Residual glasses from some alkali basaltic lavas from New South Wales

By J. F. G. WILKINSON, M.Sc., PH.D.

Department of Geology, The University of New England, Armidale, New South Wales

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Summary. The glassy residua from an alkali olivine-basalt and a nephelinebasanite are respectively alkali trachytic and phonolitic in composition and contrast strongly with the compositions of the host rocks. The analysis of the glass from the alkali olivine-basalt reveals appreciable normative corundum, which is considered a consequence of the crystallization of excessive diopsidic clinopyroxene. This results in a deficiency in lime relative to alumina during the crystallization of much of the plagioclase. A consideration of the compositions of the glasses and the salic differentiates from alkaline basic intrusions indicates that the development of either trachyte or phonolite depends on differing degrees of undersaturation of the parental basic magmas.

THE chemistries of the intersertal glasses in igneous rocks are of particular importance in petrogenesis for they provide the best indications of the compositions of liquid residua. Vincent (1950), Walker, Vincent, and Mitchell (1952), and Elliot (1956) have presented chemical data on glasses from tholeiites. However, hypocrystalline alkaline basic rocks have usually been discussed from a petrographic standpoint only.

This study deals principally with the chemistry of the glasses in two alkali basic lavas (an alkali olivine-basalt and a nepheline-basanite) from the Central Volcanic Province of north-eastern New South Wales. This Province is developed mainly on the New England Tableland, where it extends as a belt from south of Armidale north to Glen Innes and west to the Inverell area. The available data indicate that the most common lava is alkali olivine-basalt. The associated volcanic rocks include nephelinebasanites and olivine-nephelinites, analcime-basanites and olivineanalcimites, and ankaramitic types (Wilkinson, 1966). Tholeiitic lavas also occur in the Inverell area. The Central Province is a major alkali olivine-basalt province in a continental setting, the volcanic rocks outcropping over an area greater than 2000 square miles. The analcimebasalt (olivine-analcimite) from Spring Mount, west of Glen Innes (Wilkinson, 1962), is lower Oligocene. This age determination is based on K/Ar measurements on phenocrysts of titanbiotite (34.5 M yr.) and kaersutite (34.1 M yr.) (Cooper, Richards, and Webb, 1963). Additional K/Ar determinations on the volcanic rocks are necessary to establish detailed age relations, particularly between the alkali and tholeiitic suites.

The glasses were separated from rock crushes by repeated centrifuging in heavy liquids. It was not possible to completely eliminate inclusions and glass-silicate composites from the glass concentrates. The glass from the alkali olivine-basalt (table II, analysis 1) was obtained approximately 95 % pure, the principal impurities being plagioclase, apatite fibres, and occasional crystals of clinopyroxene. The glass from the nephelinebasanite (table II, analysis 2) has a higher degree of purity (97 %) but contains plagioclase, apatite, and yellow-brown mineraloid impurities.

Petrography and mineralogy of the lavas

The analysed lavas (table I, analyses 1 and 2) differ in their textures, modes, and degree of normative undersaturation. The alkali olivinebasalt comprises the lower chilled selvage of a sub-horizontal flow that is 5 to 10 feet thick as now exposed in a road cutting on the New England Highway (15), 26.5 miles north of Guyra. Unaltered euhedral phenocrysts of olivine (up to 1.0×0.5 mm), occasionally glomeroporphyritic, are moderately forsterite-rich (Fa₁₈₋₁₉ mol. %; $\beta = 1.688-1.690$), and frequently exhibit normal zoning. The olivine phenocrysts are set in a groundmass of plagioclase laths (which possess some flow orientation), clinopyroxene, olivine, titanomagnetite, and glass. The largest plagioclase laths (An₅₂₋₅₆ mol. %; $\beta = 1.558 - 1.560$) range up to 0.25×0.04 mm and represent the initial generation of groundmass plagioclase. Titaniferous clinopyroxene typically builds squat prisms up to 0.05 mm in length. Pale brown glass is either intersertal or forms a base to the silicates. The refractive index of the glass varies with its depth of colour (and presumably its iron content); the majority of fragments from the analysed sample have n = 1.530 - 1.532. Occasional amygdales of fibrous carbonate, small amounts of yellowish brown mineraloid, and needles of apatite complete the mineral assemblage. An approximate mode is: olivine 14, clinopyroxene 22, plagioclase 30, opaques 9, glass 22. others 3 vol. %.

The nepheline-basanite is coarser grained than the olivine-basalt and possesses little in the way of flow structures. The principal phenocrysts are zoned plagioclase (up to 2.5×2.0 mm), peppered with numerous inclusions of clinopyroxene and olivine, and sometimes showing glomero-

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porphyritic grouping. The plagioclase is labradorite (An₆₃; $\beta = 1.563$), zoned to oligoclase (An₂₂; $\beta = 1.544$). Zoned olivine is both a phenocryst $(0.2 \times 0.1 \text{ mm})$ and a groundmass mineral, the phenocrysts having the composition Fa_{32-33} ($\beta = 1.718 - 1.721$). Some olivine crystals are partially altered to bowlingite. The titaniferous clinopyroxene is typically confined to the groundmass where it forms prisms averaging 0.08×0.02 mm. The nepheline crystals $(1.0 \times 0.2 \text{ mm maximum dimensions})$ are prismatic in habit, the prisms being grouped commonly in a parallel or sub-parallel manner. The nepheline ($\omega = 1.531$, $\epsilon = 1.527$) is highly sodic (100 K/(K+Na) = 9.2), determined by the method of Smith and Sahama, 1954). Titanomagnetite, apatite ($\omega = 1.634$, $\epsilon = 1.631$) and small amounts of yellow-brown mineraloid are also present. The brown glass is intersertal and contains inclusions of all minerals, with the possible exception of plagioclase. The glass varies in colour from pale to dark brown and may contain sufficient dusty opaque oxide inclusions to render it almost opaque. Many glass fragments have n = 1.532. An approximate mode of the nepheline-basanite is: olivine 24, clinopyroxene 29, plagioclase 15, nepheline 14, glass 13, opaques 5 vol. %.

The chemistry of the lavas and their glasses

The lavas and the respective glasses are alkalic in their chemistry, the CIPW norms revealing olivine and nepheline (table I, analyses 1 and 2; table II, analyses 1 and 2). In composition the olivine-basalt is comparable with the average alkali basalt from oceanic islands along the mid-Atlantic ridge (table I, analysis 6), and with the 'parent' olivinebasalts in many oceanic and continental provinces (Nockolds and Allen, 1954; Turner and Verhoogen, 1960, p. 192). The average normal olivinebasalt and the average Hawaiian alkalic basalt tend to be higher in lime and magnesia, and lower in alkalis (table I, analyses 4 and 5). The composition of the nepheline-basanite is similar to the composition of its Hawaiian counterpart (table I, analysis 7).

Compared with the parent rocks, the glass analyses show marked decreases in $FeO + Fe_2O_3$, MgO, and CaO, and increases in SiO_2 , Al_2O_3 , Na_2O , and K_2O . The enrichment in potash exhibited by the glass (6.09 % K_2O) from the nepheline-basanite (0.93 % K_2O) is particularly noteworthy. Evaluation of the mode and the potash contents of the rock and its glass substantiates the highly sodic composition of the nepheline indicated by X-ray measurements. The glass from the nepheline-basanite is very similar in its chemistry to the average phonolite, especially when the analysis of this glass is recalculated on a water-free basis (table II.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--------------------------------|--------|----------|----------------|-------------|---------------|--------|-------|
| SiO, | 45.60 | 42.63 | 46.59 | 45.78 | 46.46 | 47.79 | 44.33 |
| TiO | 2.42 | 2.11 | $2 \cdot 26$ | 2.63 | 3.01 | 3.03 | 2.65 |
| Al ₂ O ₂ | 15.36 | 13.07 | 15.19 | 14.64 | 14.64 | 15.94 | 12.80 |
| Fe ₂ O ₃ | 2.44 | 2.02 | 2.96 | 3.16 | 3.27 | 3.76 | 3.38 |
| FeO | 8.89 | 10.78 | 9.89 | 8.73 | 9.11 | 7.46 | 9.14 |
| MnO | 0.12 | 0.50 | 0.18 | 0.20 | 0.14 | 0.12 | 0.12 |
| MgO | 7.36 | 10.19 | 8.74 | 9.39 | 8.19 | 6.83 | 11.05 |
| CaO | 8.99 | 10.97 | 10.02 | 10.74 | 10.33 | 9.77 | 10.52 |
| Na ₉ O | 3.13 | 3.35 | 3.01 | 2.63 | 2.92 | 3.28 | 3.60 |
| K ₂ Ö | 1.68 | 0.93 | 0.96 | 0.95 | 0.84 | 1.54 | 0.99 |
| $H_{9}O +$ | 3.27 | 1.77 | 0.05 | 0.76 | **** | - | |
| $H_2O -$ | 0.38 | 1.22 | \mathbf{nil} | _ | | - | |
| P_2O_5 | 0.80 | 1.00 | 0.29 | 0.39 | 0.37 | 0.45 | 0.43 |
| Etc. | - | | 0.06 | | - | - | - |
| Total | 100.47 | 100.24 | 100.20 | - | - | 100.00 | |
| Norms: | | | | | | | |
| Or | 10.01 | 5.56 | 5.56 | $6 \cdot 1$ | 5.00 | 8.90 | 6.12 |
| Ab | 21.48 | 8.38 | 20.96 | 18.3 | 24.63 | 25.68 | 11.53 |
| An | 23.07 | 17.79 | 25.30 | 24.7 | $24 \cdot 46$ | 24.19 | 15.57 |
| Ne | 2.56 | 10.79 | 2.27 | $2 \cdot 3$ | | 1.14 | 10.22 |
| Di | 13.57 | 25.07 | 18.51 | 20.8 | 19.08 | 17.57 | 27.18 |
| 01 | 16.40 | 20.62 | 18.21 | 16.5 | 14.17 | 10.42 | 17.60 |
| Mt | 3.48 | 3.02 | 4.41 | 4.6 | 4.64 | 5.57 | 4.87 |
| 11 | 4.56 | 3.95 | 4.26 | $5 \cdot 0$ | 5.78 | 5.78 | 5.02 |
| Ар | 2.02 | 2.35 | 0.67 | 1.0 | 1.01 | 1.01 | 1.01 |
| Rest | 3.62 | 2.99 | 0.11 | _ | | - | - |
| Total | 100.80 | 100.52 | 100.26 | | - | 100.26 | _ |

TABLE I. Analyses of alkali basalts and nepheline-basanites

1. Alkali olivine-basalt, lower selvage of flow exposed in road cut, New England Highway 26.5 miles north of Guyra. Analyst S. E. Shaw.

2. Nepheline-basanite, 7 miles west of Inverell. Analyst M. Chiba.

 Alkali basalt, 1801 lava, Hualalai, Hawaii (Yoder and Tilley, 1962, table 2, analysis 19).

4. Average normal alkali basalt (and dolerite) (96 analyses) (Nockolds, 1954, table 7).

 Average Hawaiian alkalic basalt (mostly olivine-bearing) (28 analyses) (Macdonald and Katsura, 1964, table 10).

 Average alkali basalt (water-free) from volcanic islands along the Mid-Atlantic Ridge (Engel and Engel, 1964, table 1).

7. Average Hawaiian nepheline-basanite (10 analyses) (Macdonald and Katsura, 1964, table 10).

analyses 2' and 4). In contrast the glass from the alkali olivine-basalt is less undersaturated in terms of its normative nepheline content and also contains appreciable normative corundum (3.88%) (table II, analysis 1). The composition of this glass is more akin to the composition of the average alkali trachyte (table II, analysis 3).

| | 1 | 2 | 1' | 2' | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|--------------------------------|----------------|----------------|---------------|--------------|--------------|--------------|----------|--------|---------------|--------|----------------|
| SiO ₂ | 52.84 | 52.00 | 57.04 | 56.06 | 61.95 | 56.90 | 52.61 | 50.71 | 56.86 | 61.31 | 58.36 |
| TiO ₂ | 1.05 | 0.80 | 1.13 | 0.86 | 0.73 | 0.59 | 0.38 | 0.59 | 0.53 | 0.89 | 0.48 |
| Al ₂ O ₂ | 20.63 | 19.24 | $22 \cdot 27$ | 20.74 | 18.03 | 20.17 | 18.88 | 16.72 | 20.19 | 19.44 | 15.82 |
| Fe ₂ O ₃ | 1.24 | 0.92 | 1.34 | 0.99 | 2.33 | $2 \cdot 26$ | 4.06 | 3.26 | 3.63 | 1.75 | 4.87 |
| FeO | 2.74 | 3.06 | 2.96 | 3.30 | 1.51 | 1.85 | 1.72 | 5.49 | 1.40 | 1.89 | 2.53 |
| MnO | 0.04 | 0.11 | 0.04 | 0.12 | 0.13 | 0.19 | 0.11 | 0.01 | 0.13 | 0.06 | 0.27 |
| MgO | 0.51 | 0.36 | 0.55 | 0.39 | 0.63 | 0.58 | 1.62 | 0.42 | 0.33 | 0.39 | 0.59 |
| CaO | 2.56 | 1.92 | 2.76 | 2.07 | 1.89 | 1.88 | 2.43 | 3.27 | 1.64 | 1.17 | 1.99 |
| Na ₂ O | 5.08 | 7.80 | 5.48 | 8.41 | 6.55 | 8.72 | 8.93 | 6.42 | 7.42 | 7.03 | 7.47 |
| K ₂ O | 5.07 | 6.09 | 5.47 | 6.57 | 5.53 | 5.42 | 4.08 | 5.75 | 4.39 | 4.95 | 4.31 |
| $H_2O +$ | 6.99 | 7.10 | — | _ | 0.54 | 0.96 | 3.72 | 4.07 | 3.29 | 1.63 | 2.62 |
| $H_{2}O -$ | 0.21 | 0.35 | — | _ | | | 0.67 | 0.49 | 0.05 | 0.20 | 0.72 |
| P_2O_5 | 0.89 | 0.42 | 0.96 | 0.49 | 0.18 | 0.17 | 0.55 | 0.12 | 0.05 | 0.13 | 0.32 |
| Etc. | | — | — | — | | 0.36 | — | 2.94 | | | 0.04 |
| Total | 99.85 | $100 \cdot 20$ | 100.00 | 100.00 | | — | 99.76 | 100.26 | $99 \cdot 95$ | 100.84 | $100{\cdot}42$ |
| Norms | : | | | | | | | | | | |
| Or | 30.02 | 36.14 | $32 \cdot 25$ | 38.92 | $32 \cdot 8$ | 31.7 | 24.46 | 33.92 | 26.13 | 29.47 | 25.58 |
| Ab | 42.44 | 22.01 | 46.11 | 23.58 | 54.0 | $36 \cdot 2$ | 32.49 | 33.01 | 47.67 | 56.59 | 49.78 |
| An | 7.78 | _ | 7.78 | _ | $3 \cdot 3$ | 1.7 | | | 8.06 | 5.00 | |
| Ne | 0.28 | $23 \cdot 28$ | 0.28 | 24.99 | 0.6 | 18.7 | 22.44 | 11.36 | 7.95 | 1.70 | 3.98 |
| С | 3.88 | _ | 4.49 | _ | | · | _ | _ | 0.31 | 0.61 | |
| Ac | _ | 0.92 | | 0.92 | | _ | 1.39 | | _ | _ | 5.08 |
| Di | _ | 5.29 | | 6.01 | $3 \cdot 9$ | $5 \cdot 2$ | 7.70 | | _ | _ | 6.25 |
| 01 | 2.61 | 1.71 | 3.02 | 1.71 | _ | | | 4.37 | 0.56 | 1.21 | 0.14 |
| Mt | 1.86 | 0.93 | 1.86 | 0.93 | $3 \cdot 3$ | $3 \cdot 3$ | 4.64 | 4.87 | 3.25 | 2.55 | 4.64 |
| \mathbf{Hm} | — | — | — | — | — | | 0.48 | | 1.44 | | |
| n | 2.13 | 1.52 | 2.13 | 1.67 | 1.4 | $1 \cdot 2$ | 0.76 | 1.22 | 1.06 | 1.67 | 0.91 |
| Ap | 2.02 | 1.34 | 2.35 | 1.34 | 0.4 | 0.3 | 1.34 | 0.34 | — | 0.34 | 1.01 |
| \mathbf{Rest} | 7.20 | 7.45 | — | — | | 0.7 | 4.29 | 11.34 | 3.36 | 1.83 | 3.38 |
| Total | $100 \cdot 22$ | 100.59 | 100.27 | 100.07 | _ | — | 99·99 | 100.43 | 99.79 | 100.97 | 100.75 |
| Differe | ntiation | index: | | | | | | | | | |
| | 72.7 | 81.4 | 78.6 | 87.5 | 87.4 | 86.6 | 79.4 | 78.3 | 81.8 | 87.8 | 79.3 |
| Rock p | aramete | rs in Ne | -Ks-Qz | system: | | | | | | | |
| Ne | 32.0 | 43.3 | 32.0 | 43.3 | 34.2 | 44.3 | 50.4 | 37.4 | 41.3 | 36.9 | 39.0 |
| Ks | 23.5 | 25.2 | 23.5 | $25 \cdot 2$ | 21.3 | 20.8 | 17.5 | 24.6 | 18.2 | 19.1 | 18.3 |
| Qz | 44.5 | 31.5 | 44.5 | 31.5 | 44.5 | 34.9 | 32.1 | 38.0 | 40.5 | 44.0 | 42.7 |

TABLE II. Analyses of residual glasses and salic undersaturated rocks

1. Glass from alkali olivine-basalt, New England Highway, 26.5 miles north of Guyra (table I, analysis 1). Analyst S. E. Shaw.

2. Glass from nepheline-basanite, 7 miles west of Inverell (table I, analysis 2). Analyst S. E. Shaw.

1'. Glass from alkali olivine-basalt (analysis 1) recalculated water-free.

2'. Glass from nepheline-basanite (analysis 2) recalculated water-free.

3. Average alkali trachyte (15 analyses). (Nockolds, 1954, table 3).

4. Average phonolite (47 analyses). (Nockolds, 1954, table 10.)

5. Analcime-tinguaite, Square Top intrusion near Nundle, New South Wales (Wilkinson, 1965, table 1). (Differentiate of analcime-olivine-theralite whose normative Ne = 15.90 %.) 6. Microcrystalline 'vein' mesostasis (alkali feldspar, analcime, sodie clinopyroxene, opaque

oxide), Black Jack sill, near Gunnedah, New South Wales (Wilkinson, 1958, table 6). (Differentiate of teschenite whose normative Ne = 7.38 %.)

7. Syenite (1501), Takara Bridge, Tiyo Mine, Morotu district, Sakhalin (Yagi, 1953, table 16). (Differentiate of teschenite whose normative Ne = 5.96 %.)
8. Syenite (1310), north of Tyaki, Tiyo Village, Morotu district, Sakhalin (Yagi, 1953, table 16).

(? Parent alkali dolerite has 3.12 % normative Ne).

9. Segregation in analcime-syenite, Eilean Mhuire, Shiant Isles (Walker, 1930, p. 387). (Differentiate of mildly undersaturated analcime-bearing alkali dolerite.)

It is possible that the excess alumina indicated by the norm could have resulted from two principal errors during analysis: incomplete separation of SiO₂ from the R_2O_3 precipitate, or inaccurate alkali determinations. The alkalis (Na₂O 5.08, K₂O 5.07 %) are the mean of three determinations by two analysts who used separately prepared standards: Na₂O 5.04, 5.11, 5.10 %; K₂O 5.04, 5.10, 5.07 %. A duplicate determination of Al₂O₃ using ion exchange methods yielded Al₂O₃ 20.23 %; a duplicate silica determination yielded SiO₂ 52.76 %. If the explanation of the excess alumina is to be found in underestimation of the alkalis, it would be necessary to assume an additional 1.2 % Na₂O and 1.8 % K₂O. Thus it would be necessary for there to be a deficiency of 3 % in the alkalis, which must be allowed for in other constituents.

Certain constituents of this glass were redetermined in the Australian National University by Dr. D. H. Green, using an ARL Electron Probe Microanalyser. The analyses were calibrated by direct comparison with a series of standard glasses of enstatite and hypersthene composition (En_{30}, En_{75}) with varying Al₂O₃ contents (0-20%) and CaO contents (0-4%). A second series of iron-free glasses containing various proportions of SiO₂, TiO₂, Al₂O₃, MgO, CaO, Na₂O, and K₂O, prepared from A.R. chemicals, were used also as standards. An average glass composition¹ based on the microprobe analyses of 8 'areas' of glass is: TiO₂ 1·3 (range 1·2-1·5), Al₂O₃ 22·6 (range 21·6-23·7), FeO 4·9 (range 4·3-5·3), CaO 1·6 (range 1·2-2·0 %), K₂O 4·8 (range 3·4-5·8 %). The most obvious discrepancy between the microprobe data and the chemical analysis of the separated glass relates to CaO (1·6 and 2·6 % respectively). However, agreement between the two values is better if allowance is made for apatite impurities in the chemically analysed glass.

Additional confirmation of the alumina-rich nature of this glass is furnished by microprobe analyses of clinopyroxene and plagioclase included in the glass. Plagioclase in one glass area yielded Al_2O_3 30, CaO 8:35 % (average), equivalent to $An_{41.4}$ wt. %. Comparison of these values with analyses of plagioclases with similar An contents suggests 3–4 % excess Al_2O_3 (cf. Deer, Howie, and Zussman, 1963, table 15). The bulk of the clinopyroxene contains FeO 9–9:5, Al_2O_3 3:5–4, TiO₂ 2:3–2:6, and CaO 21:6 % (average). The margins of crystals within an alumina-rich glass area (23 % Al_2O_3) contain over IO % FeO, over 6 % Al_2O_3 , and from 4 to 6 % TiO₂. The higher values of FeO and Al_2O_3 are in harmony with increases in the FeO/MgO ratio and the Al_2O_3 content of the residual liquid.

From the above discussion it would seem reasonable to conclude that the normative composition of the glass reflects an actual enrichment in alumina in the residual liquid.

General discussion

After a consideration of the chemistry of certain East African trachytes and phonolites, Bowen (1937) concluded that these rocks represented residual liquids produced by fractional crystallization of 'crystallizing magmas'. Their salic components (less anorthite) projected in the system NaAlSiO₄-KAlSiO₄-SiO₂ showed a marked concentration within the thermal valley in this system. Chemical data on trachytes and phonolites from other volcanic provinces has resulted in a consensus of opinion in accordance with Bowen's views. The parent magmas of these provinces

¹ Total Fe reported as FeO.

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generally are considered to be alkali olivine-basalts (Benson, 1941; Walker and Nicolaysen, 1954; Turner and Verhoogen, 1960; Le Maitre, 1962). Perhaps the most compelling evidence for the production of undersaturated salic residua from more basic liquids is afforded by veins and schlieren of analcime-syenite in differentiated teschenitic intrusions (Yagi, 1953; Wilkinson, 1958) and by the development of analcimetinguaite from theralite (Wilkinson, 1965). Hamilton and MacKenzie (1965) have demonstrated that the distribution of 122 analyses of extrusive rocks (Washington, 1917), carrying more than 80 % normative Ab+Or+Ne, shows a marked similarity to the low-temperature region in the system NaAlSi₃O₈-KAlSi₃O₈-NaAlSiO₄-KAlSiO₄ determined at 1000 Kg/cm² water pressure. They concluded that many phonolitic rocks have been derived by fractional crystallization of a trachytic magma, the liquidus surface near the Ab-Or join trending towards the area of lowest temperatures, which is located at more undersaturated compositions.

The differing degrees of undersaturation displayed by the two basic lavas are reflected in the differing chemistries of their residua. The slightly peralkaline glass from the nepheline-basanite plots in the field of leucite at a composition slightly more potassic than the reaction point in the dry system (close to Ne₄₆Ks₂₁Qz₃₃), and within the lowest temperature area trending parallel with the Ab–Or join at $P_{\rm H_2O}$ 1000 Kg/cm² (fig. 1). From the textural and chemical viewpoints this glass is a quenched residual liquid and indicates the degree whereby fairly rapid fractional crystallization of a basic magma may yield an alkali-rich aluminosilicate liquid (cf. Schairer, 1957; Schairer and Yoder, 1960). This liquid is relatively more potassic than the most differentiated analcimetinguaite in the Square Top intrusion (Wilkinson, 1965) where fractionation of alkali feldspar resulted in the 'orthoclase effect' (Bailey and Schairer, 1964). The composition of this glass provides an illustration of alkali enrichment in response to the 'plagioclase effect' (Bowen, 1945). The increase in potash in the residual liquid was enhanced also by the early separation of a soda-rich nepheline.

The proximity of the average phonolite, foyaite, lardalite, and tinguaite to the ternary reaction point and to the minimum in petrogeny's residua system determined at $P_{\rm H_{2}O}$ 1000 Kg/cm² has been noted previously (Tilley, 1958; Wilkinson, 1965) and attention directed to the heteromorphic felsic assemblages appropriate to these compositions Only nepheline (of the potential nepheline, alkali feldspar, or analcime) crystallized during the prevailing conditions of low water pressure, as the crystallization of alkali feldspar or analcime or both was suppressed by quenching above the stability fields of these minerals (cf. Yoder, 1958; Greenwood, 1961). The composition of the glass from the nepheline-basanite, recalculated free of TiO₂, Fe₂O₃, FeO, MgO, CaO, and P₂O₅ is SiO₂ 56·4, Al₂O₃ 20·8, Na₂O 8·5, K₂O 6·6, H₂O+7·7 % (Ne₄₂Ks₂₄Qz₃₄; cf. table II, analysis 4). This is similar to the recalculated composition of the



FIG. 1. Residual glasses from the alkali olivine-basalt (1) and the nepheline-basanite (2) and some undersaturated salic rocks (table II, analyses 1 to 9) plotted in the system Ne-Ks-Qz. Analysis 10 is the analcimic groundmass $(Ne_{43}Ks_{20}Qz_{38})$ in an olivine-analcimite (Wilkinson, 1962, table 7). R = reaction point in the dry system. M = minimum 750° \pm 7°C (Ne₅₀Ks₁₉Qz₃₁) determined at $P_{H_2O} = 1000 \text{ kg/cm}^2$ (Hamilton and MacKenzie, 1965). m = alkali feldspar minimum at 1000 kg/cm². The low temperature trough *ABCD* is shown as originally delineated for the dry system by Bowen (1937).

analcimic groundmass of the Spring Mount olivine-analcimite (Wilkinson, 1962, table 7). This groundmass composition represents possible alkali feldspar, nepheline, or analcime assemblages, whose nature can be related to the rate of cooling, temperature of final crystallization, and $P_{\rm H_sO}$ during crystallization.

In many respects the composition of the glass from the olivine-basalt is closely comparable with slightly undersaturated alkali trachytes whose felsic mineralogy is predominantly alkali feldspar plus minor feldspathoid (cf. table II, analysis 3). The alkali trachytes delineate a second maximum on the contour diagram based on the salic compositions of 122 extrusive rocks (with Ab+Or+Ne > 80 %) (Hamilton and MacKenzie, 1965, fig. 5). Although its chemistry is not entirely appropriate, the glass has been plotted in the Ne-Ks-Qz system where it falls close to the composition of the average alkali trachyte (fig. 1). Recalculation of the glass analysis (anhydrous, free of TiO₂, Fe₂O₃, FeO, MnO, and MgO, and with some CaO allotted to apatite) yields the composition: SiO₂ 62·04, Al₂O₃ 24·22, CaO 1·83, Na₂O 5·96, K₂O 5·95%. This composition when recast as an alkali feldspar on a basis of 32 (O) yields the formula: (K_{1·36}Na_{2·07} Ca_{0·35})(Al_{5·12}Si_{11·13})O₃₂. Although the X (3·78) and Z (16·25) groups differ from the generally accepted values of 4·00 and 16·00 respectively, the calculation does demonstrate the essentially alkali feldspathic composition of the liquid. Specimens of basalt higher in the flow contain less glass than in the chilled selvage and what appear to be untwinned alkali feldspar microlites have developed interstitially to the plagioclase laths.

The presence of normative corundum in this residual liquid could be explained in terms of gaseous transfer of alkalis, or assimilation of argillaceous material, or as a consequence of the chemistry of the parent magma, which possibly may be related to atypical conditions of generation, or as a result of controls exerted by the crystallization of the silicates. The first and second theories are not considered feasible for the lava shows only very minor evidence of vesiculation indicating the release of a gas phase, and does not display mineralogical or geochemical evidence suggesting assimilation. The third theory does not appear to be a suitable explanation because the total rock composition is similar to many other alkali basalts.

Modal and chemical data indicate that the fourth theory, which involves the crystallization of excessive lime-rich clinopyroxene, adequately explains the peraluminous nature of the residual liquid. The conventional derivation of the norm conceals the possibility that peraluminous liquid fractions may be produced during the crystallization of basalts, because sufficient lime to saturate the alumina remaining after forming Ab (and Ne) and Or is available from the clinopyroxene. However, where it can be shown that the modal clinopyroxene notably exceeds the normative diopside, a deficiency in lime (relative to alumina) necessary for plagioclase is produced. The mode (based on 3000 points counted on thin sections ground less than the normal slide thickness) indicates olivine 14, clinopyroxene 22 vol. %. The density of the basalt is 2.86 and hence the wt. % modal clinopyroxene exceeds 22 %. The microprobe data indicate that, on an average, the clinopyroxene contains 21.6% CaO and 4.0% Al₂O₃. Assuming 0.6% Na₂O in the clinopyroxene, the precipitation of 18 wt. % clinopyroxene containing these amounts of Al_2O_3 , CaO, and Na_2O results in an excess of 0.4% Al_2O_3 , after the formation of normative apatite and aluminosilicates with a 1:1 molecular ratio of alkalis and lime to alumina. The textures of the lava support the

data indicating precipitation of excessive clinopyroxene following the formation of clinopyroxene centres of crystallization. Some clinopyroxene crystals indent the plagioclase but the former mineral generally occurs as squat euhedral prisms concentrated as micro-aggregates (often nucleated around opaque oxide granules) in areas of glass between the plagioclase laths. At no stage is the clinopyroxene ophitic or sub-ophitic; the relatively high pyroxene ratio [100 pyroxene/(pyroxene + plagioclase) = 42] of the rock accords with comparatively high values of modal pyroxene in certain other olivine-basalts in which the clinopyroxene is also markedly euhedral (cf. Clark, 1952).

Experimental data on the Hualalai alkali basalt (table I, analysis 3) carried out at a total pressure of 1 atmosphere, indicates that olivine is the first silicate phase to crystallize at 1225° C, followed by plagioclase at 1160° C and clinopyroxene at 1155° C. The small range of temperatures separating the crystallization of the two latter phases may be noted. A reversal in the order of crystallization of plagioclase and clinopyroxene would not be unexpected. The textures of the New England olivine-basalt indicate that the phenocrysts of olivine crystallized first, and that these were followed by minor amounts of plagioclase and then by fairly rapid crystallization of clinopyroxene, which was localized in areas of close nucleation. Plagioclase had a relatively long crystallization range, indicated by several generations of feldspar microlites.

Some approximation of the liquidus temperatures of the alkali olivine-basalt ($F = 0.60_6$) and the nepheline-basalt ($F = 0.55_7$) may be derived from the respective degrees of iron enrichment [(F = (FeO + FeO))Fe₂O₃)/(MgO+FeO+Fe₂O₃); Tilley, Yoder, and Schairer, 1964)], which indicate liquidus temperatures of approximately 1180° C and 1210° C respectively. The higher temperature of the nepheline-basanite accords with the relatively higher temperature of an Oahu olivine-nephelinite, compared with other basalts, the olivine silicate liquidus being located at 1305° C (Yoder and Tilley, 1962). The data on the various basalts studied experimentally by Yoder and Tilley indicates a small total range of crystallization (135° C to 195° C), and it is likely that the olivine-basalt and the nepheline-basanite were quenched from temperatures of approximately 1000° C to 1050° C. These temperatures are not notably at variance with the temperatures indicated by the locations of the glasses in the Ne-Ks-Qz system determined at 1 atmosphere, especially when due allowance is made for the lowering of the liquidus temperatures of the residua by other components.

The trachytic and phonolitic chemistry of the two residua accord with

earlier observations (cf. Turner and Verhoogen, 1960, p. 169; Le Maitre, 1962) that the interstitial alkali feldspar, nepheline, and analcime in alkaline basic rocks represent potential trachytic or phonolitic differentiates. Indeed, most of the normative Or, Ne, and Ab (in excess of the Ab in plagioclase) in alkali basalts can be so regarded. A mesostasis of alkali feldspar, clinopyroxene (sometimes acmitic), analcime, and opaque oxides is not uncommon in teschenites and theralites (Lehmann, 1930; Walker, 1936; Wilkinson, 1958, p. 13). The chemistry (table II, analysis 6) and mineralogy of the mesostasis are similar to the veins of analcimesyenite (table II, analyses 7 to 9) that occur generally within the basic intrusions.

The development of either trachyte or phonolite has been referred on occasion to processes involving the gaseous transfer of alkalis. However, Coombs (1963) has indicated that mildly alkaline basalts (with neither significant normative nepheline nor hypersthene) tend to yield a trachytic trend of differentiation whereas a phonolitic line of descent is characteristic of relatively more alkaline basic lavas. Similar conclusions were reached by Wright (1963), following a survey of the differing differentiation trends of Cainozoic Kenyan lavas. Hamilton and MacKenzie (1965) have drawn attention to the fractionation curve extending from the minimum (m) on the Ab–Or join to near the minimum (M) on the alkali-feldspar–nepheline field boundary in the Ab–Or–Ne–Ks quadrilateral at PH_sO 1000 Kg/cm² (fig. 1). They consider that the control exerted by this curve under conditions of perfect fractionation leads ultimately to the production of phonolite from trachyte (see Le Maitre, 1962, p. 1334).

Precise identification of the parents of the various undersaturated salic members of a volcanic province is clearly difficult. The most unambiguous evidence relating parent melts and their differentiates is provided by the data from differentiated intrusions and by rocks whose residua have been quenched. The data presented in table II and figure 1 support the view that the degree of initial undersaturation of the parent magma determines the degree of undersaturation of its salic differentiates. It could be argued that the mildly undersaturated differentiates (3, 8, 7, and 9 in fig. 1) resulted from fairly rapid differentiation that was terminated by more or less complete crystallization before more fractionated liquids trending in the direction $m \rightarrow M$ (fig. 1) could be generated. However the production of phonolitic liquids by the Square Top theralite (Wilkinson, 1965) and the Inverell nepheline-basanite was also accomplished by rapid differentiation, which at Square Top is reflected in a mineral assemblage appropriate to volcanic rocks. No doubt detailed studies of individual masses of trachyte will clarify the degree to which trachytic liquids may themselves be capable of fractional crystallization.

The relative abundance of analyses of oceanic intermediate and salic lavas has led Chayes (1963) to query the thesis that crystal fractionation of basaltic magma is the effective mechanism in the generation of trachytic rocks. However, the so-called 'Daly gap' is perhaps not unexpected in view of the strongly contrasting compositions between the mesostasis in many basic alkaline rocks, the glassy residua under discussion, and the respective host rocks. It is clear that salic liquids can be produced by fractional crystallization of basic liquids and that the production of these differentiates need not be accompanied by significant quantities of differentiates with intermediate compositions. However, the equivalents of the recently designated intermediate members of the oceanic basalt-trachyte association, namely benmoreite and tristanite (Tilley and Muir, 1964), do occur as differentiates in mildly alkaline basic intrusions. An 'analcite-syenite' occurring as a segregation in analcimeolivine-dolerite at Howford Bridge, Ayrshire (Tyrrell, 1928), with SiO₂ 56.4, CaO 4.2, FeO+Fe₂O₃ 6.9, D.I. 74.8, and a 'grey vein' in the teschenite sill at Charlestown, Fife (Walker, 1926), with SiO₂ 55.3, CaO 4.1, $FeO + Fe_2O_3 6.9$, D.I. 64.6 are examples of intrusive rocks whose chemistries are appropriate to the gap of minimal frequency in the series basalt \rightarrow trachyte. Further examples are provided by some of the Morotu (Sakhalin) 'monzonites', which complete the trend from alkali dolerite to the most evolved differentiates of alkali trachytic compositions (Yagi, 1953; table II, analyses 7 and 8).

Clearly more data are necessary to ascertain whether the normative corundum in the analysis of the glass from the olivine-basalt is to any extent common in residua of this type. Many trachyte analyses reveal up to 1 % normative corundum and values of 2 % are known. Fractionation of trachytic liquids involving the precipitation of phases containing excess Al_2O_3 may decrease the Al^{3+} contents of the liquids to such an extent that the final products are not conspicuously peraluminous. Some alkali feldspars from trachytes contain small amounts of normative corundum but there appears to be little agreement whether this feature is a consequence of actual substitution in the feldspar structure or is the result of sampling and analytical procedures (Chayes and Zies, 1962; Deer, Howie, and Zussman, 1963; Carmichael and Mac-Kenzie, 1964). In intrusive rocks with trachytic compositions, analcime

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also is a phase which may show excess Al_2O_3 relative to the alkalis and lime (Saha, 1959, table 1).

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