

## FRACTIONATION TRENDS DEFINED BY RESIDUAL GLASSES IN THE LAVAS AND XENOLITHS OF PITON DE LA FOURNAISE, REUNION ISLAND

JOHN N. LUDDEN\*

*Department of Geology, The University, Manchester M13 9PL, U.K.*

### ABSTRACT

Microprobe analyses of glass which occurs as late-stage segregations in gabbroic xenoliths included within the olivine basaltic lavas of Piton de la Fournaise, Réunion Island, are used to define the closed-system, low-pressure evolutionary trend for the basaltic liquids. Glass of a trachytic composition located in a doleritic sample associated with recent scoria activity on Fournaise and hawaiitic vein segregations in an olivine basalt lava lake follow low-pressure evolutionary trends similar to those defined by the glass in the gabbroic xenoliths. Using fractional crystallization models, the Fournaise evolutionary trend has been compared to that of the adjacent volcanic centre, Piton des Neiges, which displays a sequence of lavas ranging from *ne*-normative hawaiite to *qz*-normative trachyte. This comparison shows that the chemical variation within both the Piton des Neiges Differentiated Series lavas and the Piton de la Fournaise glasses may be accounted for by low-pressure fractionation of mineral assemblages comprising olivine + clinopyroxene + plagioclase + magnetite. Rare occurrences of highly oxidized glass of a rhyodacite composition as vesicle infillings in some lavas are interpreted to have formed as a result of local development of high  $P(O)_2$  conditions, possibly by inclusion of groundwater in the basaltic melt. Alkaline glass ( $Na_2O + K_2O = 10.8$  wt. %) occurs as primary inclusions within the olivines of a dunite xenolith; these compositions may provide evidence for immiscibility between alkali-rich and basaltic liquids in the low-pressure magma reservoir.

### SOMMAIRE

Les analyses à la microsonde de verres formés par ségrégation tardive dans les xénolithes des laves basaltiques à olivine du Piton de la Fournaise, île de la Réunion, permettent de définir l'évolution de liquides basaltiques à basse pression en système fermé. Un verre de composition trachytique dans un fragment doléritique issu d'une scorie récente sur le Piton de la Fournaise et les ségrégations hawaïtiques dans un lac de lave basaltique à olivine appartiennent à la même lignée d'évolution à basse pression que les verres des xénolithes gabbroïques.

L'évolution des liquides du Piton de la Fournaise est comparée, à l'aide de modèles de cristallisation fractionnée, aux produits du volcan voisin, Piton des Neiges: association de laves allant d'une hawaïite à néphéline normative à des trachytes quartzifères. La variation en composition des liquides de la série différenciée du Piton des Neiges et des verres du Piton de la Fournaise s'explique par une séparation à basses pressions de l'assemblage olivine + clinopyroxène + plagioclase + magnétite. De rares indices d'un verre très oxydé de composition rhyodacitique, qui remplit les vacuoles de certaines laves, semblent résulter d'un développement localisé de hautes pressions d'oxygène, dues peut-être au mélange d'eau météorique à la lave basaltique. Des verres alcalins ( $Na_2O + K_2O = 10.8$  % en poids) en inclusions primaires dans l'olivine d'une enclave de dunite seraient le produit de l'immiscibilité à basse pression de liquides hyperalcalin et basaltique dans la chambre magmatique.

(Traduit par la Rédaction)

### INTRODUCTION

The geology and chemistry of the two volcanic centers, Piton (P.) des Neiges and P. de la Fournaise (Fournaise) which comprise Réunion Island have been studied by Lacroix (1936) and Upton & Wadsworth (1966, 1972a). The volcanic shield of Fournaise occupies the south-eastern third of the island, the northwestern two-thirds being occupied by the denuded volcanic shield of P. des Neiges. Both volcanic centres comprise a chemically uniform sequence of *hy*-normative olivine basalts, termed "transitional basalts" by Upton & Wadsworth (1972a). However, the P. des Neiges sequence is capped by a Differentiated Series (D. S., Upton & Wadsworth 1972a) of lavas and intrusive bodies that range in composition from hawaiite, mugearite and benmoreite to trachyte and syenite.

Glass was first reported in the basalts of Fournaise by Upton & Wadsworth (1971). They described the occurrence of a rhyodacite glass which had segregated into the vesicles of a recent lava lake. A detailed survey of the prehistoric and recent lavas of Fournaise, together with the xenoliths included within these lavas (Ludden 1976), has uncovered additional exam-

\*Present address: Département de Géologie, Université de Montréal, Montréal, Qué. H3C 3J7.

ples of rhyodacite glass as well as several glass-bearing xenoliths. The most common occurrence of glass is within gabbroic xenoliths enclosed in some basaltic-scoria eruptions of Fournaise; in these samples glass occurs interstitially and as inclusions within the minerals of the xenoliths. Glass inclusions of highly alkalic composition are found as inclusions in olivine crystals of dunite xenoliths. The xenoliths have been described by Upton & Wadsworth (1972b) and Ludden (in prep.), and are considered to represent both cumulate rocks formed at low pressure within the magma reservoir and intrusive offshoots from the low-pressure magma reservoir. Compositions similar to those of the glasses in the gabbroic xenoliths occur in two lavas: firstly, trachytic interstitial glass is found in an olivine dolerite block associated with recent scoria activity; secondly, hawaiitic vein segregations occur in an olivine-basalt lava lake.

The relationship between mineral and liquid compositions is of fundamental importance when evaluating liquid compositions inferred to represent a fractional crystallization sequence. The association of the glass with mineral phases within the gabbroic xenoliths and basaltic lavas and its compositional range are useful in making such an evaluation. In particular, due to the similarity of the glass compositions to those of the P. des Neiges D. S. lavas, the low-pressure evolutionary trend of the Réunion basaltic melts may be evaluated.

#### PETROGRAPHY

The mode of occurrence of the glass in the gabbroic xenoliths is shown in Figures 1a, b. Figure 1a shows both interstitial glass and glass included within the mineral grains of an olivine gabbro (RF47L). The glass is dark brown; in contrast to the light brown trachytic glass of the olivine dolerite RF18 (Fig. 1b), it contains few microlites. An interpretation of the timing of incorporation of the glass in the mineral phases is difficult. However, a preferred mechanism is similar to that proposed by Donaldson (1975), in which ultramafic liquids are trapped as primary inclusions along the crystal faces of anorthite megacrysts. Partial melting of the xenoliths is discounted owing to the lack of textures (*i.e.*, fritted edges and crystal embayments) indicative of such a process. Thus the glass within mineral phases of the gabbroic xenoliths and lavas probably formed as a result of static fractional crystallization. Analogous processes have been described for differentiated intrusions by Wilkinson (1966), and Thompson (1972) argued

that such a process may result in a "silica gap" when liquids are released from an intrusion 50-70% crystalline. This tendency has been further demonstrated for P. des Neiges by Upton & Wadsworth (1972a), who described syenitic veinlets and pegmatites of comenditic composition that segregated from basic sheets and microsyenite intrusions, respectively. Thus, these segregations and the formation of evolved glass within the gabbroic xenoliths may be taken as the counterparts of large-scale formation of evolved magma in a fractionating magma reservoir. The xenoliths may not represent the bulk composition of the liquid, and may therefore result from an inhomogeneous accumulation of crystals from a fractionating liquid. However, fractional-crystallization relationships between the composition of the glass, microlites within the glass and the rims of zoned mineral phases would be expected.

The rhyodacite glass was described in detail by Upton & Wadsworth (1971). The glass is pale brown and contains microlites of sodic feldspar, ferrian augite and hematite. The vesicles into which the glass has segregated are surrounded by a 2-3 cm mantle of highly oxidized basalt that contains olivine with vermicular intergrowths and coronas of magnetite (Fig. 1c), yellow "stained" clinopyroxene, and complex mixtures of magnetite, hematite and ilmenite.

The alkalic glass inclusions, which occur within olivine in the dunite xenoliths, are commonly 5-25  $\mu\text{m}$  in diameter and contain a 1-5  $\mu\text{m}$  shrinkage bubble (Fig. 1d). There appears to be no reaction with the surrounding olivine, and the glass contains no accessory mineral phases. These inclusions are comparable in morphology to primary glass inclusions reported in olivine and ilmenite from lunar basalts by Roedder & Weiblen (1970, 1971) and from Hawaiian basalts by Anderson & Wright (1972).

#### ANALYTICAL PROCEDURE

Glasses and minerals were analyzed using a Link Systems (Model 290-2KX) energy dispersive (E.D.) spectrometer attached to a Cambridge Instruments Geoscan II microprobe. The system consisted of a Kevex detector (resolution  $\sim 150\text{eV}$  F.W.H.M. at 5.9 keV; Be window of 0.3 mil.), Harwell (Model 2010) and ADC (Model 1057) processors. The digitized information was processed using a commercial version of software developed by Statham (1975) and a Nova 16K computer. The programs included an iterative stripping routine and full ZAF correction. Conditions for analysis were 15 kV

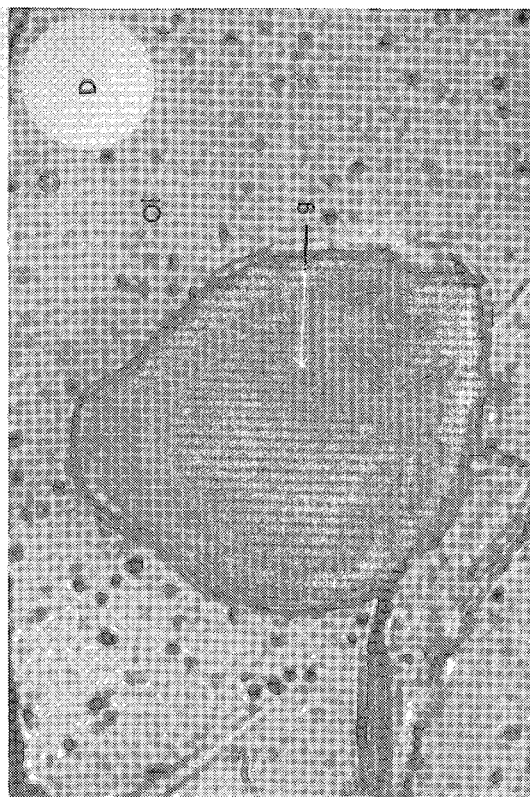
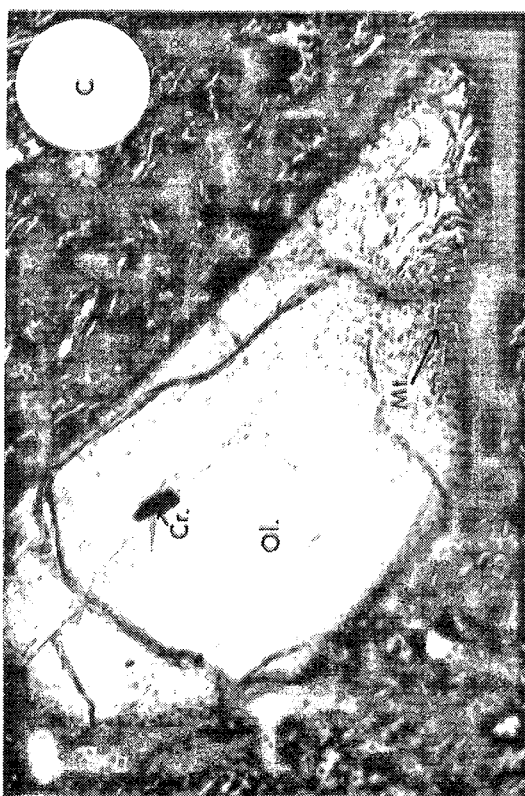
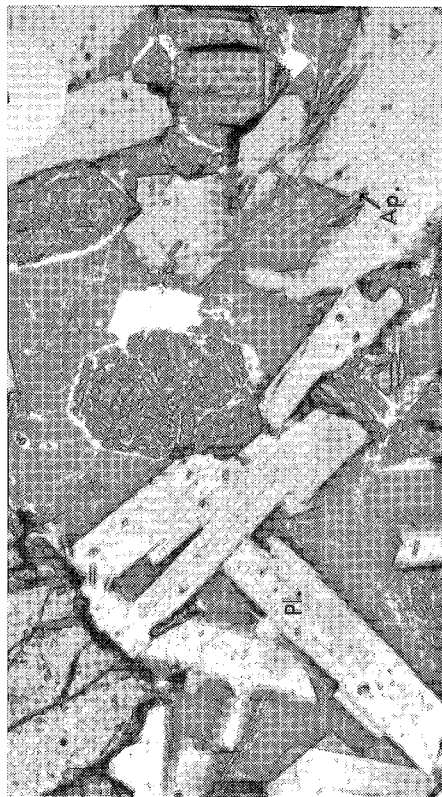


FIG. 1(a) Glass occurring as an interstitial phase and as inclusions along fracture planes in plagioclase in olivine gabbro xenolith RF47L. (Crossed polarized light; longer dimension of photograph 3mm); (b) Interstitial glass in olivine dolerite RF18. Matrix phases are titanite, plagioclase, magnetite and apatite (Longer dimension 3mm); (c) A highly oxidized olivine phenocryst within the alteration zone associated with residual glass of a rhyodacite composition in RE901. Note the vermicular intergrowth of magnetite and the magnetite-charged rim (Longer dimension 1mm); (d) Primary glass inclusion within olivine from dunite xenolith RE934. The glass inclusion is  $25\mu$  in diameter with a  $5\mu$  shrinkage bubble (g glass; ol olivine; pl plagioclase; cpx clinopyroxene; ap apatite; cr chromite).

TABLE 1. STATISTICAL DATA FOR ENERGY-DISPERSIVE MICROPROBE ANALYSES OF DIOPSIDE 65-JADEITE 35 GLASS<sup>1</sup>

	accepted comp.	mean	std. error of mean	99% conf. limits	mean	std. dev.	counting error
SiO <sub>2</sub>	56.81	56.83	0.04	56.72	56.95	0.23	0.17
Al <sub>2</sub> O <sub>3</sub>	8.44	8.91	0.02	8.85	8.97	0.11	0.07
MgO	12.39	11.94	0.03	11.87	12.02	0.15	0.10
CaO	17.23	17.14	0.03	17.06	17.22	0.16	0.10
Na <sub>2</sub> O	5.13	5.18	0.02	5.13	5.24	0.11	0.07

## CATION PROPORTIONS ON THE BASIS OF 6 OXYGENS

Si	2.000	1.999	0.001	1.996	2.001	0.004
Al	0.350	0.369	0.001	0.367	0.372	0.004
Mg	0.650	0.626	0.001	0.622	0.630	0.007
Ca	0.650	0.646	0.001	0.643	0.649	0.006
Na	0.350	0.353	0.001	0.350	0.357	0.008

<sup>1</sup> based on 30 analyses by F.C.F. Wilkinson & A.C. Dunham (pers. comm.) on the University of Manchester microprobe facility.

accelerating voltage, a specimen current of 3nA on cobalt metal and a usual analysis live-time of 100 secs. Standards were pure metals, glasses and minerals. A statistical analysis of diopside 65/jadeite 35 glass is given in Table 1

(F. C. F. Wilkinson & A. C. Dunham, pers. comm.).

By using an E.D. technique, rapid analysis with a low beam current was possible; this reduced problems of loss of light elements during analysis of the glass and microlites. During glass analysis the area of excitation of the electron beam was maintained as large as possible without overlap on to the mineral phases within or surrounding the glass. At least five determinations were made on each sample; the averages of these analyses are given in Table 2.

## CHEMISTRY

Major element analyses and CIPW normative values for the glasses are presented in Table 2. The low totals for some glass compositions, in particular RF183Y, RF18 and RE934, were verified during repeated analyses. The difference from 100% is therefore inferred to represent the volatile component of the glass.

TABLE 2. MICROPROBE ANALYSES<sup>1</sup> AND C.I.P.W. NORMATIVE VALUES OF GLASSES FROM THE LAVAS AND XENOLITHS OF PITON DE LA FOURNAISE

	RF47L (Min)	RF47L (Int)	RF183R (Int)	RF183R (Int)	RF183Y (Min)	RF183Y (Int)	RF47G (Min)	RF47G (Int)	RF18 (Int)	RE490 (Ves)	RE490 <sup>2</sup> (Ves)	RE934 (Min)
SiO <sub>2</sub>	53.45	54.31	50.61	51.73	59.97	55.60	56.86	58.94	62.14	64.65	64.94	57.38
TiO <sub>2</sub>	1.97	1.98	2.28	2.98	1.38	1.38	2.14	1.75	1.28	1.12	1.12	0.63
Al <sub>2</sub> O <sub>3</sub>	16.52	17.65	16.40	16.38	16.90	16.50	17.60	16.65	16.50	13.29	13.92	17.05
Fe <sub>2</sub> O <sub>3</sub>	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.92	2.50
FeO	5.29	4.71	8.10	7.77	4.52	4.61	5.21	5.14	0.71	0.40	0.84	1.97
MgO	4.04	3.21	3.63	3.75	2.79	1.89	2.21	2.22	0.58	1.16	1.88	2.27
CaO	7.45	7.23	7.56	7.26	5.26	5.40	5.10	4.48	0.32	2.68	3.76	2.55
Na <sub>2</sub> O	4.01	3.51	4.56	4.21	3.86	3.66	4.74	4.66	3.91	4.17	3.87	4.20
K <sub>2</sub> O	1.68	1.89	1.93	1.98	4.61	4.39	2.74	2.84	5.68	3.39	3.66	6.00
Total	96.91	96.99	97.57	98.56	96.79	95.93	99.12	99.18	93.62	93.36	96.91	95.21
qs	2.91	6.33	--	--	0.03	3.65	4.21	7.62	16.11	21.41	20.94	--
oo	--	--	--	--	--	--	--	--	3.34	--	--	--
or	9.93	11.17	11.40	11.70	27.24	25.94	16.19	16.78	33.56	17.67	21.70	39.35
ab	33.93	29.70	33.74	35.62	32.66	30.97	40.11	38.92	33.08	35.28	32.73	35.54
an	22.12	26.82	18.58	19.95	15.17	15.63	18.65	16.39	1.59	8.98	9.79	8.00
ne	--	--	2.62	--	--	--	--	--	--	--	--	--
di	11.97	7.28	15.65	13.18	8.87	9.19	5.44	4.79	--	1.54	1.62	3.65
hy	8.68	7.78	--	5.19	6.59	4.29	6.81	7.65	1.44	2.18	3.93	2.36
ol	--	--	7.61	3.63	--	--	--	--	--	--	--	1.48
mt	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	--	--	--	3.63
il	3.74	3.76	4.33	5.66	2.62	2.62	4.06	3.32	1.50	0.84	2.03	1.19
hm	--	--	--	--	--	--	--	--	2.50	2.50	2.92	--
D.I.	47	48	48	47	60	61	61	63	83	75	76	75

<sup>1</sup> Analyses are average values of at least 5 determinations; Fe<sub>2</sub>O<sub>3</sub> normalized to 2.5% for norm calculation.

<sup>2</sup> Wet chemical analysis of rhyodacite glass and included microlites (Upton & Wadsworth 1971). The higher total is due to inclusion of microlites in the analysis.

## Host-rock descriptions

RF47L: olivine-gabbro xenolith, among scoria, south of Piton Chisny. RF47G: olivine-poor gabbro xenolith, among scoria, Piton Chisny. RF183R: pyroxene-magnetite-plagioclase cumulate xenolith, Rempart de Tremblat. RF183Y: ferrogabbro xenolith, Rempart de Tremblat. RF18: olivine dolerite block among ejectamenta from the 1936 eruption (18% modal glass). RE490: residual glass segregated into vesicles in an olivine basalt lava lake, Cratère Bory (Upton & Wadsworth, 1971). RE934: glass included in olivine from a dunite xenolith from Piton Chisny.

TABLE 3. AVERAGE DIFFERENTIATED SERIES ANALYSES AND NORMS, PITON DES NEIGES, REUNION ISLAND<sup>1</sup>

	Hawaiite	Mugearite	Benmoreite	Trachyte	Syenite
SiO <sub>2</sub>	47.1	52.1	58.5	59.6	63.5
TiO <sub>2</sub>	3.7	2.3	1.3	1.1	0.5
Al <sub>2</sub> O <sub>3</sub>	15.7	17.1	17.8	16.2	17.8
Fe <sub>2</sub> O <sub>3</sub>	2.0	2.0	2.0	2.0	2.0
FeO	11.8	8.7	5.2	5.8	2.5
MgO	4.7	2.6	1.3	1.0	0.4
CaO	9.5	6.9	4.3	3.1	1.5
Na <sub>2</sub> O	3.5	4.9	6.1	6.2	7.2
K <sub>2</sub> O	1.2	2.4	2.8	3.5	4.1
P <sub>2</sub> O <sub>5</sub>	0.5	0.7	0.5	0.2	0.2
MnO	0.2	0.2	0.2	0.2	0.2
qz	--	--	0.9	1.8	4.1*
or	7.1	14.2	16.6	20.7	24.4
ab	26.6	38.2	51.6	52.5	60.9
an	23.6	17.6	12.9	6.0	--
ne	1.6	1.8	--	--	--
di	16.9	10.2	4.4	6.8	--
hy	--	--	7.2	4.6	4.5
ol	13.0	9.1	--	--	--
il	7.0	4.4	2.5	1.4	1.0
mt	2.9	2.9	2.9	2.9	2.9
ap	1.2	1.6	1.2	0.5	0.6

\* includes 2.1% corundum; <sup>1</sup> analyses recalculated to 100% on a standard Fe<sub>2</sub>O<sub>3</sub> basis (Thompson *et al.*, 1972), taken from Upton & Wadsworth (1972a).

Average major-element analyses for the D.S. lavas of P. des Neiges, taken from Upton & Wadsworth (1972a), are given in Table 3. The glass compositions have been compared with those of the D.S. in Figure 2. Relative to D.S. samples of equivalent Si saturation, (1) the glass from the gabbroic xenoliths (RF183R, RF183Y, RF47L, RF47G) and the glass of trachytic composition RF18 are comparable, and define a trend which may be interpreted in terms of fractional crystallization through (compositions equivalent to the) hawaiite, mugearite, benmoreite and trachyte lavas; (2) the rhyodacite glass RE490 (this paper and Upton & Wadsworth 1971) is depleted in Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and K<sub>2</sub>O and enriched in CaO; (3) the glass within the olivine of dunite xenolith RE934 is enriched in alkalis and depleted in total iron.

#### FRACTIONAL CRYSTALLIZATION

##### Models for Piton des Neiges

Arguments for the evolution of the D.S. have been developed by Upton & Wadsworth (1972a), Zielinski (1975) and Nativel (1976). Radiometric age determinations (McDougall 1971) indicate a period of quiescence of  $1 \times 10^5$  years between the eruption of the oldest shield basalts and youngest D.S. lavas. Upton & Wadsworth (1972a) tentatively interpreted this interval as a period during which a stagnant magma body below P. des Neiges was subject to closed-system fractionation of olivine  $\pm$  pyroxene at depths of 10–20 kbar. The *ne*-normative character of the hawaiitic and some mugearitic eruptive rocks of the D.S. was ascribed to this fractional crystal-

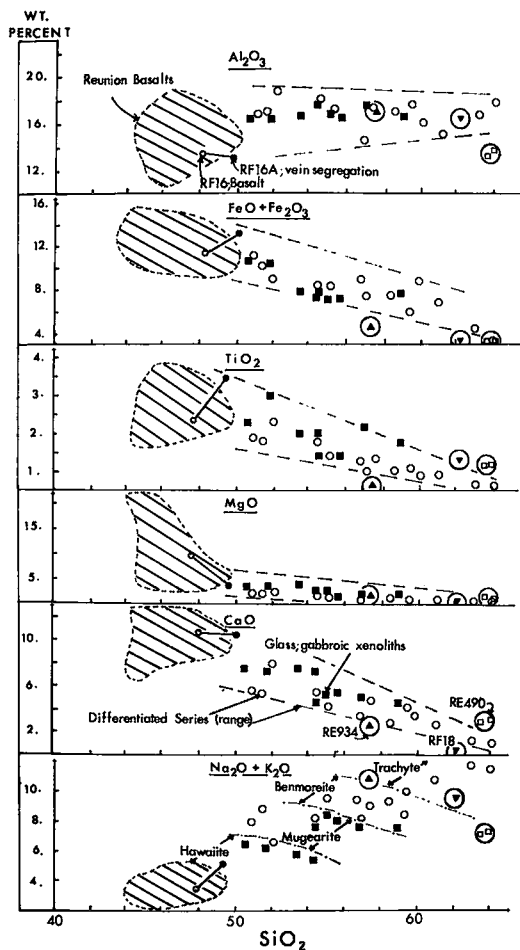


FIG. 2. Major element variation diagram showing glass compositions from Fournaise compared with the Piton des Neiges Differentiated Series lavas. Glass in gabbroic xenoliths, solid squares; RF 18 glass in olivine dolerite, inverted solid triangle; rhyodacite glass RE 490, open squares; alkali-rich glass inclusion in olivine, RE 934, solid triangle.

lization episode. Low-pressure (< 5 kbar) fractionation of plagioclase + clinopyroxene + Fe–Ti oxide assemblages was inferred to be responsible for the evolution of the more evolved D.S. liquids. Upton & Wadsworth suggested that the reversion from *ne*-normative basalts, hawaiites and mugearites of the D.S. to saturated and oversaturated mugearites and trachytes (and their intrusive equivalents) was possibly effected by both crystallization of *ne*-normative clinopyroxene and amphibole and an increase in Fe–Ti oxide precipitation; Macdonald (1974) suggested that similar reversals may be achieved by

fractionation of a non-stoichiometric, silica-deficient feldspar. Similar reversals in the normative character of the evolved liquids have been observed for other volcanic provinces, e.g., Hawaii (Macdonald 1968) and Skye (Thompson *et al.* 1972).

Data for *qz*-trachytes and comendites from the youngest D.S. eruptive rocks (Nativel 1976) largely support Upton & Wadsworth's model invoking late-stage plagioclase fractionation in a low-pressure magma reservoir system. Using rare-earth elements (REE) and quantitative models involving mass-balance equations, Zielinski (1975) defined two groups of D.S. rocks: group-1 compositions follow Upton & Wadsworth's model and show a proportional increase in total REE with differentiation index (D.I.) and an increasingly negative Eu anomaly. However, group-2 compositions, comprising both intrusive and extrusive rocks, show neither a positive correlation of REE with D.I. nor a significant Eu anomaly. In addition, La/Yb is enriched twofold (19–24) relative to 10–14 for group 1. Zielinski interpreted the group-2 liquids as partial melts from a source rich in clinopyroxene or hornblende or both, similar in character to that represented by the low-pressure cumulate xenoliths described by Upton & Wadsworth (1972b). Mixing of these partial melts with liquids having REE abundances equivalent to group 1 was expected to account for anomalous variation of REE with respect to D.I.

#### *Models for Piton de la Fournaise: major elements*

Compositions of glasses from the gabbroic xenoliths and of the trachytic glass RF18 provide an opportunity to assess the fractional crystallization of the Fournaise magma relative to that of P. des Neiges. In addition, the hawaiitic vein segregation RF16A from olivine basalt RF16 (Fig. 2) has been taken to represent the one-atmosphere evolution from basalt to hawaiite. Successive glass compositions have been considered parent and daughter; compositions of the fractionated phases have been taken from microprobe determinations of microlites in the host glass and rims of zoned phenocrysts in the host rock.

This sequence of compositions from basalt to trachyte has been assessed using a least-squares technique (e.g., Bryan *et al.* 1969, Wright & Doherty 1970). Relative to similar models (e.g., Ewart *et al.* 1973) for the Tonga islands, Zielinski & Frey (1970) for Gough Island and Zielinski (1975) for the D.S. of P. des Neiges, the relations between host rocks and

glass compositions provide an excellent control of closed-system fractional crystallization for Fournaise.

The calculations involve matrix solutions of mass-balance equations comprising compositions of a parental liquid, mineral phases and a derivative liquid. The results of five solutions for the evolved liquids of Fournaise are given in Table 4. The accuracy of a solution for element (i) is represented by the difference between the observed composition ( $B_i$ ) and the estimated composition ( $B_i^*$ ), i.e.,  $(B_i - B_i^*)^2$  is minimized. The coefficients represent either the positive or negative contribution of the parent liquid or mineral phases required for the solution. Thus the degree of crystallization (in %) and the relative proportions of mineral phases fractionated may be evaluated.

The compositional trend for *Solution 1* (olivine basalt lava-lake sample RF 16 to hawaiitic vein segregation RF 16A) is shown by the tie lines in Figure 2. The trend differs from that observed for the lavas of P. des Neiges in that it involves enrichment of Fe and Ti. Such a trend is inferred to result from fractionation of mafic minerals within the host rock and suppression of magnetite fractionation. The solution to the mass-balance equations involving the liquid, clinopyroxene, plagioclase and olivine compositions of RF 16 (olivine basalt) demonstrates this process. Ludden (1978) has shown that fractionation of significant quantities of magnetite in addition to olivine, clinopyroxene and plagioclase are required to satisfy compositional variations within the basaltic and hawaiitic lavas of Fournaise. This has been confirmed by the observation of magnetite horizons in cumulate blocks associated with basaltic eruptions on Fournaise (Upton & Wadsworth 1972a, Ludden 1976). The difference in fractionation trends (i.e., RF16→RF16A relative to Fournaise olivine basalt lavas → hawaiitic lavas) is inferred to be controlled by  $f(O_2)$ , oxygen fugacity of the melt. In the case of the vein segregation in the lava-lake sample, the liquid has fractionated under higher  $f(O_2)$  than the basaltic melts of Fournaise (i.e., the lava-lake sample is degassed relative to the basaltic melts fractionating in the low-pressure magma reservoir). Upton & Wadsworth (1972a) and Ludden (1978) have observed that, for the basaltic lavas of both P. des Neiges and Fournaise, the near-surface crystallization progression is olivine → plagioclase → clinopyroxene, whereas petrographic evidence from gabbroic and peridotitic xenoliths included in the lavas indicates the sequence olivine → clinopyroxene → plagioclase at confining pressures equivalent

TABLE 4. LEAST-SQUARES SOLUTIONS TO THE PITON DE LA FOURNAISE LOW-PRESSURE EVOLUTIONARY TREND

Solution 1: olivine basalt RF16 (D.I. 23) → hawaiitic vein segregation RF16A (D.I. 36) in olivine basalt RF16						
	RF16	cpx	plag	oliv	RF16A:(B <sub>1</sub> )	est.(B <sub>1</sub> *)
SiO <sub>2</sub>	48.33	51.71	46.42	38.61	49.41	49.65
TiO <sub>2</sub>	2.32	1.33	--	--	3.46	3.28
Al <sub>2</sub> O <sub>3</sub>	13.63	1.92	33.38	--	13.29	13.13
FeO	11.64	7.37	--	15.66	13.92	13.47
MgO	9.66	15.60	--	45.53	4.64	4.57
CaO	10.31	21.67	17.11	--	10.11	9.90
Na <sub>2</sub> O	2.64	0.30	2.07	--	3.35	3.40
K <sub>2</sub> O	0.80	--	0.35	--	1.29	1.10
P <sub>2</sub> O <sub>5</sub>	0.33	--	--	--	0.53	0.49

Coefficient<sup>1</sup>: RF16 + 1.452; cpx - 0.089; plag. - 0.194; oliv. - 0.177.

$\epsilon(B_1 - B_1^*)^2 = 0.62$ ; % crystallization = 32

Solution 2: average hawaiite A.H. (D.I. 38) → Mugearite glass RF 183R (Table 2, col. 4; D.I. 47)

	A.H.	mt	cpx	plag	RF183R:(B <sub>1</sub> )	est.(B <sub>1</sub> *)
SiO <sub>2</sub>	50.72	--	51.32	48.11	51.73	51.77
TiO <sub>2</sub>	2.89	22.36	1.34	--	2.98	2.79
Al <sub>2</sub> O <sub>3</sub>	14.55	1.56	1.75	31.91	16.38	16.20
FeO	11.16	66.41	9.72	--	10.07	10.19
MgO	4.94	3.00	14.65	--	3.75	3.47
CaO	9.86	--	20.19	16.02	7.26	7.47
Na <sub>2</sub> O	3.58	--	0.35	2.54	4.21	4.34
K <sub>2</sub> O	1.28	--	--	0.39	1.98	1.81

Coefficient: A.H. +1.298; mt -0.034; cpx -0.071; plag -0.207.

$\epsilon(B_1 - B_1^*)^2 = 0.54$ ; % crystallization = 22

Solution 3: average hawaiite (D.I. 38) → Mugearite glass RF47L (Table 2, col. 2; D.I. 48)

	A.H.	mt	cpx	plag	RF47L:(B <sub>1</sub> )	est.(B <sub>1</sub> *)
SiO <sub>2</sub>	50.72	--	51.32	48.11	54.31	54.21
TiO <sub>2</sub>	2.89	22.36	1.34	--	1.97	1.73
Al <sub>2</sub> O <sub>3</sub>	14.55	1.57	1.75	31.91	17.65	17.51
FeO	11.16	64.41	9.72	--	7.01	7.13
MgO	4.94	3.00	14.65	--	3.21	3.02
CaO	9.86	--	20.19	16.02	7.23	7.44
Na <sub>2</sub> O	3.58	--	0.35	2.54	3.51	3.68
K <sub>2</sub> O	1.28	--	--	0.39	1.89	1.79

Coefficient: A.H. + 1.362; mt. - 0.052; cpx - 0.086; plag. 0.242

$\epsilon(B_1 - B_1^*)^2 = 0.74$ ; % crystallization = 28

Solution 4: mugearite glass RF47L (D.I. 48) → benmoreite glass RF47G (Table 2, col. 8; D.I. 63)

	RF47L	mt	cpx	plag	RF47G:(B <sub>1</sub> )	est.(B <sub>1</sub> *)
SiO <sub>2</sub>	54.31	--	48.81	50.67	58.94	58.88
TiO <sub>2</sub>	1.98	19.10	1.65	--	1.75	1.98
Al <sub>2</sub> O <sub>3</sub>	17.65	3.70	2.42	29.00	16.65	16.85
FeO	7.01	68.65	9.54	--	7.44	7.28
MgO	3.21	5.46	14.61	--	2.22	2.46
CaO	7.23	--	21.90	13.84	4.48	4.13
Na <sub>2</sub> O	3.51	--	0.15	3.73	4.66	4.35
K <sub>2</sub> O	1.89	--	--	0.23	2.84	2.72

Coefficient: RF47L + 1.478; mt. - 0.029; cpx - 0.116; plag. - 0.305.

$\epsilon(B_1 - B_1^*)^2 = 0.84$ ; % crystallization = 30.

Solution 5: benmoreite glass RF183Y (Table 2, col. 6; D.I. 61) → trachyte glass RF18 (Table 2, col. 9; D.I. 80)

	RF183Y	mt	cpx	plag	oliv	RF18(B <sub>1</sub> )	est.(B <sub>1</sub> *)
SiO <sub>2</sub>	54.39	--	51.74	54.06	38.59	62.14	62.05
TiO <sub>2</sub>	1.37	19.10	0.82	--	--	1.28	1.48
Al <sub>2</sub> O <sub>3</sub>	17.71	3.70	1.48	28.85	--	16.50	16.46
FeO	7.44	68.65	13.40	--	31.16	3.01	2.95
MgO	2.95	5.46	10.90	--	31.56	0.58	0.75
CaO	4.54	--	20.85	11.07	--	0.32	0.44
Na <sub>2</sub> O	4.24	--	0.57	5.47	--	3.91	4.27
K <sub>2</sub> O	3.30	--	0.10	0.63	--	5.68	5.82

Coefficient: RF183Y + 1.874; mt. - 0.069; cpx - 0.083; plag. - 0.572; oliv - 0.121.

$\epsilon(B_1 - B_1^*)^2 = 0.79$ ; % crystallization = 45.

to the low-pressure magma reservoir (<5 kbar, Upton & Wadsworth 1972b). The evidence for the near-surface crystallization progression (RF 16 → RF 16A, this paper) and the low-pressure evolutionary trend for the basaltic melts of Fournaise and P. des Neiges (Upton & Wadsworth 1972a, b; Ludden 1978) indicates that such a change in crystallization sequence may be a result of variation in  $f(\text{O}_2)$  with confining pressure of the basaltic melts.

Transitions from hawaiite (represented by the average hawaiitic liquids erupted on Fournaise; Ludden 1978) through mugearite, benmoreite and trachyte compositions are given in Solutions 2-5. The glass represents a liquid composition and mineral analyses are taken from microlites within the glass and rims of minerals associated with the glass. All transitions involve removal of clinopyroxene, plagioclase and magnetite. The Fe content of the clinopyroxene and Na content of the plagioclase increase during fractional crystallization. Fe-Ti oxide (magnetite) compositions remain relatively constant at Usp 60-75. For comparison, the mineral end-member compositions are given for intrusive rocks from P. des Neiges (Table 5); data are taken from intrusive fragments included within the St-Pierre ash flow, Réunion (Ludden, unpubl. analyses). Fe-amphibole commonly occurs in the most evolved intrusive rocks (Table 5; Upton & Wadsworth 1972a). Trace-element evidence, cited later in this paper, requires amphibole in the fractionation sequence during evolution of the "water-saturated" syenitic melts of P. des Neiges.

Considering the implication of solutions 2-5 relative to petrographic evidence for fractional crystallization on P. des Neiges:

(1) Plagioclase dominates the fractionation sequence; the plagioclase/clinopyroxene ratio of the fractionated mineral assemblage increases

TABLE 5. COMPARATIVE MINERALOGY FOR THE DIFFERENTIATED SERIES OF PITON DES NEIGES

Sample	D.I.	cpx	plag	mt	other
RF25* (VI)	36	Fs 15-19 En 38-40 Di 42-45	An 65-25 Ab 34-65 Or 2-9	Usp 50-70	
RF25 (VII)	40	Fs 14-20 En 39-21 Di 43-46	An 50-30 Ab 40-60 Or 2-7		
RF25 (VIII)	75	Fs 18-23 En 31-37 Di 24-46	An 30-2 Ab 61-54 Or 9-44	Usp 50-70	Fe. Amph.
RF24 (VI)	79	Fs 26-27 En 27-29 Di 45-46	n.d.		Fe. Amph. Fa. Oliv.

<sup>1</sup> Total iron as FeO; coefficients refer to the fractions of liquid and crystalline phases required for the solution of the mixing calculations. B<sub>1</sub> is the actual composition of a "daughter liquid", B<sub>1</sub>\* is the composition of the "daughter liquid" predicted by the calculation.

\*RF25 (VI) - RF25 (VIII) Intrusive fragments included within the St. Pierre ash flow, P. des Neiges.

from 2.5 for hawaiitic and mugearitic compositions to 7 for trachytic compositions. The common occurrence of highly plagioclase-phyric basalts in the D.S. lava sequences (Upton & Wadsworth 1972a) and complex, plagioclase-rich (mugearitic) dykes (Upton & Wadsworth 1970) support the interpretation of the mass-balance equations.

(2) An intermediate-pressure (10–20 kbar) fractionation episode primarily involving clinopyroxene, as inferred by Upton & Wadsworth (1972a) for the evolution of the *ne*-normative hawaiitic and mugearitic liquids of P. des Neiges, would be compatible with the model. However, solutions 2–5 indicate that the complete evolutionary sequence may be achieved by clinopyroxene, plagioclase and magnetite removal at low pressures (<5 kbar). Solution 1 indicates that major changes in crystallization (fractionation) processes may result from subtle variation in fractionating regime. In addition, the normative character of the mugearitic glasses (RF 183Y, RF 183R and RF 47L) indicates that the liquids are critically situated with respect to the boundary between *hy*- and *ne*-normative liquids. Thus, it is anticipated that the complex evolution of the P. des Neiges D.S. liquids may be achieved in a low-pressure magma reservoir;

changes in the normative character of the hawaiitic and mugearitic liquids may reflect minor changes in fractionating environment. Fractionation of a relatively calcic plagioclase from mugearite liquids (*i.e.*, solution 4) would maintain the residual liquids in a *qz*-normative field. (3) Solution 5 requires removal of fayalitic olivine. The presence of olivine (Fa<sub>70</sub>) in the syenitic intrusions of P. des Neiges (Table 5) and microlites located within the glass supports this process.

#### Models for Piton de la Fournaise: trace elements

Trace element behavior during fractional crystallization may be evaluated by substituting the appropriate mineral/liquid partition coefficients (*D*) in the proportions required by the mass-balance equations. The agreement between calculated and observed compositions provides a constraint on the solutions to the mass-balance calculations. Zielinski (1975) has completed such calculations for the D.S. of P. des Neiges. Two rare-earth-element (REE) profiles taken from analytical data presented by Zielinski are shown in Figure 3 (solid symbols): RE 634, a trachyte, represents the most evolved members of Zielinski's Group 1 liquids, characterized by

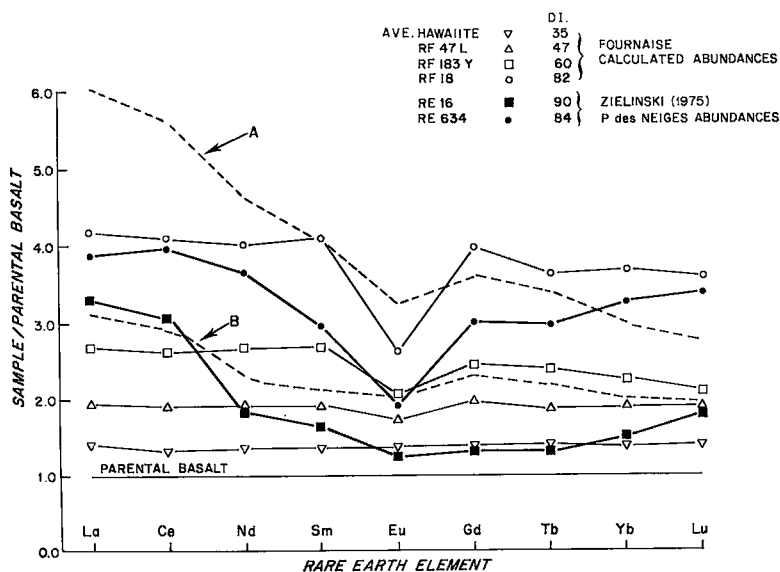


FIG. 3. Calculated REE profiles for the Fournaise average hawaiite and glass compositions (open symbols). RE 634, a trachyte, and RE 16, a syenite, from groups 1 and 2 respectively, defined by Zielinski (1975). The dotted lines represent calculated fractionated liquids. A = RF 183Y after removal of 35% clinopyroxene. B = RF 18 after fractionation of 35% amphibole. All values are normalized to the composition of the Fournaise parental basalt (Ludden 1978).



a positive correlation of D.I. with REE abundance and an increasingly negative Eu anomaly; RE 16, a quartz syenite, represents Zielinski's Group 2 liquids, characterized by high La/Yb, lack of Eu anomaly, lack of heavy-REE enrichment and non-correlation of D.I. and REE abundance. The open symbols represent the calculated compositions of the average Fournaise hawaiite (Ludden 1978) and glasses RF 47L, RF 183Y and RF 18. In this model fractionation from parental basalt compositions (Ludden 1978) through to the most evolved glass RF 18 is considered. Mineral/liquid  $D$  values have been taken from Schnetzler & Philpotts (1968, 1970), Buma *et al.* (1971) and Philpotts *et al.* (1972).

The glass compositions define a trend of increasing REE abundance and negative Eu anomaly with  $D.I.$  This trend reflects fractionation of clinopyroxene, plagioclase and magnetite, and the negative Eu anomaly is attributed to the increasing plagioclase/clinopyroxene ratio. Thus, the calculated abundances are equivalent to those of Zielinski's Group 1 D.S. compositions and confirm the low-pressure fractionating assemblage of plagioclase  $\pm$  clinopyroxene  $\pm$  magnetite for these liquids. A near-perfect match for the calculated profile for RF 18 glass ( $D.I.$  82) and the observed profile for RE 634 (trachyte;  $D.I.$  84) is obtained when 1% apatite is added to the fractionating assemblage; owing to mineral/liquid  $D$  values in the order of 50–10 (Nagasaki 1970), apatite acts as a major sink for REE.

Zielinski considered the REE abundance of Group 2 liquids to reflect partial melting of a mafic mineral assemblage similar to that reported for the cumulate rocks of P. des Neiges (Upton & Wadsworth 1972b). It is considered improbable that such a partial melting event occurred on Réunion during the evolution of the D.S. lavas, and it proposed that the REE profiles of the Group 2 liquids reflect fractionation of amphibole. Recent data for amphibole in acidic volcanic rocks (Sun & Hanson 1976; Kyle & Rankin 1976; Zielinski & Lipman 1976) indicate that amphibole may: (1) act as a major sink for REE; (2) fractionate heavy REE preferentially to light REE; (3) offset the effect of plagioclase fractionation on the Eu abundance due to a negative Eu anomaly. Data from Sun & Hanson and Kyle & Rankin give Sm/Yb ratios of 3–4 and mineral/liquid  $D$  values of 1–10. Profiles A and B shown in Figure 3 model the effect of extensive amphibole fractionation on a D.S. liquid which has already undergone some gabbroic fractionation (in this model RF 183Y and RF 18). In profile A, RF 183Y has been

subjected to 35% clinopyroxene fractionation; in profile B, RF 18 has been subjected to 35% kaersutite fractionation, with mineral/liquid  $D$  values taken from Sun & Hanson (1976). After amphibole fractionation a relatively close approximation to RE 16 is obtained. In addition, if 1–2% apatite were fractionated with amphibole, a close match to RE 16 would be obtained. Thus profile B supports an origin for the syenite liquids of Réunion by stabilization of amphibole as a fractionating phase in the D.S. liquids (see Upton & Wadsworth 1972a for petrographic arguments for such a process). Removal of small quantities of a silica-free phase having high mineral/liquid  $D$  values for REE (*i.e.*, apatite) would result in an inconsistent variation of Si-saturation ( $D.I.$ ) with total REE abundance of the liquid.

#### RHYODACITE GLASS

Upton & Wadsworth (1971) considered the origin of the rhyodacite glass in the olivine basalt lava-lake sample, RE490, in some detail. They considered the glass to have formed after a localized increase in  $P(O)_2$  of the basaltic melt, possibly as a result of inclusion of groundwater. The high  $P(O)_2$  resulted in early Fe–Ti oxide precipitation and subsequent Si-enrichment to rhyodacite compositions. The oxidized nature of the glass is indicated by microprobe determinations on oxide phases; the analyses show hematite (Usp 12%) in the glass and a gradient in oxygen fugacity (estimated using the calibration curves of Buddington & Lindsley 1964) of  $10^{-12.5}$  near the glass to  $10^{-10.4}$  in the fresh basalt.

The restricted occurrence of oxidized glass, the lack of hydrous mineral phases in the basaltic melts and the apparently low  $P(O)_2$  (non-oxidized nature) of the trachyte glass in RF18 favor a mechanism, such as that described by Upton & Wadsworth, involving a very localized process for increasing  $P(O)_2$ . Localized solution of water in the basaltic melt implies that the Fournaise basaltic melts are undersaturated with respect to water.

#### PRIMARY ALKALINE GLASS

Occurrences of large inclusions in minerals ( $>10\mu$ ) such as the glass within the olivine of dunite RE934 (Fig. 1d) are rare. However, microprobe scans across smaller inclusions indicate a similar alkali-rich nature. This paper presents data for the glass in RE934 and a preliminary interpretation of its significance: a more de-

tailed survey of similar glass occurrences is in progress.

Silicate inclusions in olivine crystals have been reported by Roedder & Weiblen (1970, 1971), Anderson (1974) and Anderson & Wright (1972). The latter two papers presented data for inclusions which, when corrected for olivine crystallization, reflect the bulk rock or primary liquid chemistry. The silica-rich "granitic" glass reported by Roedder & Weiblen (1970, 1971) is inconsistent with such an explanation.

Figure 4 shows microprobe scans across the glass. The steep crystal-glass contact indicates that no diffusion has occurred between the trapped liquid and olivine host. The peak towards the center of the glass inclusion may indicate either thinning of the glass at its centre, or a crystal-glass "edge effect" caused by differential X-ray excitement. The normative values for the crystal extract from an average Fournaise basalt composition required to form the glass composition are *ab* 21, *an* 27, *di* 33, *hy* 8, *ol* 3, *mt* + *ilm* 8. Thus, by extraction of olivine alone, it would be impossible to form such compositions after inclusion of the basaltic liquid within the olivine. The implication is that the alkali-rich liquid existed as an immiscible phase in the basaltic melt and was included in the olivine during crystal growth in the low-pressure magma reservoir.

To be considered for the origin of such liquids are: (1) melting of material from a granitic or syenitic source in the oceanic crust or volcanic superstructure; (2) the existence of immiscible alkali-rich liquids in the source region for basaltic melts; (3) partial melting of gabbroic material to yield alkalic liquids; (4) gabbroic fractionation and mechanical liberation of evolved liquids from partly crystalline cumulate horizons in the low-pressure magma reservoir.

The formation of evolved liquids in the gabbroic xenoliths and the compositional similarity of the RE934 glass to the evolutionary trend displayed by the glasses in the gabbroic xenoliths seem to indicate the fourth mechanism.

#### SUMMARY OF THE CONCLUSIONS

Fractional crystallization models based on the compositions of glass phases within gabbroic xenoliths and basaltic lavas of Fournaise indicate:

1. Differences between the near-surface sequence of crystallization and the crystallization sequence equivalent to the low-pressure magma reservoir (probably <5 kbar). This difference reflects a higher  $f(\text{O}_2)$  for magmas crystallizing at 1 atm relative to magmas fractionating in the low-pressure magma reservoir.
2. The evolution from hawaiitic to trachytic

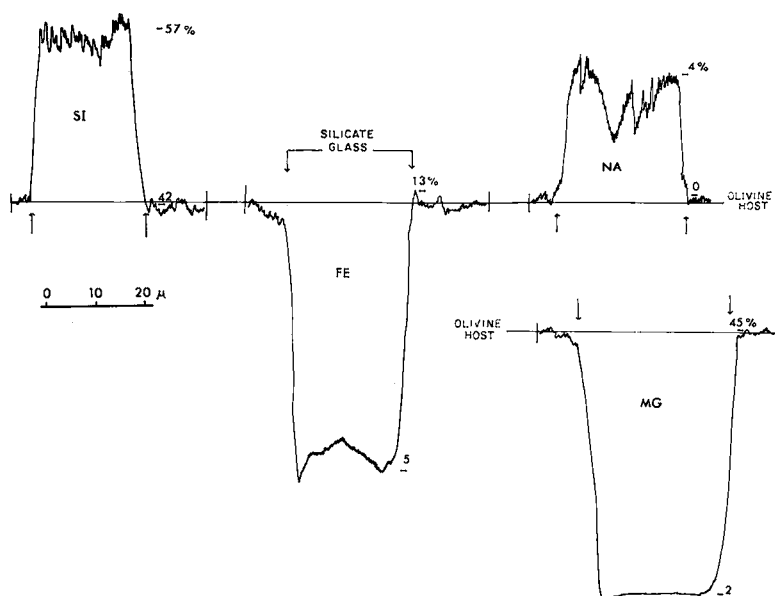


FIG. 4. Electron-microprobe scans across a 20 $\mu$  glass inclusion in an olivine crystal in dunite xenolith RE 934. Scale expansion is represented by weight % values.

compositions is controlled by clinopyroxene, plagioclase and magnetite fractionation at low pressure. The plagioclase/clinopyroxene ratio of the fractionated mineral assemblage increases from 2–5 in hawaiitic compositions to 7 in trachytic compositions.

3. Comparison with P. des Neiges indicates that a similar model will satisfy the evolution of most D.S. compositions. However, syenite generation is expected to be a result of stabilization of amphibole as a fractionating phase by introduction of water into the fractionating liquid.

4. Models based on the REE and the mass-balance equations indicate that enrichment in REE is proportional to increases in *D.I.* and an increasingly negative Eu anomaly during fractionation, from hawaiite through to trachyte. Models involving the syenitic liquids provide a good match with observed data. The introduction of amphibole as a fractionating phase in evolved liquids affects the REE pattern of the residual liquid significantly in that it reduces the overall abundance of REE, it fractionates the heavy REE preferentially to the light REE, and it offsets the Eu anomaly normally attributed to plagioclase fractionation.

5. Highly oxidized rhyodacite glass in the vesicles of some lavas is inferred to reflect the development of a high  $P(O_2)$  by localized inclusion of groundwater in the basaltic melt.

6. Primary alkaline glass inclusions in olivine crystals are tentatively inferred to represent the presence of immiscible alkali-rich liquids in the basaltic melts.

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