Trachytes and their feldspar phenocrysts

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Summary. The compositions of the groundmass and of the plagioclase and sanidine phenocrysts of a series of over- and under-saturated trachytes indicate that plagioclase will precipitate at some stage in the crystallization interval of all calcium-bearing potassic trachytes. Using this data obtained from natural salic liquids, a concept of crystallization within the system $CaAl_2Si_2O_8$ -NaAlSiO₄-KAlSiO₄-SiO₂ may be obtained.

ALTHOUGH the system $CaAl_2Si_2O_8$ -NaAlSiO₄-KAlSiO₄-SiO₂ has still to be investigated experimentally, it is possible to deduce some of the properties of this system by the study of the phase chemistry of natural rocks whose bulk composition may be expressed almost completely in terms of these four components. As a result of a study of the porphyritic rhyolites (Carmichael, 1963*a*) which plot in the over-saturated part of the four-component system, it was concluded that potassic acid liquids would, at some stage in their crystallization interval, intersect a boundary surface, and that on this surface two feldspars, a plagioclase, and a sanidine would precipitate.

This paper is concerned with the two-feldspar potassic trachytes, and therefore extends the investigated compositions of natural salic liquids in the system $CaAl_2Si_2O_8$ -Na $AlSiO_4$ -K $AlSiO_4$ -SiO_2 from the quartzfeldspar boundary surface (rhyolites) (op. cit.) across the ternary feldspar plane towards the phonolite minimum (Hamilton and Mac-Kenzie, 1965). Some of the arguments and discussion developed in a previous paper (Carmichael, 1963*a*) have been abbreviated or omitted to avoid repetition.

Petrography

The petrographic descriptions of the trachytes are given on page 124 and are summarized below. In the discussion which follows it is convenient to divide the trachytes into two types: those which are oversaturated and contain normative quartz, and those which are undersaturated and contain normative nepheline.

Phenocrysts of plagioclase and sanidine are found in all the rocks

except 8R¹; plagioclase is generally the first feldspar to precipitate, as plagioclase crystals are sometimes enclosed by the sanidine phenocrysts. With the exception of the feldspars in 5R, neither the plagioclase nor the sanidine is strongly zoned, but as plagioclase is normally the first feldspar to separate, possibly only the outer zones of the crystals are in equilibrium with the sanidine phenocrysts. This zoning has been neglected, although in general the composition of the plagioclase phenocrysts as found by analysis will be slightly more calcic than their actual composition, as the outer rims of crystals tend to be lost in separation.

Quartz can be identified in the groundmass of the more coarsely crystalline oversaturated trachytes, but is never found as a phenocryst. In the groundmasses of the under-saturated rocks, an interstitial felspathoid, probably sodalite, is present, but a feldspathoid is never present as a phenocryst.

Biotite is apparently stable in only one of the trachytes (1R), and in the remaining biotite-bearing specimens it has been resorbed and replaced by aggregates of granular iron-ore to a greater or lesser extent. Because biotites contain a significant proportion of alkali feldspar components, the incorporation of these components into the liquid may change the composition of the liquid's feldspathic components. As the intratelluric crystallization of biotite in these trachytes is taken to be broadly coeval with the crystallization of the feldspar phenocrysts, the subsequent resorption of the biotite, due possibly to release of water vapour pressure, will not greatly affect the composition of the feldspar phenocrysts. Moreover, as the modal amount of biotite is usually less than 2.5 % (table I) the incorporation of its feldspathic components into a liquid composed of over 70 % alkali feldspar components will not greatly change the liquid's composition.

A common feature in these trachytes is the almost ubiquitous presence of microphenocrysts of iron-ore enclosed in augite phenocrysts; in the more iron-rich ferroaugite phenocrysts this occurrence is less noticeable (Carmichael 1963b). A lime-poor pyroxene, either pigeonite or orthopyroxene, has not been found.

There is no petrographic evidence that any of the phenocrysts are xenocrysts; the resorption of biotite (and amphibole in 6R) by many of these trachytic liquids is not evidence of their foreign origin and no

¹ In the descriptions, the suffix R has been used for the rock, G denotes the groundmass and A and B are the alkali feldspar and plagioclase phenocrysts respectively. Thus 1A and 1B are the feldspar phenocrysts which together with the groundmass 1G (and the ferromagnesian phenocrysts) make up the rock 1R.

xenoliths have been found. In both groups of trachytes it is assumed that the rocks are non-accumulative, or in other words, that they are all capable of existing in a completely liquid state (and at some stage of their history did so) in a natural environment. It is possible to find analyses of fine-grained almost completely non-porphyritic trachytic

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	Ground- mass	Plagioclase	Sanidine	Biotite	Pyroxene	Iron Ore	Miscellaneous
1R	84.0	12.0	$0{\cdot}2$	1.1	0.8	0.6	$\left\{ \begin{array}{l} 1.3 \text{ amphibole} \\ \text{tr. sphene} \end{array} \right.$
2R	71.4	24.5	0.9*	1.4	0.6	0.9	0.3 sphene
3R	64.6	23.5	6.8	$2 \cdot 2$	1.8	0.8	0.3 sphene
$4\mathrm{R}$	86.3	0.8	12.0	tr.	0.2	0.7	
5R	91.2	1.1	$5 \cdot 2$	$1 \cdot 3$	0.7	0.4	0·1 olivine
6R	83.8	4.7	$4 \cdot 0$	5.1^{+}	1.0	1.1	$\left(\begin{array}{c} 0.3 \text{ sphene}\\ 0.1 \text{ olivine} \end{array}\right)$
7R	71.9	tr.	27.8	—	0.3	tr.	tr. sphene
8R	—	tr.	92.0	_	1.8	1.5	Rest 4.7
10R	79.3	$\operatorname{tr.}$	19.2		1.0	0.5	

TABLE I. Modal analyses of trachytes (volume per cent.)

* Underestimated as the sanidine phenocrysts are extremely large.
† Biotite and barkevikite in all stages of dissolution.

1R. Porphyritic trachyte pitchstone, Murat, Cantal, France. 3811.

2R. Porphyritic trachyte, Drachenfels, Rhine, Germany. 3111 and 1395.

- 3R. Porphyritic trachyte, Siebengebirge, Germany. BM. 1909-261.
- 4R. Cristobalite-trachyte, Jan Mayen, North Atlantic. JM-122.
- 5R. Biotite-trachyte dyke, Gough Island, South Atlantic. G-24.
- 6R. Biotite-trachyte, Tristan da Cunha. 442.
- 7R. Trachyte, Tristan da Cunha. 439.

8R. Sanidinite, Eifel, Germany. 5653.

10R. Porphyritic pitchstone, Isle of Eigg, Scotland. EC. 20.

lavas which match the analyses of the trachytes described here. The rock analyses are taken to represent the composition of initial liquids.

The modal analyses of both types of trachytes are given in table I, and the chemical analyses and CIPW norms of the oversaturated trachytes and their groundmasses are presented in table II. The data for the undersaturated trachytes are given in table III, and the localities of all the specimens are given below table I.

All of these trachytes and the sanidinite 8R have precipitated a plagioclase together with sanidine, and the purpose of this paper is to show that the resorption of plagioclase depicted so clearly in 4R, 7R, and 8R is the result of a reaction relationship common to all normative anorthite-bearing potassic trachytes, and which under equilibrium conditions, may be taken to completion.

	10G	69.4	0.59	14.3	1·3	1.0	0.11	0.41	0.92	4.7	5.9	0.10	1-4	0.2	100.3	17-8	35.0	39.8	0.3	2.7	1.6	1.2	ļ	0.2		1.6	100.2	
	10R	63-0	0.71	15.1	1.5	1.2	0.11	69.0	1.2	4.9	6.2	0.11	1.7	0.4	99.82	11-3	36.7	41-4	0.8	3.8	2.1	1.4		ļ		2.1	9.66	
	4G	71.54	0.23	14.59	1.42	0.20	0.08	0.02	0.94	5.22	5.54	0.01	0.10	0.01	$06 \cdot 66$	18.90	32.80	44.01]	1.97	0.23	0.46		1.28	ļ	0.12	27.66	
(60)	4R	65.62	0.37	16.81	3.03	0.16	0.23	0.31	1.18	6.05	6.08	0.07	0.11	0.04	100.06	5.40	36.14	50.83	0.83	2.89	0.46	0.61		2.72	!	0.22	100.10	
, see page l	3G	69.85	0.29	14.50	2.17	0.04	6-07	0.18	0.82	4.58	6.14	0.04	0.88	0.31	18.66	18.54	36.14	38.77	0.83	1.33		0.15	1	2.24	0.59	1.19	99.78	urmichael.
o analyses.	3R	64.87	0.76	16-77	2.85	0.61	0.12	0.61	1.95	5.02	5.04	0.18	0.78	0.36	99.92	11.82	29-47	42-44	8.62	1.50	ļ	1.37	0.34	2.88	0.20	1.14	87.66	I. S. E. Ca
r the key t	2G	69-42	0.20	15.52	1.76	0.07	0.02	0.26	0.81	4.67	6.06	0.04	0.73	0.30	98.66	17.10	36.14	39.30	3.34	0.60		0.15		1.76	0.39	1-07	99.85	Analyst:
(Fo	$2 \mathrm{R}$	64.40	0.80	16-71	3.13	0.47	60-0	0.65	2.36	5.06	5.04	0.20	0-67	0.38	96-66	10.68	29.47	42.97	8-06	2.64	I	1.22	0.34	3.09	0.39	1.05	16.66	
	1G	63.34	0.78	16.18	1.45	1.63	0.13	0.78	2.45	4.56	6.15	0.21	2.08	0-06	0 8-80	7-92	36.70	38-77	5.28	5.11	2.09	1.52	0.34			2.14	99.87	
	1R	60.73	1.08	16.75	2-05	2.13	0.16	1.11	3.55	4.56	5.24	0.36	1.90	0.10	99.72	6.84	30.58	38.77	10.01	5.66	3.02	2.13	1.01		I	2.00	100.02	
		SiO_2	Ti0,	Al_2O_3	$Fe_{2}O_{3}$	FeO	MnO	MgO	C_{aO}	Na_2O	$\mathrm{K}_{s}\mathrm{\tilde{O}}$	$P_{s}O_{s}$	$\mathrm{H_{3}O^{+}}$	H_{0}^{-}	Total	Qtz	0r	Ab	An	Di	\mathbf{mt}	il	ap	hm	$^{\mathrm{sb}}$	Rest	Total	

TABLE II. Analyses and norms of oversaturated trachytes

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The analyses of the feldspar phenocrysts are given in table IV; in each case, the purity of the feldspar concentrate was carefully checked in refractive index oils before analysis, and each feldspar is believed to be at least 98% pure.

TABLE III. Analyses and norms of undersaturated trachytes

	$5\mathrm{R}$	$5\mathrm{G}$	6R	6G	$7\mathrm{R}$	8R
SiO_2	60.09	60.80	56.32	59.35	62.27	62.06
TiO ₂	0.93	0.84	1.70	0.97	0.48	0.50
Al ₂ O ₃	17.95	17.40	18.11	18.73	19.47	18.99
Fe ₂ O ₃	1.39	1.74	2.02	1.47	1.44	1.59
FeO	3.36	3.16	$3 \cdot 20$	1.98	0.78	0.91
MnO	0.12	0.13	0.14	0.10	0.10	0.16
MgO	0.96	0.80	1.68	0.97	0.29	0.30
CaO	2.43	2.13	4.10	2.96	1.32	1.45
Na ₂ O	5.69	5.83	5.42	6.09	5.74	6.09
K ₂ Ō	6.51	6.57	5.94	6.62	7.28	7.12
$P_{2}O_{5}$	0.29	0.23	0.58	0.35	0.06	0.05
H,0+	0.32	0.31	0.41	0.32	0.82	0.58
H ₂ O`⁻	0.09	0.10	0.29	0.20	0.33	0.11
Total	100.13	100.04	99.91	100.11	100.43*	99.91
*]	Includes (0∙07 Cl;le	ess O eq	uivalent o	of $Cl = 0$	·05.
Or	38.36	38.92	35.03	38.92	43.37	42.26
Åb	40.87	42.97	33.54	36.68	43.49	44.01
An	4.17	1.95	7.51	4.17	5.56	3.34
Ne	3.98	3.41	6.53	7.95	2.84	3.98
Di	5.35	6.53	7.60	6.80	1.05	2.33
01	2.54	1.51	1.53			
mt	2.09	2.55	3.02	2.09	1.39	2.32
il	1.67	1.52	3.19	1.98	0.91	0.91
ap	0.67	0.34	1.34	1.01		
hm			_		0.48	_
\mathbf{Rest}	0.41	0.41	0.70	0.52	1.21	0.74
Total	100.11	100.11	99.99	100.12	100.30	99.87

(For the key to analyses, see page 109)

Analyst: I. S. E. Carmichael.

Solid solution in ternary feldspars

The extent of solid solution among anorthite, albite, and potassium feldspars depends upon the temperature of crystallization and upon the composition of the liquid from which the feldspars crystallized. By analogy with the experimental results on the system NaAlSiO₄-KAlSiO₄-SiO₂-H₂O (Tuttle and Bowen, 1958; Hamilton and MacKenzie, 1965), it is to be expected that trachytes will crystallize at higher temperatures than either rhyolites or phonolites, where the liquidus temperatures are

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Composition (recalculated to 100 wt %) 6.6 60.0 7.6 60.9 7.6 34.7 7.5 50.4 14.5 50.2 6.7 45.2 4 56.2 37.3 62.6 36.0 64.0 58.0 64.2 44.1 53.1 47.4 55.8 50.5 43 37.2 0.4 29.8 1.8 28.4 7.3 28.3 5.5 32.4 2.4 37.5 4.3 -2.3 -1 -1 -1 -1 -1 -1 -1 -	() a ₂ 0 v0 tal feldspar components	$\begin{array}{c} 1B\\ 7\cdot 56\\ 6\cdot 70\\ 1\cdot 12\\ -\end{array}$	2A 0-09 4-40 10-12 0-96 99-75	2B 5·72 7·04 1·22 	3.A 0-36 4-25 10-32 0-56 100-06	3B 5.68 7.50 1.28	4A 1.47 6.84 5.85 99.74	$\begin{array}{c} 4B \\ 5.71 \\ 7.59 \\ 1.27 \\ - \end{array}$	5A 1.11 5.25 8.60 	5B 6-64 6-38 	6A 0.49 5.61 8.52 - 100-26	6B 7-56 6-60 1-13 03	7A 0-86 6-02 7-71 - 100-79	8A 0.78 5.99 8.08
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	56.2 37.3 62.6 36.0 64.0 58.0 64.2 44.1 53.1 47.4 55.8 50.5 4 37.2 0.4 29.8 1.8 28.4 7.3 28.3 5.5 50.5 4 37.2 0.4 29.8 1.8 28.4 7.3 28.3 5.5 32.4 2.4 37.5 4.3 - 2.3 - 1.3 -		<i>h</i> .6	60-0	7.6	Comp 60-9	osition (r [.] 7.6	ecalculat(34·7	ed to 100 7.5	• wt %) 50-4	14.5	50.2	6.7	45.2	46.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	37.2 0.4 29.8 1.8 28.4 7.3 28.3 5.5 22.4 27.5 4.3 $ -$		56.2	37.3	62.6	36.0	64.0	58.0	64.2	<u>44</u> ·1	53.1	47-4	55.8	50.5	49.5
	2.3 1.3 1.3		37.2	0.4	29.8	1·8	28.4	7-3	28.3	5.5	32.4	2.4	37.5	$4\cdot 3$	3.8
	1A. Sanidine determined by X-ray method, $20\overline{1}$; Or_{55} . 10A. Sanidine $Or_{22,4}Ab_{51,5}An_{6,1}$ (Carmichael, 1963 <i>a</i>). 10B. Plagioclase An_{12} (optically) (<i>op. cit.</i>). * Contains quartz impurity.		I	2.3]	1.3]]		١		1]]	I
	Analyst, I. S. R. Comminhael					Δ.	nalvet. T	S F Co	laehaimr						

TABLE IV. Partial analyses of feldspar phenocrysts from trachytes

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lowered by silica and nepheline respectively, so that in trachytes, the phenocrysts of plagioclase should contain larger proportions of potassium, and the alkali-feldspar phenocrysts larger amounts of calcium than the corresponding phenocrysts in rhyolites and phonolites.



FIG. 1. Coexisting feldspar phenocrysts of oversaturated trachytes (solid circles) and undersaturated trachytes (open circles) plotted in the ternary feldspar diagram. The dashed line represents the limit of ternary solid solution in natural feldspars (Smith and MacKenzie, 1958; Tuttle and Bowen, 1958). *m* represents the minimum on the alkali feldspar join at 500 kg/cm² water vapour pressure (Tuttle and Bowen, 1958). The sanidine 1A, which has not been analysed (table IV), is assumed to have a similar calcium content to the sanidines 2A and 3A.

The analysed coexisting feldspar phenocrysts (table IV) of the trachytes described here have been plotted in fig. 1, and 5A-5B is the only plagioclase-sanidine pair where each feldspar shows greater ternary solid solution than the coexisting feldspars in rhyolites (Carmichael, 1963*a*). The other plagioclase phenocrysts have similar contents of potassium to the plagioclase phenocrysts of the two-feldspar rhyolites, and this correspondence suggests that the temperature difference between the liquidus temperatures of two-feldspar rhyolites and of trachytes may not be generally large enough to affect the potassium content of a plagioclase. The trachytes generally contain more normative anorthite than the rhyolites (fig. 2: Carmichael, 1963*a*) and this would have the effect of raising their liquidus temperatures; this may account for the generally different trend of the trachyte feldspar tielines (fig. 1) compared to the trend of those of rhyolites, where the plagioclase is typically more sodic.



FIG. 2. The normative ternary feldspar of the under- and oversaturated trachytes (open circles, suffix R) and their groundmasses (oversaturated, filled circles; undersaturated, filled triangles) plotted in the ternary feldspar diagram. The lower dashed line represents part of a generalized equilibrium path on the solidus of an alkali feldspar crystallizing in 4R or 10R. The upper dashed line represents the limit of ternary solid solution (fig. 1). The solid curve is the projection on to the ternary feldspar plane of the two-feldspar surface as defined by the groundmasses of the trachytes 1R, 2R, 3R, 5R, and 6R.

The more potassic of the sanidine phenocrysts from trachytes (fig. 1 nos. 1A, 2A, 3A) have similar amounts of calcium to the sanidine phenocrysts of the two-feldspar rhyolites. Of the remaining alkali feldspar phenocrysts, 4A and 10A have the largest anorthite content. It has previously been suggested that the anorthite content of 10A is higher than the more potassic sanidines found in rhyolites because the lower content of silica in the rock 10R had raised the liquidus temperature (Carmichael, 1963*a*). This suggestion is now considered to be erroneous, as will be shown below when considering the feldspar-liquid relationships in 4R, and the anorthite content of both 4A and 10A (fig. 1) is considered to illustrate the progressive solubility of anorthite in an alkali feldspar as it becomes more sodic by continuous reaction with the liquid. A generalized path on the solidus of an alkali feldspar crystallizing from a trachyte similar to 4R would therefore run from 3A towards 10A and 4A (figs. 1, 2), until such time as the liquid becomes virtually of constant composition with respect to Na₂O:K₂O ratio, whereupon the solidus path of the alkali feldspar would change direction towards the alkali-feldspar join (fig. 4).

The two-feldspar surface and its extent

The boundary curve which represents liquids in equilibrium with a plagioclase and a sanidine in the system CaAl₂Si₂O₈-NaAlSi₃O₈-KAlSi₃O₈ becomes a surface in the system CaAl₂Si₂O₈-NaAlSiO₄-KAlSiO₄-SiO₂, and it will be defined by under- or over-saturated salic liquids in equilibrium with plagioclase and sanidine. It has previously been shown that the two-feldspar surface in the system CaAl₂Si₂O₈-NaAlSi₃O₈-KAlSi₃O₈-SiO₂ extends, in projection, over the potassic side of the feldspar field in the system NaAlSi₃O₈-KAlSi₃O₈-SiO₂. The trachytic liquids defining this surface have been projected on to the CaAl₂Si₂O₈-NaAlSi₃O₈-KAlSi₃O₈ plane in fig. 2 (oversaturated liquids, solid circles; undersaturated liquids, filled triangles). The two-feldspar surface in the system $CaAl_2Si_2O_8$ -NaAlSiO₄-KAlSiO₄-SiO₂ is unlikely to project on to the ternary feldspar plane (CaAl₂Si₂O₈-NaAlSi₃O₈- $KAlSi_{3}O_{8}$) as a line, but rather as an area, so that the variation in anorthite content of the trachytic liquids which define this surface (fig. 2) may be real. Analytical error, however, will account for some of the variation in the anorthite content, for the calculation of the CIPW accumulates most of the normal errors of chemical analysis on the presence or amount of normative anorthite. In order to simplify a later discussion, an approximate curve has been drawn in fig. 2 through the under- and oversaturated liquids projected on to the ternary feldspar plane, and represents liquids (in terms of the three feldspar components) in equilibrium with plagioclase and sanidine. Even with this approximate curve it is clear that for the three initial oversaturated compositions 1R, 2R, and 3R, a plagioclase would precipitate before an alkali feldspar, and the same is true for the undersaturated rock 6R.

The two oversaturated trachytes 4R and 10R (fig. 2) have the least amount of normative anorthite, and yet they have sanidine phenocrysts 4A and 10A with the highest anorthite content (fig. 1). To understand this apparent paradox, it is necessary to illustrate a course of equilibrium crystallization for a liquid similar to 4R.

The composition 4R (in projection) falls near the intersection of the



FIG. 3. The normative salic constituents (less anorthite) of the salic phases of twofeldspar oversaturated trachytes plotted in the system NaAlSi₃O₈-KAlSi₃O₈-SiO₂. Groundmass compositions are represented by open circles (suffix G) and are joined to their respective sanidine and plagioclase phenocrysts (represented as pure albite). The rocks are represented by solid circles with suffix R. The composition 4R (and 10R, not plotted) falls outside the triangle whose apices represent the groundmass 4G, the sanidine 4A and the plagioclase (pure albite), because the sanidine (4A) contains significant amounts of the anorthite component (table IV) and it has been plotted only in terms of its Or content. The boundary curve and minimum (represented by +) at 500 kg/cm² water vapour pressure are taken from Tuttle and Bowen (1958), together with the thermal valley, represented as a dashed line.

thermal valley¹ with the alkali-feldspar join (fig. 3) and Tuttle and Bowen (1958) have discussed at length the crystallization of calcium-free synthetic liquids of otherwise similar salic composition to 4R. They have shown that the first feldspar to precipitate from the synthetic equivalent of 4R would be considerably more potassic than the initial composition

¹ It has been assumed that the unique fractionation curve and the 'thermal valley' (Tuttle and Bowen, 1958) are coincident in both the over- and undersaturated parts of petrogeny's residual system (NaAlSiO₄-KAlSiO₄-SiO₂).

of the liquid, so that it is reasonable to suppose that the composition of the first crystals of sanidine to precipitate from 4R would also be more potassic, and could be similar to the sanidines 1A-3A (fig. 3). It is therefore possible to deduce a generalized path on the solidus of an alkali feldspar precipitating under equilibrium conditions from a liquid similar to 4R (fig. 4).

As the initial composition of 4R plots between the alkali-feldspar solidus path and the alkali-feldspar join (fig. 4), it is possible to express the feldspathic components of this rock solely in terms of a calciumbearing alkali-feldspar, so that the plagioclase phenocrysts 4B (fig. 4) will be resorbed at some stage during equilibrium crystallization (Tuttle and Bowen, 1958).

Following Tuttle and Bowen (1958), it may be concluded that a potassic alkali-feldspar was the first feldspar to precipitate from 4R, and with continued equilibrium cooling, the sanidine, moving along the solidus path in fig. 4, becomes more sodic, and at the same time is progressively enriched in anorthite.

At some stage the liquid intersects the two-feldspar surface so that a plagioclase begins to precipitate together with the sanidine. The apparent paradox is the result of the low content of anorthite in the initial liquid delaying the precipitation of the plagioclase so allowing the sanidine to become increasingly sodic and at the same time enriched in anorthite.

The petrographic evidence obtained from a study of 4R indicates that the plagioclase enclosed in some of the sanidine phenocrysts has been partially resorbed. Therefore with the continued precipitation of sanidine and its reaction with the liquid to become increasingly sodic, the accompanying plagioclase will begin to be resorbed. As the tie-line between plagioclase 4B and the liquid 4G also contains the sanidine 4A (fig. 4), it is possible to express the composition of 4R, which also lies (within experimental error) on the solid-liquid tie-line 4B-4A-4G, either in terms of plagioclase 4B and liquid 4G, or of sanidine 4A and liquid 4G. However, it has been shown before that for salic liquids which plot on the potassic side of the thermal valley, it is the plagioclase rather than the sanidine which is resorbed (Carmichael 1963a).

Perhaps it may be suggested that when the solidus path of the alkali-feldspar intersects the plagioclase-liquid three-phase boundary 4B-4G, or, in other words, when the three-phase triangle of liquid, sanidine and plagioclase becomes a straight line with liquid remaining, the resorption of one of the solids, namely plagioclase, should be

complete under equilibrium conditions, and the liquid can then leave the two-feldspar surface. It is difficult to assess whether or not, or to what extent, the partial resorption of plagioclase has contributed to the composition of the sanidine 4A.

With continued equilibrium cooling, the plagioclase will be completely resorbed, and the incorporation of its components into the liquid may



FIG. 4. The plagioclase (4B) and the sanidine (4A) phenocrysts of the trachyte 4R are plotted in the ternary feldspar diagram together with the normative ternary feldspar of 4R and the groundmass 4G. The dashed curve represents the limit of ternary solid solution (fig. 1); the dash-dot curve S-4A-4R represents an equilibrium path on the solidus of an alkali feldspar crystallizing from a liquid represented by 4R; the dash-dot curve P-4B represents an equilibrium solidus path of the plagioclase phenocrysts. The alkali-feldspar minimum at 500 kg/cm² water vapour (double arrows) is taken from Tuttle and Bowen (1958).

keep the sanidine more or less constant in composition, for the precipitation of sanidine 4A (fig. 3) tends to enrich the liquid in potassium, and impoverish it in anorthite, whereas the resorption of plagioclase tends to enrich it in sodium and anorthite, so that for a time these two effects may balance. With continued cooling and precipitation of sanidine, the liquid moves towards higher silica contents, until quartz or tridymite precipitate. With the precipitation of a silica mineral, the sanidine, having become steadily impoverished in anorthite by continuous reaction with the liquid, will now reverse its initial trend of sodic enrichment, and become increasingly potassic (fig. 4). The composition 4R will become all solid when the tie-line (in the system $CaAl_2Si_2O_8$ -NaAlSi₃O₈-KAlSi₃O₈-SiO₂) from the sanidine, plotted on the ternary feldspar plane, to the silica apex intersects the initial salic composition plotted in terms of these four components.

The initial liquids 2R and 3R (fig. 3) also lie near the thermal valley, and an equilibrium course of crystallization similar to 4R is to be expected for both of them. However, as both of these liquids contain more anorthite than 4R (fig. 2), and plot above the two-feldspar boundary surface (in projection), plagioclase is the first feldspar to precipitate. Moreover, as the anorthite content of the initial liquids is greater than that held in the sanidine phenocrysts, plagioclase will continue to be present throughout the crystallization interval.

The initial precipitation of plagioclase from 2R and 3R enriches the liquids in potassium and impoverishes the liquids in anorthite until they impinge on the two-feldspar surface, where potassic sanidines begin to precipitate (fig. 3; 2A, 3A). Thereafter the precipitation of plagioclase exerts a continuous tendency to enrich the liquids in potassium and so prevents the sanidine phenocrysts becoming increasingly sodic. It is suggested, therefore, that in liquids of similar composition to 2R and 3R, the composition of the early sanidine will not change markedly in terms of its Na₂O: K₂O ratio during the crystallization interval, but the continued reaction of this feldspar with the liquid to maintain equilibrium will progressively decrease its anorthite content. The plagioclase will similarly decrease in anorthite, but the Na₂O: K₂O ratio may also only change within narrow limits until the liquid has been used up (Carmichael, 1963a).

These two equilibrium courses of crystallization illustrate the general conclusion that the crystallization of normative anorthite-bearing potassic trachytes, which in projection plot on the potassic side of the thermal valley in fig. 3, cannot be described solely in relation to the system $NaAlSi_{3}O_{8}-KAlSi_{3}O_{8}-SiO_{2}$.

The two undersaturated trachytic liquids 5G and 6G (table III), which are in equilibrium with plagioclase and sanidine phenocrysts, have been plotted in fig. 5, and indicate that the two-feldspar surface extends in projection towards the nepheline-feldspar boundary.

The lateral extent of this surface towards the thermal valley is unknown, because it has been shown that the thermal valley and the minimum on the nepheline-feldspar boundary curve (fig. 5) are considerably displaced (in projection) towards more potassic compositions for undersaturated liquids which plot in the feldspar field and contain normative anorthite (Carmichael, 1964).

The two undersaturated initial liquids 7R and 8R have a similar composition (table III), although 7R does contain a little more normative anorthite (fig. 2). However the sanidinite 8R, which has presumably cooled slowly and therefore approached equilibrium conditions, has only very rare remnants of partially resorbed plagioclase enclosed by sanidine, so that the sanidine 8A (table IV) corresponds closely to the composition of the normative feldspar in the initial liquid (8R, table III). This correspondence indicates that as an undersaturated liquid crystallizes under equilibrium conditions and moves towards the nepheline-feldspar boundary (fig. 5), the plagioclase will, depending upon the liquid's initial composition, be completely resorbed.



FIG. 5. The normative salic constituents (less anorthite) of the groundmasses of the undersaturated trachytes plotted in the system $NaAlSiO_4$ -KAlSiO₄-SiO₂. The nepheline-feldspar field boundary and minimum at 1000 kg/cm² are taken from Hamilton and MacKenzie (1964) together with the position of the thermal valley (dashed line). The alkali feldspar minimum and the minimum on the boundary curve are represented by double arrows.

Although the assemblage nepheline plus plagioclase plus sanidine in equilibrium with liquid is apparently rare in nature, this does not necessarily indicate that the two-feldspar surface does not extend to the nepheline-feldspar boundary (in projection in fig. 5), but rather that the composition of most undersaturated salic liquids (which plot in the feldspar field in fig. 5) requires that if plagioclase is precipitated, it is subsequently resorbed. The incorporation of the plagioclase components as a result of resorption may affect the compositions of both the alkali feldspar and the nepheline, but assuming that nepheline contains approximately the same amount of the anorthite molecule as an alkali feldspar, then the criterion, that if there is more anorthite in the initial liquid than in the sanidine phenocrysts, then a plagioclase will exist throughout the crystallization interval, is still valid.

The precipitation of plagicclase and its later resorption during the equilibrium crystallization of many oversaturated potassic salic liquids indicates that plagioclase will behave similarly in the undersaturated

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potassic salic liquids, so that depending upon the composition of the initial liquid, the two-feldspar surface is either a co-precipitation or a resorption surface, or changes from one to the other during crystallization. The two feldspar surface is taken here to extend in projection to the nepheline-feldspar boundary curve (fig. 5).

The salic tetrahedron: the system CaAl₂Si₂O₈-NaAlSiO₄-KAlSiO₄-SiO₂

With the data provided by the compositions of the salic phases of volcanic rocks whose composition can be expressed almost completely in terms of the above four components, it is possible to represent schematically some of the relationships in this four-component system, at unknown but moderate water vapour pressures.

In fig. 6, a hypothetical representation of the salic tetrahedron is given, and is similar to that described by Sobolev (1959). The base of the tetrahedron is the system NaAlSiO₄-KAlSiO₄-SiO₂ and within the tetrahedron the surface ABCDE represents the two-feldspar surface. This surface cannot intersect the base of the tetrahedron, however closely it may approach it, as the equilibria of the alkali feldspars either alone or with nepheline or silica are characterized by minima rather than by eutectics, which would be necessitated if AE intersected the base of the tetrahedron. The two-feldspar surface must fade out along AE as it approaches the minima (M, M' and M'') in the base of the tetrahedron. At high pressures of water vapour the minima will of course be replaced by eutectic relations (Tuttle and Bowen, 1958).

The curve ED represents the intersection of the two-feldspar surface with the boundary surface separating the silica volume from the plagioclase volume, and will be defined by liquids in equilibrium with quartz, sanidine, and plagioclase, namely the porphyritic rhyolites (Carmichael, 1963*a*).

The curve BC represents liquids in equilibrium with plagioclase, sanidine, and leucite. From B a four-phase curve (now shown) extends upwards into the tetrahedron and is defined by liquids in equilibrium with plagioclase, nepheline, and leucite. This four-phase curve is at the apex of two intersecting surfaces, the nepheline-plagioclase surface and the leucite-plagioclase surface. The point B is an invariant point (in a condensed system) where liquid is in equilibrium with nepheline, leucite, sanidine, and plagioclase, all of fixed composition. A trachyte from Rome, Italy, in the Imperial College collections has leucite, sanidine, and plagioclase phenocrysts with nepheline surrounding some of





FIG. 6. A generalized schematic representation of the system CaAl₂Si₂O₈-NaAlSiO₄-KAlSiO₄-SiO₂ as deduced from porphyritic salic volcanic rocks. M, M', and M'' represent the minima on the quartz-feldspar boundary curve, the alkali feldspar join and the nepheline-feldspar boundary curve respectively. ABCDE represents the two-feldspar surface above the base of the tetrahedron (see text). The relationships for the system KAlSi₂O₆-CaAl₂Si₂O₈-SiO₂ have been taken from Schairer and Bowen (1947); for the system CaAl₂Si₂O₈-NaAlSiO₄-SiO₂ from Schairer (in Roedder, 1959), and for the base of the tetrahedron from Tuttle and Bowen (1958) and Hamilton and MacKenzie (1964).

the sanidine, which indicates that the liquid may have a composition close to B, on the curve BC.

The curve AB is the trace of the intersection of the two-feldspar surface ABCDE with the boundary surface separating the nepheline volume from the plagioclase volume. AB will be defined by liquids in equilibrium with plagioclase, sanidine and nepheline.

Natural salic liquids which in projection plot in the feldspar field on the sodic side of the three minima M, M', and M'' in the base of the tetrahedron are rhyolites, trachytes, and phonolites with phenocrysts of the plagioclase–anorthoclase solid solution series. At no time in the crystallization interval of these liquids will the plagioclase–anorthoclase feldspar be joined by a potassic sanidine (Carmichael, 1963a).

The addition of anorthite to compositions in the base of the tetrahedron (NaAlSiO₄-KAlSiO₄-SiO₂) raises the liquidus temperature (unpublished work) so that liquids, corresponding to the restricted range of composition of natural salic rocks, will all tend to move towards the base of the tetrahedron. The greater the degree of fractionation, the greater the tendency for the liquid to reach the base of the tetrahedron.

Conclusions

Fractional crystallization of liquids in the salic tetrahedron depletes the liquids in the anorthite component, so that derivative liquids may become completely free of the anorthite molecule. An example of a trend in this direction is given by the volcanic rocks of Gough Island, where the plagioclase-sanidine trachytes (5R, table III) are considered to be higher up a liquid line of descent than the anorthoclase-aegirineaugite trachytes (Le Maitre, 1962).

The crystallization of plagioclase and its later complete or partial resorption in many salic liquids may be accentuated, or even caused, by the preferential incorporation of calcium (vis à vis anorthite) from the liquid; this has been called the 'plagioclase effect' (Bowen, 1945; Carmichael and MacKenzie, 1963). Indeed the two-feldspar surface may only become a resorption surface where calcium (other than as a constituent of the anorthite molecule) is present in the liquid, but whether or not this is so cannot be shown with the data of natural salic liquids. The fractional crystallization of salic liquids where calcium has been preferentially incorporated into the plagioclase will produce undersaturation of Al₂O₃ with respect to total alkalis in the derived liquids, so that alkali pyroxenes and/or amphiboles may become products (cf. Le Maitre, 1962).

It has previously been suggested (Carmichael, 1963*a*) that fractional crystallization of 'normal' basaltic magma would only produce onefeldspar salic liquids, the feldspar being a member of the plagioclaseanorthoclase solid solution series. If two-feldspar salic, particularly oversaturated, liquids are accounted derivatives by fractional crystallization of basaltic magma, then the parental basalt must itself be potassic. The problem of the origin of the two-feldspar potassic salic liquids therefore becomes a problem of the origin of the potassic nature of the parental basalt, which in the continental areas, may be conveniently ascribed to sialic contamination.

In the oceanic areas where sialic contamination is less easily accepted, Chayes (1963) found a relative paucity of intermediate rocks in the basalt-trachyte series, and concluded that 'the relative abundance of salic oceanic lavas does not tell us whether crystal fractionation of basaltic magma is necessary for their generation but suggests very strongly that it is insufficient'.

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Petrographic appendix

The oversaturated trachytes. Phenocrysts of weakly zoned plagioclase (1B) form interlocking crystal clusters in the pitchstone IR. Pale green augite, biotite, brown amphibole (barkevikite), and rare sanidine (1A) occur as smaller well-scattered phenocrysts and are all enclosed by a brown vesicular glass (1G). Phenocrysts in minor amounts are sphene, apatite, zircon, and iron-ore, the last commonly being enclosed by the augite phenocrysts. Neither the biotite nor the amphibole phenocrysts show any evidence of resorption by the glass, which has congealed with scattered minute feldspar laths together with pyroxene and iron-ore granules.

2R is the celebrated trachyte from Drachenfels, Germany, which has large idiomorphic sanidine phenocrysts (2A) up to 2 in. in length that may enclose plagioclase, biotite, and sphene. The abundant plagioclase phenocrysts (2B) commonly cluster, and together with augite, and biotite in all stages of resorption and replacement by aggregates of iron-ore, are enclosed in a groundmass (2G) of alkali feldspar laths, rare plagioclase and irregular interstitial quartz. Sphene and iron-ore microphenocrysts also occur and glass may also be found interstitially in the groundmass.

The phenocrysts of sanidine (3A) are smaller in 3R than in 2R, and occur as interlocking crystal clusters with plagioclase (3B) but predominantly as independent crystals. Augite, and biotite with only an indefinite rim of granular magnetite, are the principal ferromagnesian phenocrysts, the pale green pyroxene containing microphenocrysts of iron-ore. Sphene and iron ore are common microphenocrysts. The groundmass (3G) is very fine grained with laths of alkali feldspar, interstitial glass, a silica mineral, and granules of pyroxene and iron ore.

The biotite phenocrysts in 4R are almost completely resorbed and replaced by aggregates of minute iron-ore grains, and together with phenocrysts of perthitic alkali feldspar (4A), plagioclase (4B) and ferroaugite are enclosed by a fine-grained groundmass (4G). A few of the alkali feldspar phenocrysts have cores of partially resorbed plagioclase, and the pyroxene phenocrysts invariably have an outer rim of granular iron-ore. The groundmass is made up of alkali feldspar, cristobalite (Carstens, 1961) pyroxene, iron ore, brownish amphibole, and rare interstitial glass.

The sub-acid pitchstone 10R has been described elsewhere (Carmichael, 1963a) and the published data for this rock have been included in the tables and diagrams for completeness.

The undersaturated trachytes. Phenocrysts of alkali feldspar (5A), plagioclase (5B), biotite, augite, olivine, and iron ore are found in 5R. The alkali feldspar has an unusually patchy extinction, and both the zoned plagioclase and alkali feldspar phenocrysts are mantled by a thin zone of alkali feldspar crowded with iron-ore inclusions. The biotite is strongly pleochroic with a thin rim of granular iron-ore around each crystal. The groundmass (5G) is made up of fine laths of alkali feldspar, granules of pyroxene and iron-ore, and a rare interstitial feldspathoid, possibly sodalite.

Sanidine phenocrysts (6A) may occur as independent crystals or enclose normally independent plagioclase phenocrysts (6B) in 6R, and the phenocrysts of biotite are almost completely resorbed and replaced by aggregates of iron-ore, which have in turn been disintegrated and strewn throughout the groundmass. Barkevikite phenocrysts have been partially resorbed and replaced by iron-ore, and the sphene microphenocrysts also have a rim of granular iron-ore. Pale greenishyellow augite and rare olivine phenocrysts are unaffected by the groundmass, which is crystalline and full of iron-ore grains from the disintegration of the biotite ironore aggregates. The groundmass is composed of alkali feldspar, pyroxene, and apatite which is unusually abundant.

The trachyte 7R has abundant phenocrysts of sanidine (7A) showing all gradations in size to the sanidine of the ground-mass. The larger phenocrysts may form interlocking clusters of crystals, a few of which have cores of plagioclase (An_{27}) . Sparse phenocrysts of ferroaugite, sphene, zircon, and iron-ore together with sanidine are enclosed by a trachytic groundmass of sanidine ($Or_{46^{+5}}$), interstitial glass, and granular pyroxene and iron ore; there is a little interstitial feldspathoid in the groundmass.

8R is a sanidinite composed predominantly of interlocking sanidine crystals (8A) of varying size, together with sodic ferroaugite, sphene, and iron-ore. Partially resorbed oligoclase is rarely found as cores to the sanidine crystals, and nepheline altered to zeolites is present interstitially to the sanidine. Apatite, zircon, sodalite, and a hastingsitic amphibole are accessory.

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