00	0.04	0.06	0.00
Y_2O_3	14.97	17.52	91.53	93.61	97.76	97.34	99.24	96.83
La_2O_3	2.23	1.74						
Ce_2O_3	8.13	6.82						
Pr_2O_3	1.40	1.21						
Nd_2O_3	7.77	7.53						
Sm_2O_3	3.42	3.55						
Eu_2O_3*	0.08	0.29						
Gd_2O_3	4.43	4.88						
Tb_2O_3	0.49	0.74						
Dy_2O_3	3.17	3.48						
Ho_2O_3*	2.12	2.55						
Er_2O_3*	1.51	1.52						
Tm_2O_3*	0.17	0.54						
Yb_2O_3*	0.77	0.89						
Lu_2O_3*	0.15	0.13						
ThO_2	1.66	1.95						
UO_2	0.45	0.59						
F	5.79	4.82						
O=F	2.43	2.02						
	103.49	102.19						

	Cation proportions			
Si	1.830	1.734	1.756	1.742
Ti	0.025	0.026	0.003	0.005
Al	0.209	0.331	0.234	0.259
Fe^{3+}	0.166	0.264	0.369	0.406
Fe^{2+}	0.605	0.629	0.474	0.557
Mn	0.000	0.034	0.044	0.045
Mg	0.200	0.042	0.135	0.037
Ca	0.880	0.824	0.862	0.790
Na	0.086	0.116	0.122	0.159
K	0.004	0.019	0.003	0.003
P	0.000	0.001	0.002	0.000
O	6.000	6.000	6.000	6.000

Brith: britholite, mag: magnetite, fas: Na-rich ferroan fassaitic pyroxene. The high totals for britholite are due to uncorrected overlap of the rare-earth peaks (see text). The first column gives an average of two data-sets. The low totals for pyroxene are probably due to the presence of elements not determined (such as Li and trace elements). * Concentrations uncorrected for overlap with other REE (Roeder 1985); the actual values may be significantly lower. Eu, Ho, Tm and Lu are probably close to 0.

MINERALS OBSERVED IN THE INCLUSIONS

Most of the melt inclusions contain 1) trapped crystals, that were fully grown when enclosed in the host phenocryst, and 2) daughter minerals, that nucleated upon cooling once the melt was trapped in the inclusion (Clocchiatti 1975, Roedder 1979). The daughter minerals occur as fibres, which commonly radiate from a point-source, generally consisting of an opaque speck on the wall of the bubble (Fig. 4A). In contrast, the trapped minerals, typically perfectly euhedral, display sharp edges and well-developed faces (Figs. 4B,C,D).

Three types of trapped minerals were identified: magnetite, clinopyroxene and britholite. The clinopyroxene occurs as elongate, bright green to yellowish green to yellowish brown prisms; these measure up to 60 μm in length (Fig. 4B). Their composition is intermediate between hedenbergite and fassaite, and corresponds closely to a sodic ferroan fassaite: $(Ca_{0.8-0.9}Na_{0.2-0.1})(Fe^{2+}_{0.5-0.7}Fe^{3+}_{0.5-0.2}Mg_{0-0.1}Al_{0-0.1})(Si_{1.7-1.9}Al_{0.3-0.1})O_6$; 3.6 to 6.8 wt.% Al_2O_3, 1.1 to 2.0 wt.% Na_2O (Table 1; Deer *et al.* 1978, 1980). Most of the pyroxene compositions (Table 1) yield low totals of 97 to 98%, which may be due to the presence of elements not determined, such as Li and Y. The values of the ratio 100 Mg/(Mg + total iron) recorded in the pyroxene range from 4 to 20, which is a reflection of the highly

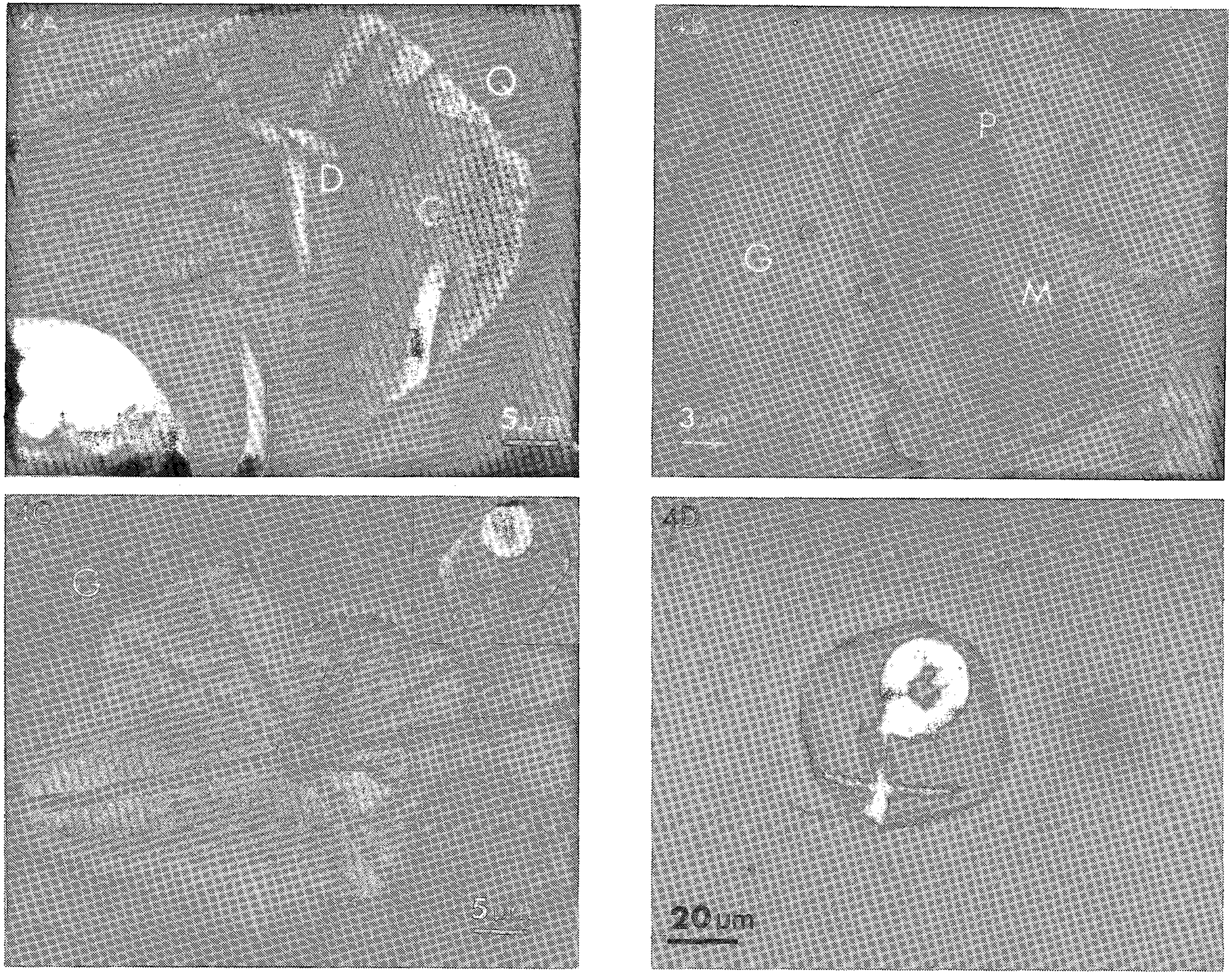

FIG. 4. SEM pictures of the minerals observed in the inclusions. Daughter minerals: A. acicular minerals (D) set in glass (G), possibly amphibole(?); Q: quartz host-crystal (scale bar 5 μm). The darker elongate "patches" were caused by etching of the glass with HF to emphasize the daughter minerals. Trapped minerals: B. Pyroxene (P) and magnetite (M) set in glass (G) (scale bar 3 μm). The acicular crystals to the left are most probably britholite. C. Britholite fibres set in glass (G) (scale bar 5 μm). Inset, same inclusion (180 μm across) before etching of the glass. D. Unidentified coil-like mineral in glass (G) in a quartz phenocryst (scale bar 20 μm).

evolved nature of the melt. The ratio (Na + K)/Al varies from 0.36 and 0.88, which illustrates the aluminous nature of this pyroxene.

A colorless, prismatic, hexagonal, 60-μm-long rare-earth-rich silicate–phosphate has been found and tentatively identified as britholite, which has the idealized formula $(Ce,Y)_3Ca_2(Si,P)_3O_{12}(OH,F)$ (Vasil'eva 1978, Fleischer 1980, Nekrasova & Nekrasov 1980; Table 1). Britholite has an apatite-type structure (Ito 1968, Griffin *et al.* 1979) and varies significantly in composition, which has led to the introduction of a complex scheme of classification. The variant identified in this study corresponds best to Y-britholite (Kupriyanova & Sidorenko 1963), of intermediate composition between lessingite (Ce-rich end-member) and abukumalite (Y-rich member; Nekrasova & Nekrasov 1980). The britholite crystals contain a minimum of 48 to 50 wt.% of the rare-earth elements expressed as oxides, Y, U and Th, but none (or only traces) of Al, Na, K, Sr, Zr and Cl; they are extremely enriched in F. Ion-microprobe data indicate the presence of Li in very small concentrations. In view of the very small size of the crystals, only the 60-μm prisms were analyzed from polished sections; for some elements, the rare-earth concentrations reported in Table 1 are uncorrected for overlap with other *REE*; in those cases, the actual concentrations may be significantly lower. Hydroxyl groups may be present, but only in small amounts owing to the extreme enrichment in F. Most compositions of britholite reported contain up to 2 or 2.5% F (Vlasov 1966, Bailey 1977, Griffin *et al.* 1979). The Harvey britholite contains 3.5 to 7.5% F, thereby reflecting a strong degree of F enrichment of the melt. Britholite may also be present in the form of small green needles, identified on the basis of the presence of Y and rare-earth peaks in the SEM X-ray spectrum. It has also been observed as thin brown rod-like hexagonal fibres associated with a Ca-rich silicate nucleus (Fig. 4C) and with small Si–Fe-rich deposits (not identified) along the fibres.

TABLE 2. CHEMICAL COMPOSITION OF THE GLASS AND COMPARISON WITH BULK ROCK, TOPAZ RHYOLITE AND ONGONITE

	1	2	3	4	5	6
SiO_2 %	71.1	71.4	79.5	80.0	76.0	71.0
TiO_2	0.04	0.04	0.08	0.08	0.6	-
Al_2O_3	14.7	14.9	10.8	10.6	13.0	16.0
Fe_2O_3	-	-	1.5	1.3	1.0	0.1
FeO	0.6	0.4	-	-	-	0.5
MnO	0.03	0.03	0.01	0.02	0.06	0.2
MgO	0.01	0.01	0.2	0.02	0.08	0.1
CaO	0.5	0.3	0.3	0.1	0.6	0.5
Na_2O	3.5	3.6	1.5	2.4	4.0	5.9
K_2O	6.4	6.7	4.9	4.5	4.8	3.5
P_2O_5	0.01	0.01	0.01	0.01	-	0.1
F	0.5*	0.2*	-	-	0.3	2.0
Cl	0.23*	0.2*	-	-	-	-
L.O.I.	-	-	1.4	0.8	-	1.0
total	97.6	97.8	100.2	99.8	100.4	100.9
A/CNK	1.12	1.11	1.34	1.19	1.06	1.15
Qtz	25.49	24.50	51.73	49.08	32.91	22.03
Ab	30.57	31.28	12.85	20.51	33.80	51.04
Or	39.03	40.65	29.31	26.85	28.32	21.14
D.I.	95	96	94	96	95	94

1. Average of 30 compositions of the glass included in quartz phenocrysts containing no trapped or daughter minerals, but only a contraction bubble (type-2 inclusion). Samples 2 and 13 (Fig. 1). Total iron expressed as FeO.
2. Average of 67 compositions of the glass included in quartz phenocrysts containing trapped and daughter minerals (melt inclusions of types 3 and 4). Samples 2 and 13 (Fig. 1). All concentrations were obtained by electron-microprobe analysis; total iron expressed as FeO.
3, 4. Average bulk-rock chemical composition of the devitrified quartz-feldspar porphyry, sampled at two different locations (Fig. 1): 2 (column 3) and 13 (column 4). Obtained by X-ray fluorescence. L.O.I. loss on ignition. Total iron expressed as Fe_2O_3.
5. Average composition of glassy topaz rhyolite (bulk rock) from the western United States (Christiansen *et al.* 1983). Total iron expressed as Fe_2O_3.
6. Average composition of crystalline (devitrified) ongonite (Kovalenko *et al.* 1971).
* Average fluorine content of the glass in the inclusions. The F content is variable, and attains 2 wt.% in the inclusions devoid of trapped and daughter minerals (*i.e.*, type 2). -: not determined.

Other trapped mineral phases were observed but remain unidentified: euhedral colorless (bipyramidal?) crystals, round opaque grains, green needles and various dendritic and coil-like forms (Fig. 4D).

The following assemblages were commonly encountered: 1) Clinopyroxene and magnetite, commonly with green needles (britholite?) (Fig. 4B). 2) Magnetite and unidentified colorless bipyramidal crystals, commonly occurring with colorless to green needles. 3) Stubby prisms of britholite (60 μm), usually found as solid inclusions in quartz, with little or no associated glass. Their habit differs from that of the radiating fibres (Fig. 4C) within glass-bearing inclusions. This difference in crystal habit suggests that britholite crystallized at more than one stage in the magma prior to trapping. Assemblages 1 and 3 (radiating fibres) may occur in the same quartz phenocryst, but not in the same inclusion.

The daughter minerals are long, acicular, brown fibres without crystalline faces (Fig. 4A). They are less common than the trapped minerals, and their amount varies from inclusion to inclusion. The daughter minerals were not analyzed by electron microprobe owing to their small size, but were found to contain Si, Al, Na, K and Fe using by an EDS system attached to the SEM (see Appendix); they may be amphibole (R. Clocchiatti, pers. comm.).

THERMOMETRY

Theoretically, the homogenization temperature T_h, the minimum temperature at which all constituents (glass, crystals and gas bubble) become one phase, should be nearly identical to the temperature of trapping and, thus, of formation of the host mineral (Roedder 1979). Daughter phases should dissolve *before* complete homogenization, and the trapped minerals *after* T_h is reached.

The inclusions were initially heated to 550°C for one hour (see Appendix), and then kept 30 minutes to equilibrate at every additional 50°C step. Heating-stage studies indicate that melting begins between 700 and 750°C (indicating a low volatile content: R. Clocchiatti, pers. comm.); small bubbles start appearing, but these do not coalesce or redissolve upon cooling. The melt does not homogenize, even at temperatures above 1000°C; this may be due to leakage of the melt through small fractures in the host phenocryst (R. Clocchiatti 1975, pers. comm., Takenouchi & Imai 1975). Upon heating, some of the mineral phases dissolved, the first ones being the fibres of daughter mineral(s) (Fig. 4A) at ~900°C. However, the opaque speck to which they were "attached" remains intact, and most of the trapped minerals are still not dissolved at ~1150°C. Studies over a long time-span or at a higher temperature were not carried out, largely because of the kinetic problems expected in working with such high-viscosity compositions.

COMPOSITION OF THE GLASS

The composition of the glass phase was determined by electron-microprobe analysis (see Appendix). The average composition (on the basis of 97 analyses) is SiO_2 71.3, TiO_2 0.04, Al_2O_3 14.8, MgO 0.01, FeO 0.4, MnO 0.03, CaO 0.4, Na_2O 3.6, K_2O 6.5, P_2O_5 0.01, Cl 0.2–0.5% and variable F contents, total 97.1 wt.% (Table 2). The range of compositions observed is as follows: SiO_2: 67 to 74%, TiO_2: 0 to 0.11%, Al_2O_3: 13 to 16%, MgO: 0 to 0.06%, FeO: 0.11 to 1.10%, MnO: 0 to 0.08%, CaO: 0.1 to 0.8%, Na_2O: 2.5 to 4.5%, K_2O: 5 to 7.8%, P_2O_5: 0 to 0.07%. The totals range from 91.96 to 100.55%, not including F. The glass seems to be inhomogeneous relative to F, as very different concentrations (0 to 1.97%) were obtained on various inclusions (see Clocchiatti & Nativel 1984). The Cl content is constant, at 0.15 to 0.25, and averages 0.21 wt.%, with a few values attaining 0.30 wt.%. Totals below 99 to 100% (97.8%, 97.6%, Table 2) are taken to reflect

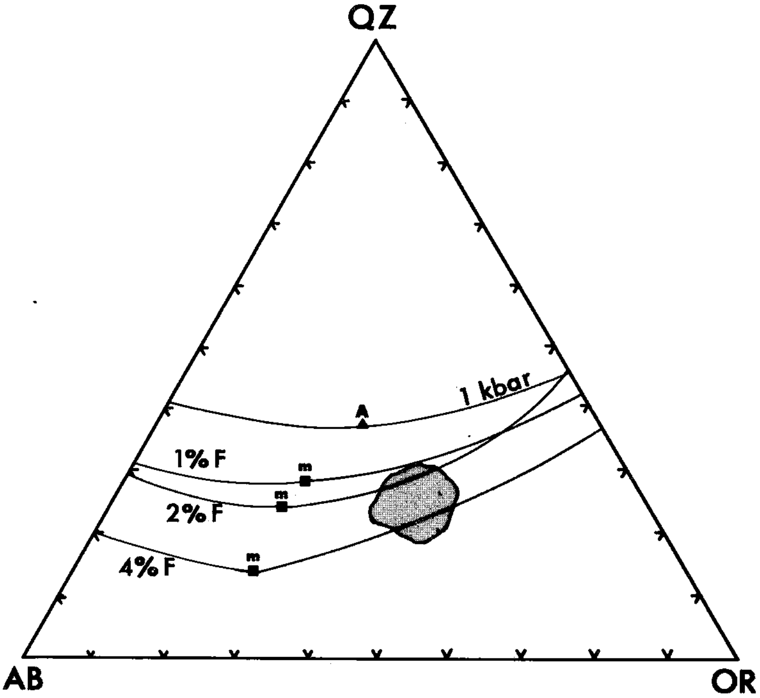

FIG. 5. Composition of the glass in terms of normative quartz, albite and orthoclase (Table 2) superposed on the experimentally determined curves with 1, 2 and 4% F and the cotectic in the water-saturated haplogranite system at 1 kbar (after Luth 1976, Manning 1981). m: minimum in the fluorine-bearing system; A: minimum in the fluorine-free system.

the presence of dissolved volatiles, largely water (Anderson 1973, Sommer 1977, Chaigneau *et al.* 1980, Laridhi 1981, Beddoe-Stephens *et al.* 1983), F and Cl (Naumov *et al.* 1984, Clocchiatti & Nativel 1984). The average content of dissolved volatiles is thus about 2 to 3%. The trace-element concentrations could not be determined. The peraluminous character of the glass is indicated by the A/CNK ratio, which varies from 1.0 to 1.4 (average 1.1), and is consistent with the presence of a fassaitic pyroxene. Except for the fluorine content, the compositions of glass in columns 1 and 2 are remarkably similar, and quite different from the bulk rock (compositions 3,4), which presumably should have a composition similar to the melt trapped in the quartz phenocrysts (see also Payette & Martin 1986). We contend that the viscosity of such an evolved melt is so great that any phenocrysts in the bulk rock crystallized *in situ*. The Harvey magma shows a strong affinity to ongonite and topaz rhyolite (compositions 5 and 6, Table 2), except that it is distinctly potassic. This is best illustrated in a triangular plot of normative quartz, albite and orthoclase (Fig. 5), on which are superposed the compositions of the glass listed in Table 2 (columns 1 and 2).

DISCUSSION

Minerals observed in the inclusions

Britholite has never been described as a liquidus phase in rhyolitic magmas. Rather it typically is an accessory phase in alkaline rocks, related pegmatites and metasomatic rocks, albitites and nepheline syenites. It has been reported, for example, in carbonatite (Oka, Quebec: Hughson & Sen Gupta 1964), in hydrothermal veins in peralkaline felsic complexes (Mount Prindle, Alaska; Mountain Pass, California: Mariano 1981) and pegmatites [Baikal area, USSR: Glushchenko & Li (1966); Reiarsdal, Vest-Agder, Norway; Griffin *et al.* (1979)]. Its presence is generally considered to reflect formation under conditions of sodium metasomatism, with the participation of fluorine (Vasil'eva 1978, Vasil'eva & Tsepin 1980); this is corroborated by its paragenetic association with fluorite in areas affected by high-temperature hydrothermal solutions (Kozlova & Gurvich 1979, Mariano 1981). The Harvey example shows that this rare-earth-rich phase has a field of stability that extends to magmatic temperatures. Furthermore, it can occur in a potassic environment and is evidently not restricted to peralkaline media. As the Harvey britholite does not contain much Na, K and Al, and as it is enriched in calcium, similar to several published compositions (Vlasov 1966, Glushchenko & Li 1966, Vrublevskii *et al.* 1984), its role as a liquidus phase could perhaps be expected in peralkaline as well as peraluminous systems.

The variety yttrobritholite, which typically contains between 37 and 47% $Y_2O_3 + Dy_2O_3 + Ce_2O_3$, occurs in alkali granite pegmatites with fluorite, magnetite and zircon (Vlasov 1966); there, as at Harvey, it may reflect enrichment of the environment in the heavy rare-earths. It could perhaps be expected in topaz rhyolites, which also display an enrichment in Y and the heavy rare-earths (Christiansen *et al.* 1984).

The presence of magnetite trapped in melt inclusions has been reported in plagioclase phenocrysts in andesite (Clocchiatti 1975, Babanskiy *et al.* 1980) and as a daughter mineral in inclusions in quartz phenocrysts in ongorhyolite, along with biotite, K-feldspar, albite, fluorite and quartz (Naumov *et al.* 1984). As in the case of andesite, its appearance on the liquidus of the Harvey rhyolite presumably indicates a relatively high fugacity of oxygen.

It should be noted that britholite, fassaitic sodium-bearing iron-rich pyroxene and magnetite were not found as microphenocrysts in the bulk rock (Payette & Martin 1986); the samples are strongly oxidized, hematite-bearing, and generally devoid of primary assemblages except for the quartz phenocrysts. These phases were presumably destroyed and the feldspar phenocrysts modified as the rock cooled and recrystallized in the presence of water.

Thermometry

The aim of heating-stage studies is 1) to determine the possible trapping temperature of the melt, 2) to distinguish daughter (subliquidus) from trapped mineral phases (liquidus phases) and 3) to establish their sequence of crystallization, indicated by their dissolution temperature. This approach assumes that the temperature of disappearance of the trapped minerals upon reheating should be representative of the temperature at which they had initially crystallized on cooling, at equilibrium (Roedder 1979). In similar studies, Gigashvili (1969), in Bailey (1977) reported a melting temperature of 700°C for solid inclusions in quartz from a pegmatite; he identified mica, albite, topaz, lepidolite and alunite(?) coexisting with a vapor phase (15–25 vol. %); most of these trapped phases had melted by 960°C. Naumov *et al.* (1971) reported melting of the glass phase in melt inclusions from topaz phenocrysts from ongonites at 550 to 600°C. The inclusions homogenized in the interval 920–1020°C. Upon heating, a few bubbles appeared, and upon cooling, remained in fixed positions. Naumov *et al.* (1984) reported temperatures of homogenization of 760–830°C for melt inclusions from quartz phenocrysts from ongorhyolites. Experimental studies on the granite–H_2O–F system suggest minimum melting temperatures of 690–730°C for a water-saturated melt containing 2% F at 1 kbar

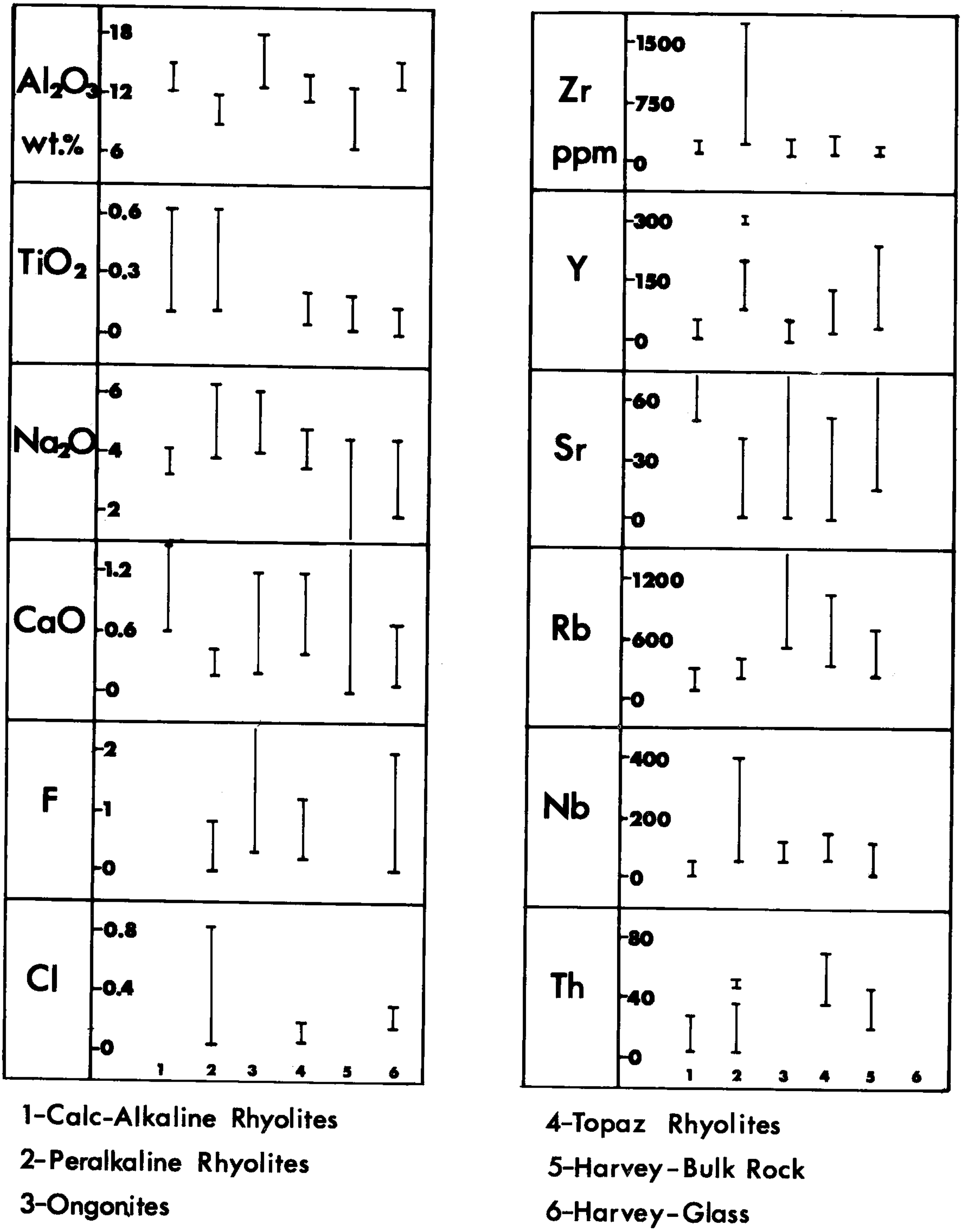

FIG. 6. Comparison of the chemical composition of rhyolitic glass and bulk rocks encountered at Harvey with the major and trace-element contents typical of calcalkaline rhyolite, peralkaline rhyolite, topaz rhyolite and ongonite (modified after Christiansen *et al.* 1983).

(Manning 1981). Equilibration temperatures calculated from two-feldspar and Fe–Ti oxide geothermometry for topaz rhyolites range from 600 to 850°C (Christiansen *et al.* 1983, 1984). In studies of rhyolites and porphyries, Clocchiatti (1975) obtained a T_h lower than 850–900°C for volatile-rich inclusions, and T_h from 900 to 1200°C for volatile-poor melts, similar to the results of Takenouchi & Imai (1975) for rhyolites from Japan; they also reported inclusions in which T_h was not reached by 1200°C; they attributed this result to the escape of volatiles in cracks in the host phenocryst. The temperature of initiation of melting reported here for the melt inclusions in the Harvey rocks (700–750°C) corresponds well with experimental results obtained both on synthetic and natural melts; T_h for the Harvey rocks should therefore be expected to be lower than 1100–1150°C. T_h was not reached, probably owing to the very high viscosity of the melt, precluding coalescence of the bubbles, extensive SiO_2 crystallization on the walls, an inclusion size too large, insufficient time for equilibration (see Appendix), or most likely, leakage of the melt into small fractures in the host phenocryst, (re)opened at the time of the α–β quartz transition.

Differences in composition between the bulk rock and the glass

The compositions of the included glass and the bulk rock are compared in Table 2 and Figure 6. The glass shows higher concentrations of Al, Na and K than in the bulk rock and less Si and Fe. The high variability in the composition of the glass is typical of old glasses (R. Clocchiatti, pers. comm.). The minor elements Ti, Mg, Mn, Ca and P show similar low concentrations, which are indicative of a highly evolved rhyolite (Miller & Mittlefehldt 1984). The F and Cl contents are most probably larger in the glass than in the bulk rock. This is as expected from the findings of Noble *et al.* (1967), who have documented a common loss of halogens (up to ~50% loss of F and 80% of Cl) upon devitrification of similar silicic welded tuffs.

The amount of volatiles modifies the concentrations of all elements by "dilution", a fact also reported by Naumov *et al.* (1984). The melt inclusions devoid of mineral phases tend to have a higher volatile (H_2O) content, although this difference tends to disappear when F and Cl are taken into account. The difference may indicate the presence of a zonation(?) in the magma chamber, with the upper level richer in volatiles and the lower level, richer in small crystals (such as the trapped minerals).

Comparison with topaz rhyolite

A comparison of the Harvey rhyolite (bulk rock 5, and glass 6 in Fig. 6) to other types of rhyolite (calcalkaline 1, peralkaline 2, ongonite 3 and topaz rhyolite 4) emphasizes its similarity with topaz rhyolite and ongonite (Table 2). A slightly aluminous character in both the glass and bulk rock, high concentrations in F, Rb, U and Th, and very low concentrations in Ba and Sr are characteristic of F-rich (topaz) rhyolites, ongonites and ongorhyolites (Christiansen *et al.* 1983, 1984, Naumov *et al.* 1984). The Al_2O_3 content (15%) of the Harvey magma (glass) is slightly higher than the average content for topaz rhyolites (13%; Christiansen *et al.* 1983), but Kovalenko *et al.* (1971), Herrera *et al.* (1984) and Kontak *et al.* (1984) reported values similar to those of Harvey (Table 2) (except for their Na/K ratio, which is characteristically greater than 1, opposite to that at Harvey). The F/Cl ratio of the glass at Harvey is variable, from <1 to ~6.7. Christiansen *et al.* (1983) emphasized that the F/Cl ratio should exceed 3 for topaz rhyolite, but this ratio is ~2–3 in ongorhyolites (Naumov *et al.* 1984; a value below 3 is typical of peralkaline rhyolites). A low F/Cl value in the Harvey rocks (usually close to 3) could perhaps account for the apparent absence of topaz. On the other hand, the variability of the F content in the glass may be due to the local formation of high-temperature F-rich minerals such as britholite.

In the Qtz–Ab–Or diagram (Fig. 5), the composition of the Harvey glass is displaced toward the Or apex, away from the minimum in the Qtz–Ab–Or–H_2O systems at 1 kbar (A). As the specimen contain quartz *and* a K-rich feldspar as phenocryst phases, the trapped melt must plot close to the cotectic. However, for the cotectic to pass through the melt compositions, the primary field of quartz must be considerably expanded with respect to the situation in the haplogranite system at a $P(H_2O)$ of 1 kilobar. An increase in water pressure to 2 kbar may be a step in the right direction, but cannot explain the anomaly.

Manning (1981) has shown that the addition of fluorine to the haplogranite system does lead to a marked expansion of the field of primary crystallization of quartz. On Figure 5, the cotectic curves for the cases of 1, 2 and 4% F are also shown (minimum, m). The addition of fluorine has the effect of lowering the solidus (see also Luth 1976, Bailey 1977, Wyllie 1979) and shifting the location of the minimum toward the Ab apex. Minor elements such as Li, B and Cl may also affect the location of the cotectic relevant to the Harvey samples. The data points cluster around the cotectic curves for 2 and 4% F, in accordance with the measured fluorine content of the glass (up to 2%).

The melt continued to crystallize quartz on the walls of the inclusion (Fig. 3), whose shape evolved progressively to that of a negative crystal. How much of this later growth took place is generally not clear, so that it is difficult to correct the composition of the melt and its co-ordinates in Figure 5. One possible test in future studies will be to attempt much longer heating experiments, to allow the new wall-material to redissolve into the melt. A microprobe determinatin of the composition of the quenched melt after such an experiment will presumably provide a more accurate composition of the melt. At this point, however, we can only state our opinion that such a correction will be minor, and that the influence of fluorine will still be necessary to explain the expanded primary field of quartz.

Whatever the correction to the silica content of the melt, there is no reason to correct its measured K/Na ratio (if no volatile loss occurred), which would not change as a result of deposition of silica on the walls. There may be parts of the ignimbritic system at Harvey that contain melt inclusions closer to the minimum composition in terms of K/Na ratio. These remain to be discovered.

In the absence of isotopic data for the Harvey rocks, we tentatively assign the generation of a potassic, peraluminous, granitic liquid to the anatexis of continental crust containing metapelitic rocks. The heat source for this anatectic reaction could be provided by mantle-derived basalts that intruded the area in the incipient stages of rifting that led to the formation of the Central Carboniferous basin in New Brunswick.

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REFERENCES

ANDERSON, A.T., JR. (1973): The before-eruption water content of some high-alumina magmas. *Bull. Volc.* **37**, 530-552.

BABANSKIY, A.D., SOLOVOVA, I.P., RYABCHIKOV, I.D. & BOGATIKOV, O.A. (1980): Parental magma of rocks of the alkaline-earth series, as shown by study of melt microinclusions. *Dokl. Acad. Sci., Earth Sci. Sect.* **253**, 162-164.

BAILEY, J.C. (1977): Fluorine in granitic rocks and melts: a review. *Chem. Geol.* **19**, 1-42.

BEAUDIN, J., LEGALLAIS, C. & SCHIMANN, K. (1980): Rapport final des travaux de la campagne 1979. Groupe de claims Manners Sutton. Projet 24-147, comté York, Nouveau-Brunswick, Vol. 1. Rapport interne (non publié), SERU Nucléaire du Canada Ltée, Montréal.

BEDDOE-STEPHENS, B., ASPDEN, J.A. & SHEPHERD, T.J. (1983): Glass inclusions and melt compositions of the Toba tuffs, northern Sumatra. *Contr. Mineral. Petrology* **83**, 278-287.

CHAIGNEAU, M., MASSARE, D. & CLOCCHIATTI, R. (1980): Contribution à l'étude des inclusions vitreuses et des éléments volatils contenus dans les phénocristaux de quartz de roches volcaniques acides. *Bull. Volc.* **43**, 233-240.

CHRISTIANSEN, E.H., BIKUN, J.V., SHERIDAN, M.F. & BURT, D.M. (1984): Geochemical evolution of topaz rhyolites from the Thomas Range and Spor Mountain, Utah. *Amer. Mineral.* **69**, 223-236.

______, BURT, D.M., SHERIDAN, M.F. & WILSON, R.T. (1983): The petrogenesis of topaz rhyolites from the western United States. *Contr. Mineral. Petrology* **83**, 16-30.

CLOCCHIATTI, R. (1975): Les inclusions vitreuses des cristaux de quartz. Etude thermo-optique et chimique. Applications géologiques. *Soc. Géol. France Mém.* **122.**

______, HAVETTE, A., WEISS, J. & WILHELM, S. (1978): Les bytownites du rift d'Asal. Etude des verres basaltiques inclus dans les mégacristaux: nouvelle approche pour la connaissance de certains processus pétrogénétiques. *Bull. Minéral.* **101**, 66-76.

______ & MASSARE, D. (1985): Experimental crystal growth in glass inclusions: the possibilities and limits of the method. *Contr. Mineral. Petrology* **89**, 193-204.

______ & NATIVEL, P. (1984): Etude minéralogique et découverte de reliquats magmatiques silicosodiques hydratés dans les phénocristaux de quartz de la syénite de Cilaos (Ile de la Réunion). *C.R. Acad. Sci. Paris* **299** (II), 451-456.

DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1978): *Rock-Forming Minerals. 2A. Single-Chain Silicates (2nd edition).* Longman, London.

______, ______ & ______ (1980): *An Introduction to the Rock-Forming Minerals (2nd edition).* Longman, London.

FLEISCHER, M. (1980): *Glossary of Mineral Species 1980.* The Mineralogical Record, Tucson, Arizona.

GIGASHVILI, G.M. (1969): Primary gas–solid inclusions in quartz from the Volyn pegmatites. *Mineral. Sb. (Lvov)* **23**(4), 398-404 (in Russ.).

GLUSHCHENKO, A.A. & LI, A.F. (1966): Britholite from an alkaline massif in the Northern Baikal area. *Nauch. Tr. Irkutsk. Gos. Nauch. — Issled. Inst. Redk. Tvsvet. Met.* **14,** 100-107 (in Russ.).

GRIFFIN, W.L., NILSSEN, B. & JENSEN, B.B. (1979): Britholite(-Y) and its alteration: Reiarsdal, Vest-Agder, south Norway. Contributions to the mineralogy of Norway, no. 64. *Norsk Geol. Tidsskr.* **59,** 265-271.

HERRERA, J.V., PICHAVANT, M. & ESTEYRIES, C. (1984): Le volcanisme ignimbritique peralumineux plio-quaternaire de la région de Macusani, Pérou. *C.R. Acad. Sci. Paris* **298** (II), 77-82.

HUGHSON, M.R. & SEN GUPTA, J.G. (1964): A thorian intermediate member of the britholite–apatite series. *Amer. Mineral.* **49,** 937-951.

ITO, J. (1968): Silicate apatites and oxypatites. *Amer. Mineral.* **53,** 890-907.

KONTAK, D.J., PICHAVANT, M. & CLARK, A.H. (1984): Petrology of the Pliocene peraluminous volcanics from Macusani, SE Peru. *Amer. Geophys. Union Trans.* **65,** 299 (abstr.).

KOVALENKO, V.I., KUZ'MIN, M.I., ANTIPIN, V.S. & PETROV, L.L. (1971): Topaz-bearing quartz keratophyre (ongonite), a new variety of subvolcanic igneous vein rock. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **199,** 132-135.

KOZLOVA, P.S. & GURVICH, M.YU. (1979): The behaviour of uranium on postmagmatic alteration of potassic alkali rocks. *Geochem. Int.* **16**(4), 109-117.

KUAN, S. (1970): *The Geology of Carboniferous Volcanic Rocks in the Harvey Area, New Brunswick.* M.Sc. thesis, Univ. New Brunswick, Fredericton, N.B.

KUPRIYANOVA, I.I. & SIDORENKO, G.A. (1963): Minerals of the britholite group. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **148,** 109-111.

LARIDHI, N. (1981): *Contribution à l'Etude des Laves Hyperalcalines de l'Ile San Piétro (Sardaigne).* Thèse de 3^e cycle, Université de Paris-Sud, Centre d'Orsay, Paris.

LUTH, W.C. (1976): Granitic rocks. *In* The Evolution of the Crystalline Rocks (D.K. Bailey & R. Macdonald, eds.). Academic Press, London.

MANNING, D.A.C. (1981): The effect of fluorine on liquidus phase relationships in the system Qz–Ab–Or with excess water at 1 kb. *Contr. Mineral. Petrology* **76,** 206-215.

MARIANO, A.N. (1981): Rare earth mineralization in Mount Prindle, Alaska. *Internal report for Mapco Inc.*, Tulsa, Oklahoma.

MILLER, C.F. & MITTLEFEHLDT, D.W. (1984): Extreme fractionation in felsic magma chamber: a product of liquid-state diffusion or fractional crystallization? *Earth Planet. Sci. Lett.* **68,** 151-158.

NAUMOV, V.B., KOVALENKO, V.I., CLOCCHIATTI, R. & SOLOVOVA, I.P. (1984): Crystallization parameters and phase compositions for melt inclusions in ongorhyolite quartz. *Geochem. Int.* **21,** 451-463.

______, ______, KUZ'MIN, M.I., VLADYKIN, N.V. & IVANOV, G.F. (1971): Thermometric study of inclusions of melt in topaz from topaz-bearing quartz keratophyre (ongonite). *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **199,** 104-106.

NEKRASOVA, R.A. & NEKRASOV, I. YA. (1980): New data on minerals of the britholite group. *Geokhim., Mineral.* 170-176 (in Russ.).

NOBLE, D.C., SMITH, V.C. & PECK, L.C. (1967): Loss of halogens from crystallized and glassy silicic volcanic rocks. *Geochim. Cosmochim. Acta* **31,** 215-223.

PAYETTE, C. & MARTIN, R.F. (1986): The Harvey volcanic suite, New Brunswick. II. Postmagmatic adjustments in the mineralogy and bulk composition of a high-fluorine rhyolite. *Can. Mineral.* **24,** 571-584.

PETROV, P. & MARCHEV, P. (1981): Glass inclusions in quartz phenocrysts from acid volcanic rocks (Borovitsa volcanic region, Bulgaria). *Dokl. Bolg. Akad. Nauk* **34,** 1425-1427.

ROEDDER, E. (1979): Origin and significance of magmatic inclusions. *Bull. Minéral.* **102,** 487-510.

ROEDER, P.L. (1985): Electron-microprobe analysis of rare-earth elements using calculated peak-overlap corrections. *Can. Mineral.* **23,** 263-271.

RUITENBERG, A.A. & MCCUTCHEON, S.R. (1985): Tungsten, molybdenum and tin deposits in New Brunswick. *Geol. Assoc. Can - Mineral. Assoc. Can., Guidebook Excursion* **13.**

SOBOLEV, V.S. & KOSTYUK, V.P., eds. (1975): Magmatic Crystallization Based on Study of Melt Inclusions. *Trudy Inst. Geol. Geofiz., Sib. Otd., Akad. Nauk SSSR* **264** (in Russ.; translation in Fluid Inclusion Res. **9,** 182-253).

SOMMER, M.A. (1977): Volatiles H_2O, CO_2, and CO in silicate melt inclusions in quartz phenocrysts from the rhyolitic Bandelier air-fall and ash-flow tuff, New Mexico. *J. Geol.* **85,** 423-432.

TAKENOUCHI, S. & IMAI, H. (1975): Glass and fluid inclusions in acidic igneous rocks from some mining areas in Japan. *Econ. Geol.* **70**, 750-769.

VASIL'EVA, Z.V. (1978): Chemical composition and typomorphic features of britholite. *In* Sostav Strukt. Mineral. Pokazateli Ikh Genezisa (F.V. Chukhrov & N.V. Petrovskaya, eds.). Izd. Nauka, Moscow (in Russ.).

______ & TSEPIN, A.I. (1980): Zoned britholite. *Geokhim.*, 730-738 (in Russ.).

VINCENT, D. (1982): *Datation des Quartz Volcaniques par la Méthode des Traces de Fission. Le Problème des Nappes de Ponces du Mont Dore.* Thèse de 3e cycle, Université de Paris-Sud, Centre d'Orsay, Paris.

VLASOV, K.A., ed. (1966): *Chemistry and Mineralogy of Rare Elements and Genetic Types of their Deposits. I. Geochemistry of Rare Elements. II. Mineralogy of Rare Elements.* Nauka, Moscow (translated by Israel Program for Scientific Translations, Jerusalem).

VRUBLEVSKII, V.A., KOROLYUK, V.N., PAL'CHICK, N.A. & REVERDATO, V.V. (1984): Britholite from nepheline syenites of the Berikul region (Kuznetsk Alatau). *Zap. Vses. Mineral. Obshchest.* **113**(1), 59-61 (in Russ.).

WHITE, S.H., GRANT, P.R. & BRODIE, K.H. (1980): Application of electron microscopy in geology. Short Course Notes, Imperial College of Science and Technology, London.

WYLLIE, P.J. (1979): Magmas and volatile components. *Amer. Mineral.* **64**, 469-500.

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APPENDIX

Sample preparation

For microprobe, heating-stage and SEM studies, samples were selected from doubly polished sections (150–250 μm in thickness). For the SEM study, the procedure followed is modified after that of Vincent (1982). The most representative samples of the mineral phases observed in the melt inclusions were chosen. The samples selected were polished until the desired section of the magmatic inclusion showed on the surface of the small polished slab. The inclusions were analyzed at this point, before any further treatment. They were then etched with HF (50–55%) vapor for a few seconds to a few minutes, depending on the thickness of the inclusion and the amount of glass that had to be dissolved. A thin film of carbon was then evaporated onto the surface of each sample.

The main advantages of this method are 1) the possibility of selecting the inclusion and mineral phase to be examined and 2) the ability to insure that no mineral phases are lost upon opening and polishing of the inclusion; they may, unfortunately, be dissolved by HF, sometimes as fast as the enclosing glass phase.

Scanning-electron microscopy

The scanning-electron microscope (SEM) part of a scanning–transmission electron microscope JEOL 100 CX TEMSCAN was used in conjunction with an energy-dispersion system (EDS) PGT System 4 in order to identify the major elements present in mineral phases too small to be analyzed by electron microprobe. The three-dimensional imaging capabilities of the SEM allow the observation of deep-seated minerals within the inclusion cavity. The main advantages of an EDS is that a complete X-ray spectrum of all elements with an atomic number of 11 or greater is obtained from a single point on a sample (White *et al.* 1980). The disadvantages are 1) its poor resolution of energy, *i.e.*, overlapping of peaks of interest (*e.g.*, Ce, Nd) (White *et al.* 1980, Roeder 1985) and, 2) mainly, its inability to provide direct quantitative analysis.

The analytical conditions used were an accelerating voltage of 80 kV and a current of 80 nA with a beam size of 100–150 Å in diameter. The magnification ranged from 10× to 50 000×.

A number of analytical problems were encountered with this method. To be detected, an element normally must have a concentration greater than 5% or an atomic number greater than 11; however, in some instances, Fe was detected at a concentration lower than 1% (*e.g.*, in the rhyolitic glass, and also in britholite). Moreover, the tilt angle of the specimen influences the number of counts obtained. If the mineral is located deep within a cavity, the X-rays produced may rebound within the cavity and may not be recorded by the detector.

Electron microprobe

The electron microprobe was used in order to obtain precise compositions of the glass phase and of the larger grains of included mineral phases; however, the size of the trapped and daughter-mineral phases sets limits on its applicability. An accelerating voltage of 15 kV, a current of 8 nA, a beam diameter of 5 μm and a counting time of 10 seconds were chosen to avoid volatilization of the alkalis; for all other elements, a counting time of 20 seconds was used.

There are problems associated with an analysis by electron microprobe. Firstly, the size of inclusion or its depth (if the inclusion is thin) may lead to an overlap with the host crystal, thus giving an intermediate composition. Reported compositions of glass are thus from the central portion of large inclusions, in order to avoid any overlap with the host crystal and any compositional gradient possibly caused by SiO_2 deposition on the walls. Also, for the mineral phases, there may be overlap with the enclosing glass; for a clinopyroxene, this would increase Si, Al, Na, K and decrease Fe, Mg, Mn, Ca. An analysis of very thin crystals (a few μm thick) would have the same drawbacks;

in addition, there may be a thin film of glass partly covering the trapped crystal. Finally, the common association of clinopyroxene and magnetite enhances the possibility of overlap.

Heating stage

The heating stage used was a Leitz Heating Stage 1350°C coupled with a Pt - Pt 10% Rh thermocouple and water cooling system. The stage was calibrated against the melting points of pure substances and compounds such as $K_2Cr_2O_7$ (398°C), Ag (962°C) and Au (1063°C). The samples were initially kept at 550°C for 1 hour, and for 30 minutes at every additional 50°C step.

The homogenization temperature T_h may be higher than the actual temperature of trapping, possibly by up to 100°C (Roedder 1979). Highly viscous melts, high content of water in the glass, thermal gradients in the stage, inadequate time for equilibration and loss of hydrogen (Sobolev & Kostyuk 1975) or water from the melt may all contribute to this bias (Roedder 1979). The use of small inclusions eliminates most of these problems.