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The feldspar phenocrysts of some Tertiary acid glasses.

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Summary. The feldspar phenocrysts of some British and Icelandic Tertiary acid glasses have been studied optically and chemically. Six new analyses of the feldspar phenocrysts are presented together with an anorthoclase from a glassy pantellerite. The analysed feldspars and all the other feldspar phenocrysts that have been examined show high-temperature optics, and confirm the results of previous investigations of plagioclase feldspar determinative curves. The relationship of the feldspar phenocrysts to the plagioclase components in the analysed residual glasses conforms to the synthetic plagioclase system, and the crystallization of feldspar in natural acid melts is considered.

S INCE the clear recognition of high-temperature optics of volcanic plagioclases by Kohler (1941, 1942) and Tertsch (1942), little work has been done on the plagioclase feldspars of the British Tertiary volcanic province, although Bradley (1953) has reported that the plagioclase phenocrysts of a pitchstone from Brodick, Arran, have high-temperature optics as may the plagioclase phenocrysts of an Arran felsite. Tuttle and Bowen (1958) have shown the transitional nature of the optics (and the structure) of the plagioclase and alkali feldspars of the Beinn an Dubhaich granite, Skye, as have Emeleus and Smith (1959) for the alkali feldspar phenocrysts of a porphyritic felsite from Slieve Gullion, Northern Ireland. The optical data for the alkali feldspars of the Mourne Mountains granite (G1) given by Brown (1956, table 7) suggest that they also are intermediate between the low-sanidine-anorthoclase and orthoclase-low-albite series (Tuttle, 1952). This paper is concerned with the feldspar phenocrysts of ten pitchstones from the North Atlantic Tertiary volcanic province, the pyroxene and olivine phenocrysts of which have been separated, analysed, and described (Carmichael, 1960).

Of the ten pitchstones, six come from the east coast of Iceland where they occur in association with the Thingmuli central volcano as an acid dyke (G. 151) and as a pitchstone margin of an acid lava (G. 87); as high-level acid intrusions at Sellatur (E. 868) (Walker, 1959, p. 379), at Bondolfur (P. 186), and at Skruthur (P. 258); and as the chilled margin of a dacitic lava at Rauthaskritha (IC. 3) (Hawkes, 1924). The pitchstones from the British Tertiary all come, with one exception, from the island of Arran, where they form dykes, and have been described by Tyrrell (1928, pp. 210–235). The Arran specimens come from behind the schoolhouse at Brodick (AC. 6), from Glen Shurig (AC. 7), and from the Tormore shore (Judd's No. 1 dyke) (AC. 12). The remaining pitchstone forms the Sgurr of Eigg (EC. 20), which has been described in detail by Harker (1908, pp. 170–174).

The enumeration of the feldspars described here is the same as that of the pyroxenes, olivines, residual glasses, and pitchstones (Carmichael, 1960). Thus, for example, 1F is the analysed alkali feldspar (table III), 1P the optically determined plagioclase (see below), 1 and 1A the analysed pyroxenes, and 1G the analysed residual glass, all of which make up the analysed pitchstone (1R) that forms the Sgurr of Eigg.

The nomenclature of the high-temperature sodic alkali feldspars has been discussed by Smith and MacKenzie (1958), who have suggested that calcium-bearing alkali feldspars may be distinguished from potassic albite and oligoclase by the presence or absence of a change in symmetry on heating. Unfortunately no X-ray study has been made on these feldspars, nor apparently can a distinction be made by the refractive indices or optic axial angle. However, the development of various twin laws suggests a classification, for four of the analysed feldspars, 1F, 4F, 7F, and 3112F (table III and fig. 5), twin only on the Carlsbad, Manebach, and Baveno laws, although very fine shadowy but optically indeterminate lamellar twinning is persistent. The three feldspars 2F, 6F, and 8F (table III and fig. 5) twin on the above laws and also on the albite, albite-Ala, and Carlsbad-albite laws, and very fine lamellar twinning is rare or absent. The feldspars that twin on the complex laws (2F, 6F, and 8F) are for the purposes of this study called plagioclases, whereas the remainder are alkali feldspars, and either sanidine or anorthoclase according to their symmetry. Both the plagioclases and the sodic alkali feldspars as defined here fall into the corresponding

composition fields of high-temperature plagioclase and anorthoclase suggested by Smith and MacKenzie (1958, fig. 1).

Petrography.

It is hoped to publish a more detailed account of the petrography of these pitchstones later, so only a very brief summary, mainly concerning the feldspar phenocrysts, is offered here.

The pitchstone of Eigg contains abundant phenocrysts of slightly zoned alkali feldspar (1*F*, table III), together with considerably rarer phenocrysts of augite and orthopyroxene, and opaque iron ores. A dull brown microcrystalline glass with perlitic fracture encloses the phenocrysts. The alkali feldspar may show small and sporadic patches of unmixed sodic feldspar, which is well shown on staining, with very rare crystals having cores of plagioclase. Some of the alkali feldspar phenocrysts have very fine lamellar twinning, which is variable in thickness and extent and is possibly gradational to the clearly developed crosshatched microcline twinning that may rarely be found bordered by untwinned alkali feldspar. Independent plagioclase is extremely rare, shows well developed lamellar twinning, and has the following optical properties:¹ (1*P*) $\alpha = 1.534$ (An₁₂), $\gamma = 1.543$ (An₁₄).

The pitchstone dyke from Tormore, Arran, (AC. 12) contains scattered phenocrysts of slightly zoned plagioclase (2*F*, table III) together with less common ferroaugite and orthopyroxene. The glassy ground mass is pale in colour, and has abundant spiculites, which define the flow banding. The plagioclase phenocrysts are often well rounded, and are twinned on the normal parallel and complex laws. The dyke at Brodick, Arran, (AC. 6) presents a most striking display of scopulites within the glass, which encloses phenocrysts of ferroaugite, olivine, quartz, and weakly zoned plagioclase. The plagioclase phenocrysts, which have not been analysed, have been examined on the universal-stage and the Kohler twin-angle values determined together with the optical constants. As with all the other optically-determined plagioclase phenocrysts, these show high temperature optics:² (5*F*) $\alpha = 1.538$ (An₂₃), $\gamma = 1.550$ (An₂₈), $2V_{\alpha} = 68^{\circ}$ (An₂₆); U-stage = An₂₆.

The Glen Shurig dyke (AC. 7) is the richest in ferromagnesian

¹ The high-temperature plagioclase refractive index and 2V curves of Smith (1958) have been used for this and all subsequent optical determinations.

² U-stage = An_{26} refers to the average value of An % of the Kohler twin-angles for the high-temperature plagioclase curves (Tröger, 1956), the abbreviation U-stage being used subsequently.

phenocrysts of all the glasses examined and they consist of olivine, ferroaugite, and xenocrystic orthopyroxene, together with quartz and plagioclase. The plagioclase phenocrysts, which are of variable size, have the following optical properties: $(10F)\alpha = 1.540 (An_{23}), \gamma = 1.551 (An_{30}), 2V_{\alpha} = 69^{\circ} (An_{27})$; U-stage = An₂₇.

The Icelandic glasses typically have fewer microlites in the glass and are all devoid of quartz as a porphyritic element. Basaltic xenoliths often in advanced stages of digestion are not uncommon, and are particularly frequent in P. 258 and G. 87. The acid lava from Rauthaskritha (1C. 3) contains phenocrysts of plagioclase (9*F*, U-stage = An₃₄), olivine, and ferroaugite, all being enclosed in a hyalopilitic glass with rhombs of alkali feldspar (Hawkes, 1924). The acid lava from Thingmuli (G. 87), which rests in the centre of a zone of intense hydrothermal alteration, has well-developed perlitic texture in a pale-coloured glass. Enclosed in the glass are phenocrysts of weakly zoned plagioclase, together with ferroaugite and basaltic material, which may remain coherent or may be scattered throughout the glass as independent minerals. The plagioclase phenocrysts have the following properties: $(3F) \alpha = 1.546$ $(An_{34}), \beta = 1.551$ $(An_{37}), \gamma = 1.554$ $(An_{36}), 2V_{\alpha} = 79^{\circ}$ (An_{34}) ; Ustage = An₃₃.

The glassy margins of the acid intrusions contain phenocrysts of feldspar together with one or more ferromagnesian silicates and opaque iron oxides. The pitchstone margin of the Sellatur plug (E. 868) has phenocrysts of anorthoclase (4F, table III) and ferroaugite, which are enclosed in a pale brown glass. The anorthoclase phenocrysts show a great deal of very fine twinning, often cross-hatched, but not quite coarse enough for optical determination. The well flow-banded pitchstone (P. 186) has phenocrysts of plagioclase (8F, table III), together with less abundant ferroaugite and olivine, enclosed in a pale brown glass. The plagioclase phenocrysts are twinned on the normal, parallel, and complex laws, and the very fine twinning characteristic of many of the anorthoclases is not noticeably present. Weakly birefringent spherulites are abundantly developed in P. 258 and may surround many of the phenocrysts of anorthoclase (7F, table III) and ferroaugite. The feldspar phenocrysts show extremely fine twinning, which is usually optically indeterminate and which may be cross-hatched. Extremely rare olivine and microphenocrysts of opaque iron oxides are contained in a pale brown glass with well developed perlitic structure.

The Thingmuli acid dyke (G. 151) has phenocrysts of plagioclase (6F, table III), which are the most strongly zoned of all the analysed

feldspars, with a probable range of about 6 % anorthite. The contiguous twin lamellae of this plagioclase are sometimes of different composition, and gave consistently large triangles of error for the twin axes (cf. Game, 1957, p. 663). Olivine and ferroaugite, together with the plagioclase phenocrysts, are set in a glassy microlitic groundmass with abundant tiny feldspar laths.

All the feldspar phenocrysts are extremely fresh, and with the exception of no. 6F only slightly zoned. No study has been made of the habit of the phenocrysts, but the feldspars vary in habit from the slender laths typical of many of the plagioclase phenocrysts to the stumpier, almost equi-dimensional habit of some of the alkali feldspars.

TABLE I. Modal analyses (vol. %). For the key to these analyses, see below.

No.	Glass	Plagio- clase	Alk. feld- spar	Quartz	Pyro- xene	Olivine	Iron oxides	Basaltic xenoliths
EC. 20 (1R)	79·3	trace	19.2	_	1.0		0.5	trace
AC. 12 (2R)	97.1	2.5		— <u> </u>	0.2	_	0.2	_
E. 868 (4R)	92.0		6.0	_	0.4		0.4	1.2
G. 151 (6R)	89.0	8.1	_		1.6	0.7	0.6	_
P. 258 (7R)	86.7	_	9.2		0.5		0.2	3.4
P. 186 (8R)	89.6	8.9	_		0.8	0.2	0.3	0.2

KEY to TABLES I-V

- IF Sanidine from Sgurr of Eigg pitchstone (Harker, 1908, pp. 170-174). EC. 20.
- 1G Residual glass from EC. 20.
- 2F Plagioclase (with analysis recalculated after subtraction of 13 % of 2G) from Judd's No. 1 dyke, Tormore shore, Arran (Tyrrell, 1928, pp. 218–235). AC. 12.
- 2G Residual glass from AC. 12.
- 4F Anorthoclase from pitchstone margin of Sellatur plug, E. Iceland. E. 868.
- 4G Residual glass from E. 868.
- 6F Plagioclase from glassy margin of dyke, Thingmuli, E. Iceland. G. 151.
- 6G Residual glass from G. 151.
- 7F Anorthoclase from pitchstone margin of intrusion, Skruthur, E. Iceland. P. 258.
- 7G Residual glass from P. 258.
- 8F Plagioclase from pitchstone margin of intrusion, Bondolfur, E. Iceland. P. 186.
- 8G Residual glass from P. 186.

3112F Anorthoclase from glassy porphyritic pantellerite, Pantelleria. 3112.

3112G Residual glass from 3112.

Analyst: I. S. E. Carmichael. The analyses of the residual glasses nos. 1G to 8G are taken from Carmichael, 1960 (table VI).

The modal analyses of these porphyritic pitchstones are given in table I, and are slightly different from those given previously (Carmichael, 1960, table I) as the composition of the feldspar phenocrysts was unknown at that time.

The optics of the analysed feldspars.

The refractive indices were determined by the immersion method using sodium light, and care was taken to keep the refractometer at the same temperature as the microscope stage. Although the repeated determinations of refractive index made on different days showed satisfactory precision, it is not believed that the determined values are more accurate than ± 0.002 . A comparison of the refractive indices of the analysed plagioclases (2*F*, 6*F*, and 8*F*, table III) with the high-temperature curves published by Smith (1958, fig. 3) shows satisfactory agreement, especially if allowance is made for the higher Or content of these plagioclases by recalculating their composition to mol. % An/(An+Ab). This new refractive index data therefore lends support to Smith's suggestion (1958, p. 1190) that the refractive index curves of Schwarzmann (1956) for the high-temperature sodic plagioclases are too low.

The refractive indices of the alkali feldspars are, with the exception of 3112F, anomalous. All three indices of 4F and 7F (table III) are above those of the most sodic of the alkali feldspars (Tuttle, 1952) and an approximate idea of their An content may be derived from the hightemperature plagioclase curves of Smith (1958). The refractive indices of 3112F are appropriate to an alkali feldspar of that composition (table III), and the low lime content is similar to that of the high temperature alkali feldspars used for the refractive index variation curves (Tuttle, 1952). As the refractive indices of 1F (table III) are comparable with, and lie within the experimental error of, the refractive indices of 3112F (table III) it would seem probable that the unusually high content of lime in 1F (and in 4F and 7F) is responsible for the otherwise anomalously high refractive indices (Tuttle, 1952, p. 559). Until the exact structural state of these alkali feldspars is known, they cannot reliably be used for optical determinative curves, but eventually the optical properties of the high-temperature calcic anorthoclases and potassic plagioclases will have to be drawn on a ternary feldspar diagram.

The optic axial angle of all the feldspar phenocrysts was measured directly on a Leitz 4-axis universal stage using the orthoscopic procedure, for many feldspars have noticeable dispersion, and the final setting was made using a yellow optical filter. The average value and the range of 2V is given in table III. The range in values for 1F may indicate that it is intermediate between the low-sanidine-high-albite and orthoclaselow-albite series (Tuttle and Bowen, 1958; Emeleus and Smith, 1959), whereas the variation in 2V of 6F (table III) is caused by zoning over a range of about 6 % An.



FIG. 1. Stereogram showing the migration of twin-axes of parallel and complex twin laws with change in composition for high- and low-temperature plagioclases. The twin axes of the plagioclase phenocrysts of these acid glasses are plotted.

The average figure for 2V of the analysed plagioclases shows satisfactory agreement with the high-temperature plagioclase values of Smith (1958, fig. 2), whereas the alkali feldspars, with the exception of 3112F, are again anomalously high. It is presumed that the high content of lime has had similar influences on the optic axial angle and on the refractive indices of the alkali feldspars (cf. Tuttle and Bowen, 1958, p. 108).

The orientation of the indicatrix with respect to the crystallographic directions of the feldspar phenocrysts was determined by the Fedorov

method on twinned crystals, using the twin axes of the various twinlaws. The crystallographic directions are not precisely obtained from the cleavages, and the commonly vicinal twin composition planes are of little use for precise determination.



FIG. 2. Stereogram showing the position of the twin-axes of the alkali feldspar phenocrysts (dots) together with the albite twin-axes of the plagioclase phenocrysts (crosses).

The optical directions of both members of a twinned crystal were plotted stereographically, the twin-law identified, and the position of the twin axis after rotation of β to the centre of the stereogram determined. The position of the transposed twin-axis enables the composition of a plagioclase to be determined, using the migration curves of van der Kaaden (1951), published by Tröger (1956). The migration curves for the various twin-laws for the high-temperature plagioclases are displaced from the corresponding migration curves for the low-temperature

plagioclases, and it may be seen (figs. 1 and 2) that the twin axes of the plagioclase phenocrysts of these acid glasses all fall on or near the hightemperature migration curves. The average position of the twin axes of each determined twin-law of the analysed plagioclases (2F, 6F, and8F, table III) is given in table II. It is suggested that the hightemperature migration curve for the Carlsbad-albite twin-law should be slightly lower, as all the determined twin axes fall below the curve (fig. 1). The Carlsbad and Manebach twin axes of one plagioclase (8F)fall among those of the alkali feldspars, and nearer to the low-temperature plagioclase migration curves than the high-temperature (fig. 1), and is possible that the optical properties of this feldspar are in some measure similar to those of the alkali feldspars. The twin axes of the alkali feldspars scatter around the position of triclinic anorthoclase. All the alkali feldspars show inclined extinction in the zone [010], but 1F usually, although not invariably, shows straight extinction indicating monoclinic symmetry, although the average position of the Manebach and Carlsbad twin axes (table II) lies outside the α - β plane, and points to triclinic symmetry; this of course may be experimental error.

The composition of plagioclase may also be derived optically by the values of the Kohler twin-angles. These are the angles between each axis of the indicatrix of one twin member and the corresponding axis of the indicatrix of the other member, viz the angles $\alpha \alpha'$, $\beta \beta'$, and $\gamma \gamma'$ where $\alpha\beta\gamma$ are the indicatrix axes for one member and $\alpha'\beta'\gamma'$ the axes for the other member of a twinned individual. Additional values may be obtained if the positions of the optic axes of both members are plotted. Thus if A and B are the two optic axes of the first member, and A'B' the optic axes of the second member, then three independent values may be obtained, namely AA', BB', and A'B (the last being theoretically equal to AB'). These twin-angle values for various twin-laws of the analysed plagioclase feldspars are given in table II (2F, 6F, and 8F) and generally correspond with the published high-temperature twin-angles (Tröger, 1956) for plagioclases of similar composition. Few values for AA', BB', and A'B for high-temperature sodic plagioclase for some twin-laws have been published, so that comparison is impossible. There is a definite tendency for the twin-angles of the Carlsbad-albite law to give aberrant results, and the values read from the high-temperature curves (Tröger, 1956) may indicate a difference of up to 10 % An from the analysed plagioclase composition.

Although no curves of variation of twin-angles with composition for the alkali feldspars have been drawn, it may be seen that the alkali

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TABLE II. Twin angle values $\alpha \alpha', \beta \beta', \gamma \gamma', AA', BB'$, and A'B (see text) for the analysed feldspars. λ and ϕ are the polar coordinates of the relevant twin-axes, with $+\gamma$ at $\lambda = 0^{\circ}$ and $\phi = +90^{\circ}$, and β (at the centre of the stereogram) at $\lambda = 0^{\circ}$ and $\phi = 0^{\circ}$. All values are the average of between two and eight determinations on different crystals. For the key to these feldspars, see page 591.

					Albite				
		αα΄	ββ'	YY'	AA'	BB'	A'B	λ	φ
2F		174°	37°	37°	72 1 °	62°	21°	— 3°	_71 ∔ °
6F		176	40	411				-2	-69
8 F		171	15	19	_		_	-4	-81
					Carlsbad				
1 <i>F</i>		36	36	2	32	33	59	+18	+1
2F	•••	48	57	30	21	57	82	+24	+16]
4F		40	41	3 1	36	37	63	+20	$+2\frac{1}{2}$
6 <i>F</i>		51	62	$3\overline{2}$	19	62 1	83	+24	+18
7F		41	41	7	37	38	59	+20	+4
8F		43	43	9	32	41	74	+21	+4
3112.	F	34	34	4	32	31	55	$+16\frac{1}{2}$	+11
				Ca	urlsbad-alb	ite			
2F		131	136	20	114	80	41	-65	+25
6F		132	136	19	114	80	40	-66	+25
8F		136 1	139	15	120	92	38	-68	+21
					Manebach				
1 <i>F</i>		15 1	16	3	16	12 1	50	-8	+1
4F		13	12 1	3	11	11	48	-6	+1
7F		12	12	3	11	12	47	-6	+1
8F		12	10	6	10	11	114	-5]	+1
31 12	F	19	19	2	20	20	50	—9 <u>1</u>	- † •1
				Pe	ricline-acli	ine			
6 <i>F</i>		4	46	45 1	60	73	28	$-2\frac{1}{2}$	67
					Albite-Ala	,			
6 F	•••	3 1	41	41 1	25 1	27	69 1	+1	+ 20 🛔

feldspars (1F, 4F, 7F), and 3112F, table II) show some variation in these values for the Carlsbad and Manebach twin-laws, so that with further data the twin-angles of the alkali feldspars may possibly be used for the determination of their ternary composition.

Chemical analyses.

The feldspar phenocrysts were separated in the Frantz isodynamic separator and by centrifuging in methylene iodide. It was often quite difficult to separate composite grains of feldspar and glass, but it is

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Twin law.

believed that with the exception of 2F, the feldspars were at least 98 % pure.

			1F	2F	4F	6F	7F	8F	3112F
SiO ₂		•••	64.58	61.5	66.08	60.39	65.32	63·44	66.75
Al_2O_3			20.30	23.7	20.27	24.35	20.69	$22 \cdot 37$	18.84
Fe ₂ O ₃		•••	0.43	0.2	0.42	0.44	0.53	0.35	0.88
FeO	•••		n.d.	<u> </u>	n.d.	n.d.	nil	nil	n.d.
CaO	•••		1.26	5.4	1.58	6.21	2.18	3.42	0.06
BaO		•••	n.d.	0.07	0.30	tr.	n.d.	n.d.	0.08
Na ₂ O			6.06	7.9	9.11	7.70	9.14	9.17	7.41
K20			7.12	1.1	2.36	0.60	2:01	0.86	6.12
$H_2O +$		•••	0.24		0.17	0.24	0.14	0.23	0.18
$H_{2}O -$		•••	0.10		0.11	0.09	0.11	0.09	0.09
Total	•••	•••	100.09	99-9	100.40	100.02	100.12	99.93	100-41
			Compo	sition (re	calculated	l to 100 v	vt. %)		
Or	•••	•••	42.4	6.7	14.0	3.3	11.7	5.0	36.3
Ab	•••	•••	51.5	66.5	77.4	$65 \cdot 6$	77.5	77.9	63·2
An	•••	•••	6.1	26.6	7.8	31.1	10.8	17.1	0.3
Cn		•••		0.2	0.8				0.2
α			1.525	1.541	1.533	1.543	1.529	1.537	1.525
β			1.530	1.547	1.538	1.548	1.536	1.543	1.529
γ			1.532	1.550	1.541	1.552	1.539	1.546	1.530
$2V_{\alpha}$ av.		•••	47°	72°	48°	74 °	41°	58°	45°
Range	of $2V_{\alpha}$	•••	$45^{\circ}-52^{\circ}$	70°73°		68° -77°	_	$56^{\circ}-60^{\circ}$	43°-47°

TABLE III. Analyses and optical properties of feldspars. Refractive indices ± 0.002 , $2V_{\alpha} \pm 2^{\circ}$. For the key to these analyses, see page 591.

Normal semi-micro techniques were used for the analysis of these feldspars (table III), and the minimum material was used so that it would later be possible to determine colorimetrically some of the trace elements. The determination of BaO was made in the filtrate from the lime precipitate after destruction of the ammonium salts; it was precipitated and weighed as barium chromate. Barium was also sought in the ignited lime precipitate, and the amount found (very small) subtracted from the figure for lime. TiO₂ and MnO were sought but are absent from all the feldspars. FeO was determined in two feldspars (7F and 8F) but with a negative result, and the writer concludes that the iron in these feldspars is all trivalent. It is of interest that the iron content of 3112F (table III) is very much greater than that of the other feldspars, possibly as a result of the very much higher iron content of the pantelleritic residual glass (3112G, table V) compared with the other glasses. The analytical methods for the residual glasses have already been briefly described (Carmichael, 1960).

The atomic ratios of the feldspars on a basis of 32 oxygen are set down

in table IV and show a satisfactory balance. However, the composition (as wt. %) of the feldspars computed from the molecular proportions of Na₂O, K₂O, and CaO generally give totals of less than 100 %, which may be the result of glass impurity in the analysed specimens.

		1F	2F	4 <i>F</i>	6F	7 <i>F</i>	8F	3112F
Si		 11.653	10.983	11.702	10.804	11.598	11.291	11.924
Al		 4.314	4.982	4.234	5.138	4 ·332	4.683	3.972
Fe‴	•••	 0.065	0.021	0.064	0.064	0.064	0.043	0.129
Ca		 0.238	1.031	0.298	1.193	0.416	0.652	0.011
Ba		 —	0.004	0.021				0.004
Na		 2.125	2.727	3.127	2.666	3.137	3.165	2.575
K	•••	 1.648	0.258	0.532	0.129	0.448	0.192	1.395
z		 16.03	15.99	16.00	16.01	15.99	16.02	16.02
xy		 4.01	4.02	3.98	3.99	4.00	4.01	3.98

 TABLE IV. Formulae of the analysed feldspars on the basis of 32 oxygens.

 For the key to these analyses, see page 591.

The residual glasses.

It is proposed to confine this discussion of the residual glasses to those aspects of their chemistry that are believed to be of importance in the crystallization of feldspar. The analyses of the residual glasses of the pitchstones from which the feldspar phenocrysts have been separated and analysed are set down in table V. With the exception of the residual glass from a pantellerite (3112G, table V) the analyses are taken from Carmichael (1960). The relationship of the residual glasses to the analysed pitchstones is shown in fig. 3 (taken from Carmichael, 1960) where the analyses have been plotted in the system NaAlSi_aO₈-KAlSi_aO₈-SiO₂-H₂O together with the quartz-feldspar boundary curves under various water-vapour pressures (Tuttle and Bowen, 1958, pp. 54-56). The anomalous position of 3R-3G (G. 87) (fig. 3) is due to a low content of K_2O , which is considered to be the result of subsequent hydrothermal alteration. Although the geological environment of 9R-9G (1C. 3) (fig. 3) is not well known to the writer, this acid lava may be similarly affected. The residual glass of the pantellerite (3112G, table IV) has not been plotted in fig. 3 and its composition is in marked contrast to the other residual glasses but generally typical of other analysed pantellerites (Washington, 1914).

The relationship of the feldspar phenocrysts to the residual glasses.

In order to assess whether or not the feldspar phenocrysts are in equilibrium with their respective glasses, the phenocrysts have been plotted on the synthetic plagioclase solidus (fig. 4) (Bowen, 1913) together with the corresponding plagioclase components of the residual glasses, the feldspar-glass pairs being connected by horizontal tie-lines.



F10. 3. Normative quartz, orthoclase, and albite of the analysed pitchstones and residual glasses are plotted in the system $NaAlSi_3O_8-KAlSi_3O_8-SiO_2-H_2O$. O Analysed pitchstones; • analysed residual glasses, nos. 1*G*, 2*G*, 4*G*, 6*G*, 7*G*, and 8*G* being presented in table V. The boundary curves for various water vapour pressures (in Kg/cm.²) have been plotted; + indicates position of the minimum on the boundary curves (Tuttle and Bowen, 1958). The diagram is taken from Carmichael, 1960 (fig. 5), as are the rock and residual glass analyses not given here (table V). In the text a pitchstone-residual-glass pair has been referred to as, for example, the pair 3R-3G.

It may be seen that the plagioclase components of seven of the residual glasses fall very near the synthetic plagioclase liquidus, and it is considered that these phenocrysts are in equilibrium with the plagioclase components of their respective residual glasses. Of the aberrant residual glasses, 3G and 9G have both been shown to be poor in potash (fig. 3) and the undoubted alteration of one (3R-3G) suggests the possible alteration of the other (9R-9G). This deficiency of potash in the residual

			1G	2G	4G	6G	7G	8G	3112G
SiO ₂			69·4	74.0	71.5	72.3	67 ·0	74.2	70.1
TiO ₂			0.59	0.14	0.22	0.22	0.55	0.19	0.41
Al ₂ O ₃	•••	•••	14.3	11.8	12.2	12.1	$12 \cdot 2$	11.6	7.6
Fe ₂ O ₃			1.3	0.39	0.9	0.4	$1 \cdot 2$	0.6	2.9
FeO			1.0	0.84	1.7	1.4	3.9	1.0	5.6
MnO	•••		0.11	0.03	0.09	0.05	0.20	0.05	0.34
MgO			0.41	0.10	0.21	0.09	0.32	0.04	0.04
CaO			0.92	0.62	0.62	1.0	1.4	0.71	0.53
Na ₂ O		•••	4.7	3.9	5.0	4.9	3.9	4·3	7.1
K ₂ O			5.9	`4 ∙8	3.5	3.5	4.4	$4 \cdot 2$	4 ·6
$P_{2}O_{5}$	•••		0.10	0.02	0.02	0.04	0.11	0.04	0.05
$H_20 +$			1.4	3.6	4 ·1	3.8	$4 \cdot 3$	2.8	0.23
$H_{2}O -$			0.2	0.1	0.1	0.1	0.1	0.1	0.04
Total	•••	•••	100.3	100.3	100.2	99·9	99 ·6	99·8	99·8 *
				Norr	native feld	lspar			
Or			46 ·6	45.8	$32 \cdot 4$	32.8	42.1	40.8	66.7
Ab	•••		53.0	$53 \cdot 2$	66.7	65.9	$53 \cdot 4$	$59 \cdot 2$	33.3
An	•••		0·4	1.0	0 ∙9 `	1.3	4.5		

 TABLE V. Analyses of the residual glasses. For the key to these analyses, see page 591.

* Includes 0.28 % ZrO₂.

glasses increases the amount of normative anorthite, and leads to the anomalous composition of the plagioclase components of the residual glasses (fig. 4). No such explanation can be offered for the feldspar-glass pair 7F-7G (fig. 4), as the composition of the pitchstone-glass pair 7R-7G (fig. 3) is not particularly unusual. Perhaps part of the high content of basaltic material contained in this pitchstone (table I) may have become digested and thus modified the glass composition causing the unusually high content of both iron and magnesia, and perhaps lime (7G, table V).

It is of interest to compare the stage of fractionation with respect to the An/(An+Ab) ratio of the feldspar phenocrysts with the stage of fractionation with respect to the (Fe'' + Fe''' + Mn)/(Fe'' + Fe''' + Mn + Mg)ratio of both the olivine and pyroxene phenocrysts. In an account of the ferromagnesian silicate phenocrysts of these acid glasses (Carmichael, 1960) it was suggested that the calcium-rich pyroxene phenocrysts were in equilibrium with the ferromagnesian constituents of the residual glasses, and the phenocrysts and rocks were numbered in all the tables of that account in order of increasing relative enrichment of iron of the calcium-rich pyroxenes, with the exception of no. 10. This same enumeration has been used here, so that, for example, the plagioclase

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1P (fig. 4) comes from a pitchstone whose pyroxene is the most magnesian of those examined. Thus the numerical order of the feldspar phenocrysts (fig. 4) represents the relative iron enrichment of the pyroxene phenocrysts, and it may be immediately seen that the stage



FIG. 4. Part of the synthetic plagioclase diagram (Bowen, 1913) with the feldspar phenocrysts plotted on the solidus and joined to the corresponding plagioclase components of the residual glasses, which lie near the synthetic plagioclase liquidus. O, analysed feldspar phenocrysts (table III) plotted as weight per cent. An/(Ab+An); **x**, optically determined plagioclase phenocrysts; **•** normative plagioclase of the residual glasses (table V). The normative plagioclase of the residual glasses for 3F, 5F, 9F, and 10F are taken from Carmichael, 1960, table VII. The alkali feldspars 1F and 3112F (table III) have not been plotted, the optically determined co-existing plagioclase 1P being used instead of 1F. In the text a feldspar-residual-glass pair has been referred to as, e.g., the feldspar-glass pair 8F-8G.

of fractionation with regard to the An/(An+Ab) ratio of the feldspar phenocrysts does not correspond with the fractionation stage of the pyroxene phenocrysts. As all the pitchstones with the possible exception of 1R-1G (fig. 3) have a generally similar chemical composition, and as both the feldspar and pyroxene phenocrysts are believed to be in equilibrium with their glasses, this lack of equivalence of the two fractionation stages is unusual. In the author's view this may be explained if the temperature of crystallization of either the pyroxene or the feldspar phenocrysts was above the crystallization temperature of the other. This would allow a certain degree of reaction (both the feldspars and the calcium-rich pyroxenes forming continuous solid solution series) of the early formed crystals with the liquid before these crystals were joined by the other member of the pair. The early separation of a calcium-rich pyroxene in varying amounts may cause variation in the CaO:Na₂O ratio of the liquid, so that to a limited extent the anorthite content of a later-separating plagioclase may be controlled by the amount of the calcium-rich pyroxene separating. It is possible that the influence of water in depressing the crystallization temperatures of the pyroxenes and particularly of the feldspars will in some way contribute to or cause the suggested effect. As the temperature of crystallization of the feldspar phenocrysts is unknown and the partial pressure of water also unknown, the temperature scale of the plagioclase system (Bowen, 1913) has been omitted (fig. 4); in this context it may be misleading.

The crystallization of feldspar in natural acid melts.

The crystallization of ternary feldspars (An-Ab-Or) in acid melts has been treated in great detail by Vogt (1926, 1931) who examined the coexisting plagioclase and alkali feldspar phenocrysts of acid and subacid rocks, and calculated the composition of the groundmass feldspar. From this and other data, he was able to delineate an 'individualization boundary', which separated the field of potash feldspar from the field of plagioclase. This boundary, later defined as a cotectic by Vogt (1929, pp. 61--64; 1931, p. 225), extended from the Ab-Or sideline (fig. 5) at Or40 Ab60 to about Or 47 Ab28 An25, and then possibly to the An-Or sideline. Bowen (1928) has also discussed the crystallization of ternary feldspars, and Tuttle and Bowen (1958) provide the latest account in which they trace the course of feldspar crystallization using data from the literature on the composition of coexisting plagioclase and alkali feldspar phenocrysts and the host rock or groundmass. This discussion was with reference to trachytic rocks, where, it is suggested, the extent of solid solution of potassium in the plagioclase and of calcium in the alkali feldspars is greatest, the temperature of trachytic crystallization being higher than that of rhyolites or phonolites (Tuttle and Bowen, 1958, pp. 131-137).

The general relationships of the crystallization of ternary feldspar



FIG. 5. Ternary diagram of anorthite-albite-orthoclase with the feldspar phenocrysts plotted and joined by tie-lines to their corresponding feldspar components in the residual glasses. O, analysed feldspar phenocrysts, 1F to 8F (table III); J, Jafnadal anorthoclase (Hawkes, 1932); a and b, San Juan plagioclase and sanidine phenocrysts respectively (Larsen et al., 1938, p. 235, table 5, no. 7, and p. 418, table 10, no. SCXX); **x**, optically determined plagioclase phenocrysts, all with an unknown potash content; • normative feldspar components in the residual glasses (table V), the glasses of 5F and 10F being taken from Carmichael (1960, table VII) and c from Larsen and Cross (1956, table 21, no. 48). The Jafnadal anorthoclase is joined to the bulk normative feldspar of the unaltered interior felsite (Hawkes, 1932). - - possible feldspar solidus; \leftarrow feldspar cotectic. M is the minimum at 500 kg./cm.² in the system KAlSi₃O₈-NaAlSi₃O₈-H₂O (Tuttle and Bowen, 1958). In the text a phenocryst feldspar-residual-glass pair is referred to as, for example, the pair 2F-2G.

deduced by Tuttle and Bowen are applicable to all salic rocks, and are applied here to the porphyritic pitchstones.

The analysed feldspar phenocrysts (table III) have been plotted in the ternary An-Ab-Or diagram together with the feldspathic constituents of the residual glasses (table V, and fig. 5). A line (dashed) has been drawn through the plotted phenocrysts, and represents the feldspar solidus, which in the case of these acid rocks is displaced towards the Ab corner with respect to the feldspar phenocrysts of the trachytes, and therefore may indicate a lower temperature of crystallization. Intersecting and crossing the solidus is a field boundary (cotectic) which represents the composition of various liquids in equilibrium with both plagioclase and alkali feldspar phenocrysts. The position of this cotectic (fig. 5) has been defined by a San Juan acid residual glass which is in presumed equilibrium with both plagioclase¹ and sanidine, and by the sub-acid residual glass 1G (table V), which is in assumed equilibrium with both an alkali feldspar (1F, table III) and a plagioclase (1P, p. 589). None of the other pitchstones contains two co-existing feldspar phenocrysts and therefore their residual glasses do not lie on the feldspar cotectic. This cotectic (fig. 5) has a different orientation from the one suggested for trachytic rocks by Tuttle and Bowen and in contrast runs to the Ab-Or sideline. Using the data of the feldspar-phenocryst-glass relationships (fig. 5) it is possible to generalize on the possible feldsparliquid equilibrium relations during cooling, the subsequent changes of exsolution and inversion of the feldspars that take place at temperatures below the solidus being neglected. It is assumed that, as the pitchstones have a generally similar composition, the deduced cooling history could be common to them all. It is also assumed that the alkali feldspar solidus does not intersect the underlying solvus.

In tracing a course of crystallization in any phase diagram, it is necessary to know the composition of the initial liquid, which in the case of these porphyritic pitchstones corresponds to the bulk normative ternary feldspar (Carmichael 1960, table VII).

The initial liquids of the pitchstones have been plotted in fig. 6, and with the exception of 3R and 9R, lie within or very near to the area bounded by the feldspar solidus, the cotectic, the Ab-Or sideline and the Ab-An sideline. The probable alteration of the glasses of 3R and 9Rhas already been discussed, and it is believed that originally the bulk normative feldspar would correspond approximately to that of the others, as the abstraction of potash has increased the amount of normative anorthite. It is considered that as the normative bulk feldspar of the unaltered pitchstones falls below the feldspar solidus (fig. 6), all these

¹ Although the plagioclase is assumed here (also Tuttle and Bowen, 1958) to be in equilibrium with the sanidine, Larsen *et al.* (1938, p. 256) have expressed some doubts.

rocks could solidify with a single alkali feldspar, and the possible means of attaining this are discussed below.



FIG. 6. Ternary feldspar diagram (An-Ab-Or) with the normative feldspar of the analysed rocks (pitchstones) plotted. •, 1R to 10R normative feldspar of pitchstones (Carmichael, 1960, table VII); \circ , analysed alkali feldspar phenocrysts of the Slieve Gullion felsite (Emeleus and Smith, 1959, table 2); PL is range of optically determined plagioclase phenocrysts of unknown potash content from the Slieve Gullion felsites (op. cit., p. 1189); 3112F and 3112G are anorthoclase phenocrysts (table III) and residual glass (table V) respectively from glassy pantellerite.

A pitchstone liquid on cooling to the temperature of the plagioclase liquidus will start to crystallize a plagioclase feldspar on the solidus, which may contain about 5 % Or (e.g. 2F and 6F, fig. 5). With further cooling the plagioclase phenocrysts will react with the liquid and moving down the solidus will become more sodic (e.g. 8F, fig. 5); the liquid, which continuously reacts with the phenocrysts with falling temperature, will change in composition, and will move on a curved course (concave to the An corner) towards the cotectic. If at any time the reaction of the plagioclase and the liquid is impeded, plagioclase enclosed by alkali feldspar perhaps in granophyric intergrowth with quartz will result. This texture is typical of many of the Icelandic granophyres. With continued cooling under equilibrium conditions, the plagioclase, moving along the solidus, becomes at once more sodic and potassic, and will lose the distinguishing optical features of plagioclase feldspar and become a sodic anorthoclase (e.g. 4F and 7F, fig. 5). In the case of liquids represented by these acid residual glasses, the liquid may not yet have reached the cotectic, although the sub-acid liquid of the Eigg pitchstone, which is crystallizing a plagioclase (1P, fig. 5) and an alkali feldspar (1F, fig. 5), has reached the cotectic a little before the liquids crystallizing feldspars 4F and 7F (fig. 5); this anomaly may be due to the rather different chemical composition of the Eigg residual glass (1G, table V).

Within the temperature interval from the initial crystallization of plagioclase to just above the temperature at which an alkali feldspar may be expected to commence crystallization, the feldspathic composition of the residual glasses (fig. 5) does not seem to change in a consistent direction even though, as noted above, the plagioclase components of the phenocrysts and residual glasses conform to the synthetic system.

Further discussion of the changes on cooling can only be speculative, but the general relationships deduced by Tuttle and Bowen (1958) may again be applied. With a further drop in temperature, the plagioclase may have become more potassic than 4F (fig. 5), while the liquid, which has reached the cotectic, begins to precipitate a relatively potassic alkali feldspar. With further cooling, both feldspars continue to react with the liquid, and moving along the solidus, the sodic anorthoclase (original plagioclase) becomes more potassic, and the potassic alkali feldspar becomes more sodic, so approaching one another in composition. Eventually the original plagioclase may completely disappear, and only one alkali feldspar is precipitated. The anorthoclase from Jafnadal, Iceland (Hawkes, 1932), may represent the stage where only one feldspar crystallizes, but unfortunately the composition of the residual glass is unknown, and the phenocryst feldspar is joined (fig. 5) to the composition of the bulk normative feldspar of the unaltered central felsite. It is to be expected that the composition of the Jafnadal liquid will lie nearer the cotectic than is shown. This one-feldspar stage of crystallization may also be represented in some of the Tertiary granite dykes of Skye (Tuttle and Bowen, 1958, tables 17 and 19). However the onefeldspar margins of the Beinn an Dubhaich, Skye, granite are of alkaline facies and unrepresentative of the original magma (Tilley, 1949).

The two-feldspar porphyritic felsites of Slieve Gullion (Emeleus and Smith, 1959) may represent the two-feldspar stage of crystallization noted above. The higher potash-soda ratio of the host rock (op. cit., table I) and presumably the groundmass (liquid) compared to the pitchstones may place the liquid very near the cotectic so that the two feldspars will begin to crystallize within a smaller temperature interval. The smaller amount of calcium in the alkali feldspars of the Slieve Gullion felsite (fig. 6) suggests that the temperature of crystallization may be lower than that of the porphyritic pitchstones that contain alkali feldspars, whereas the plagioclase phenocrysts of the felsite are considerably richer in lime (fig. 6) than the feldspar deduced to co-exist with an alkali feldspar in the discussion above, under pitchstone conditions of cooling and composition.

In the author's view, the two-feldspar felsites and rhyolites are critical for the elucidation of the crystallization of feldspar in acid melts, for the feldspathic constituents of the groundmass lie on and define a cotectic, and the composition of the phenocrysts may indicate the degree of solid-liquid reaction, which may be considerably different in extent and direction to that suggested here for the feldspar-phenocryst-liquid relations of the porphyritic acid glasses.

It is to be expected that an increase in water-vapour pressure will decrease the crystallization temperature of the feldspars, and will also displace the feldspar solidus towards the Ab corner (fig. 5) (Tuttle and Bowen, 1958, p. 135) so that the composition of a single alkali feldspar at the one-feldspar stage of crystallization may vary, although it is considered that a single alkali feldspar while in equilibrium with liquid will conform more or less in composition to that of the minimum in the system NaAlSi₃O₈-KAlSi₃O₈-H₂O as may the liquids. It is unusual that the anorthoclase phenocrysts from a glassy pantellerite (3112*F*, table III and fig. 6) that have a composition very near that of the minimum should be in presumed equilibrium with a glass (3112*G*, table III and fig. 6) that is so far displaced from the minimum. It can only be concluded that a potential solid phase other than feldspar may take up potash for which biotite seems suited.

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