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FELDSPAR-LIQUID EQUILIBRIA IN PERALKALINE ACID LIQUIDS: AN EXPERIMENTAL STUDY

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ABSTRACT. The liquidus surfaces of four pseudoternary joins have been determined at $P_{H_2O} = 1000$ bars. These are:—

Join (A) $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2, plus 5 percent Na_2SiO_3
Join (B) $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2, plus 5 percent $NaFeSi_2O_6$
Join (C) $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2, plus 5 percent K_2SiO_3
Join (D) $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2, plus 5 percent $NaKSiO_3$

Liquidus temperatures are slightly lower than in "Petrogeny's Residua System". Primary feldspar-liquid relationships are shown by means of diagrams and tabulated alkali ratios. Joins A, C, and D may be used to visualize liquidus phase relations in part of the feldspar and quartz primary phase volumes in the quaternary condensed portion of the system SiO_2–Al_2O_3–Na_2O–K_2O–H_2O. With increasing alkali silicate enrichment, the "low-temperature zone" in this volume (equivalent to the "thermal valley" in Ab–Or–Qz) migrates rapidly toward the SiO_2–Al_2O_3–Na_2O plane. The "orthoclase effect", noted by Bailey and Schairer (1964), is discussed. It may be clarified by considering the position of the low temperature zone and fractionation curves associated with it in relation to planes of equal Na_2O:K_2O ratio in the SiO_2–Al_2O_3–Na_2O–K_2O tetrahedron.

A plot of the molecular ratio $(Na_2O + K_2O)/Al_2O_3$ (peralkalinity) versus $Na_2O/(Na_2O + K_2O)$ (sodicity) for peralkaline acid volcanic and plutonic rocks shows a distribution of points closely corresponding to that predicted from the experimental results. This gives support to the hypothesis that crystal-liquid processes have played important parts in the genesis of these rocks. Fractional crystallization or partial melting of any slightly alumina-undersaturated, silica-saturated trachyte or syenite, or of a similarly alumina-deficient rhyolite or granite, would be likely to give rise to a sodic peralkaline acid liquid.

INTRODUCTION

The peralkaline acid rocks have long interested petrologists. They are characterized chemically by containing insufficient alumina to accommodate all their alkalis in feldspar. In the C.I.P.W. norm this situation leads to the formation of the normative mineral acmite (*ac*) or of sodium metasilicate (*ns*) in extreme cases, such as the pantellerites. The usual mineralogical expressions of peralkalinity in acid rocks are the appearance of a relatively sodic alkali feldspar and mafic minerals such as aenigmatite (cossyrite), sodic amphibole (riebeckite/arfvedsonite), and pyroxene with an appreciable sodium content.

In recent years a number of detailed studies have been made of peralkaline acid rocks from widely separated occurrences. These include the Younger Granites and associated lavas of Northern Nigeria (Jacobson, MacLeod, and Black, 1958), the granites of New England (Chapman and Williams, 1935), the trachytes, rhyolites, and coarse-grained inclusions of Ascension (Daly, 1925; Cann, 1965), and the pantellerites and comendites of Pantelleria (Carmichael, 1962; Zeis, 1960; Chayes and Zies, 1962, 1964).

Carmichael showed that if analyses of pantellerite glasses (liquids) were recalculated according to the C.I.P.W. norm procedure and plotted on a ternary *ab–or–Q* diagram, the tie-lines between them and their alkali feldspar phenocrysts would have very different orientations from

those between liquids and their primary feldspar crystals in the synthetic system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O (Tuttle and Bowen, 1958). Accordingly, he and MacKenzie (1963) made an experimental study of this problem, by adding first 4.5 percent and then 8.3 percent each of acmite and sodium metasilicate gels to synthetic gels prepared in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2. They compared their liquidus temperature and primary phase data at 1000 bars P_{H_2O} with those of Tuttle and Bowen by projecting them, using the C.I.P.W. norm procedure, from an *ac* + *ns* + H_2O tetrahedral apex onto the *ab*–*or*–*Q* plane. In this projection the minimum melting composition and the "thermal" valley crossing the feldspar field appear to migrate progressively toward the *or*–*Q* side-line. Pantellerite glasses show a considerable range of compositions, whereas their feldspar phenocrysts vary little. Carmichael and MacKenzie's results led them to suggest that pantellerites were in a thermal valley in the multicomponent natural system analogous to that in their synthetic peralkaline systems.

Subsequently Bailey and Schairer (1966) have published a study of the system Na_2O–Al_2O_3–Fe_2O_3–SiO_2 at 1 atm. They emphasize that while the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 is "Petrogeny's Residua System" for acid liquids with an alkali/alumina ratio of 1:1, it is not so for peralkaline acid liquids. These do not trend toward the liquidus minimum in the Ab–Or–Qz[1] plane but away from this plane and probably toward a eutectic involving quartz, alkali feldspar, and alkali silicates, analogous to the quaternary invariant point quartz-albite-acmite-sodium disilicate in the system Na_2O–Al_2O_3–Fe_2O_3–SiO_2.

Bailey and Schairer (1964) have also criticized Carmichael and MacKenzie's work on several grounds, asserting that by plotting their results recalculated from oxides into the arbitrary minerals of the C.I.P.W. norm they introduce certain systematic distortions of the data which may obscure or even reverse trends shown by the experimental results. Furthermore, by adding acmite to compositions containing quartz and alkali feldspar, they increase the number of components from four to six: SiO_2–Al_2O_3–Na_2O–K_2O–Fe_2O_3–FeO; acmite being partially reduced at high water vapor pressure in stellite bombs (Nolan 1966). This makes their results impossible to analyze rigorously by phase diagrams.

Bearing this last point particularly in mind, it seemed opportune to make a further experimental study to extend and clarify the previous results. Accordingly, liquidus temperatures at 1000 bars P_{H_2O} have been determined for the following four pseudoternary joins:

Join (A): $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 plus 5 percent sodium metasilicate (Na_2SiO_3)

Join (B): $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 plus 5 percent acmite ($NaFeSi_2O_6$)

[1] In this paper *ab*, *or*, and *Q* refer, as usual, to the *normative* minerals albite, orthoclase, and quartz. Ab–Or–Qz is used as an abbreviation for $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2.

Join (C): $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 plus 5 percent potassium metasilicate (K_2SiO_3)

Join (D): $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 plus 5 percent $NaKSiO_3$.

EXPERIMENTAL TECHNIQUES

The initial materials used for this work were coprecipitated gels, prepared by slight modifications of the method described by Roy (1956). Twenty one of these, whose compositions lie in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2, were kindly provided by I.S.E. Carmichael. To these were added the required amounts of gels of sodium metasilicate (Na_2SiO_3) composition provided by I.S.E. Carmichael, acmite ($NaFeSi_2O_6$) composition provided by J. Nolan, and potassium metasilicate (K_2SiO_3) composition. Potassium metasilicate proved difficult to handle, as it is extremely hygroscopic (Kracek, Bowen, and Morey, 1937) and must be kept in an oven. The 5 percent weight of $NaKSiO_3$ added in join D was made by using sodium and potassium metasilicate gels in a 1:1 molecular ratio. The gels were mixed by prolonged grinding together in an agate mortar.

All the experiments were performed by the quenching technique in Tuttle cold-seal pressure vessels (Tuttle, 1949) made from 1¼ inch diameter rods of Haynes alloy 25. The charges were sealed, together with excess water, in gold tubes (Goranson, 1931), and any found to have leaked during runs were discarded. All experiments were made at a water pressure of 1000 ± 30 bars. Temperatures were measured with internal inconel-sheathed chrome-alumel thermocouples and continuously recorded on a Honeywell Brown recording potentiometer. The sheathed thermocouple was sealed into the bomb through a T-joint behind the main seal, so that its tip lay in the middle of the cluster of gold capsules. By using an internal thermocouple, the problem of estimating the temperature gradient across the bomb wall during runs was eliminated. The thermocouples were calibrated at the melting point of sodium chloride (801°C) at 1 atm, and temperatures are thought to be within ± 5°C of the stated values.

In all the joins except B, quartz and feldspar were the only solid phases produced in runs. These were examined and easily differentiated in crushed oil-mounted fragments under a petrographic microscope. Quartz formed minute hexagonal bipryramids, typical of the high-quartz polymorph, whereas feldspar formed larger, extremely thin, equant, or elongated tablets. Compositions of feldspars were determined from X-ray powder diffraction patterns by the $\bar{2}01$ method (Bowen and Tuttle, 1950) using a Phillips diffractometer and $KBrO_3$ as an internal standard (Orville, 1963).

RESULTS

A total of 71 liquidus determinations were made in the four joins. Equilibrium was quickly reached, except in runs at temperatures below 750°C and with compositions near the orthoclase-quartz join (compare, Tuttle and Bowen, 1958, p. 77.) The shortest runs were for 2 days dura-

tion, the longest 8 days, most were for 3 to 4 days. Equilibrium was checked in several instances by approaching a liquidus temperature from both above and below.

There is no evidence that the silica or alkali contents of the synthetic alkali feldspars formed in these experiments vary significantly from stoichiometric amounts (see discussion by Luth and Tuttle, 1966). Bailey and Schairer (1966) discovered appreciable solid solution of Fe_2O_3 in albite at 1 atm. However Nolan (1966) found no evidence for this solid solution at 1000 bars P_{H_2O}, and it appears to be negligible in the present study.

Representation of results.—Although Bailey and Schairer (1964) criticized Carmichael and MacKenzie's (1963) method of representing their results, they refrained from suggesting an alternative because of the large number of components. However, in three of the newly determined joins the number of components may be taken as only four, SiO_2, Al_2O_3, Na_2O, and K_2O, and the results treated in a quaternary (condensed) system.

The method used here is to supplement diagrams with numerical data. The alkali contents of liquids and feldspars are emphasized, because these show the largest proportional changes between "normal" and peralkaline acid rocks. The diagrams are constructed in terms of theoretical mineral molecules, in order that they may more easily be compared with analytical data from rocks and the condensed system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 (Tuttle and Bowen, 1958). In the diagrams (figs. 2, 3, 4, and 5) the triangle is the plane of the bulk compositions. Therefore, its apices are not Ab, Or, and Qz, but, for instance in join A (fig. 2) 95 percent Ab + 5 percent *ns*, 95 percent Or + 5 percent *ns*, 95 percent Qz + 5 percent *ns*. Similarly, the base of the triangle is not the feldspar join, and liquid-feldspar tie lines cannot terminate along it. Instead, a purely diagrammatic alkali feldspar base line is drawn below the triangle, and tie lines are shown running to this. It is hoped to emphasize in this way that the liquids and feldspars are not coplaner. Some aspects of their relationships may be shown numerically.

The system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O.—As the present study is simply an extension of Tuttle and Bowen's (1958) work, it seemed appropriate to make some runs in the acid part of the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O, using the original Ab–Or–Qz gels without additives, and data for this purpose are given in table 1. Figure 1 shows the feldspar-liquid tie lines at $P_{H_2O} = 1000$ bars, together with those of Tuttle and Bowen (1958). The isotherms are taken from Carmichael and MacKenzie (1963). Such liquidus temperature data as were obtained in this system agreed well with those of previous authors if external thermocouples were used but were appreciably lower (20-30°C) when determined with internal thermocouples.

Join A.—The 21 compositions used to determine this join were made up in Ab–Or–Qz with 5 percent sodium metasilicate added to them.

TABLE 1

Experimental data for the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 and the pseudoternary joins:

(A) 95% $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 + 5% Na_2SiO_3
(B) 95% $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 + 5% $NaFeSi_2O_6$
(C) 95% $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 + 5% K_2SiO_3
(D) 95% $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 + 5% $NaKSiO_3$
at a water vapor pressure of 1000 bars.

Composition				$NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2				
Ab	Or	Qz	Liquidus temperature	Primary phase	First feldspar	K_2O/Na_2O in liquid	K_2O/Na_2O in feldspar	K_2O/Na_2O in liquid less K_2O/Na_2O in feldspar
55	10	35		Feldspar	Or_4	0.26	0.06	+0.20
45	20	35		Quartz	$Or_{8.5}$	0.64	0.13	+0.51
37	28	35		"	Or_{55}	1.08	1.75	−0.67
29	36	35		Feldspar	Or_{77}	1.78	4.79	−3.01
21	44	35		"	$Or_{85.5}$	3.00	8.44	−5.44
12	53	35		"	$Or_{92.5}$	6.32	17.66	−11.34
67	10	23		"	$Or_{2.5}$	0.21	0.04	+0.17
55	22	23		"	$Or_{11.5}$	0.57	0.19	+0.38
44	33	23		"	$Or_{55.5}$	1.07	1.79	−0.72
34	43	23		"	Or_{80}	1.81	5.73	−3.92
22	55	23		"	Or_{86}	3.58	8.79	−5.21
70	20	10		"	Or_{13}	0.41	0.21	+0.20
60	30	10		"	Or_{28}	0.72	0.56	+0.16
50	40	10		"	Or_{50}	1.15	2.06	−0.91
40	50	10		"	Or_{73}	1.79	3.87	−2.08
95%			5%	Join A				
55	0	45	Na_2SiO_3	835°	Quartz			
37	18	45	Na_2SiO_3	815°	"			
19	36	45	Na_2SiO_3	790°	"			
0	55	45	Na_2SiO_3	780°	Feldspar + quartz	Or_{95}		
65	0	35	Na_2SiO_3	800°	Feldspar			
55	10	35	Na_2SiO_3	765°	"	$Or_{2.5}$	0.18	0.04	+0.14
45	20	35	Na_2SiO_3	750°	"	Or_9	0.42	0.14	+0.28
37	28	35	Na_2SiO_3	693°	Feldspar + quartz	$Or_{42.5}$	0.67	1.06	−0.39
29	36	35	Na_2SiO_3	760°	Feldspar	Or_{71}	1.00	3.50	−2.50
21	44	35	Na_2SiO_3	785°	"	$Or_{80.5}$	1.44	5.91	−4.47
12	53	35	Na_2SiO_3	815°	"	$Or_{88.5}$	2.19	11.02	−8.83
0	65	35	Na_2SiO_3	850°	"	Or_{93}	4.12	19.02	−14.90
67	10	23	Na_2SiO_3	805°	"	Or_4	0.16	0.06	+0.10
55	22	23	Na_2SiO_3	790°	"	$Or_{10.5}$	0.41	0.17	+0.24
44	33	23	Na_2SiO_3	785°	"	Or_{49}	0.71	1.38	−0.67
34	43	23	Na_2SiO_3	820°	"	Or_{70}	1.09	3.34	−2.25
22	55	23	Na_2SiO_3	860°	"	$Or_{84.5}$	1.77	7.80	−6.03
70	20	10	Na_2SiO_3	825°	"	Or_{13}	0.31	0.21	+0.10
60	30	10	Na_2SiO_3	810°	"	Or_{25}	0.52	0.48	+0.40
50	40	10	Na_2SiO_3	825°	"	Or_{51}	0.79	1.49	−0.70
40	50	10	Na_2SiO_3	865°	"	Or_{72}	1.14	3.68	−2.54
					Join B			
37	18	45	$NaFeSi_2O_6$	775°	Quartz*			
0	55	45	$NaFeSi_2O_6$	815°	Feldspar + quartz*			
55	10	35	$NaFeSi_2O_6$	785°	"	Or_4	0.24	0.06	+0.18

TABLE 1 (continued)

Composition Ab	Or	Qz		Liquidus temperature	Primary phase	First feldspar	K_2O/Na_2O in liquid	K_2O/Na_2O in feldspar	K_2O/Na_2O in liquid less K_2O/Na_2O in feldspar
95%		5%							
45	20	35	$NaFeSi_2O_6$	755°	Feldspar*	$Or_{10.5}$	0.56	0.17	+0.39
37	28	35	$NaFeSi_2O_6$	747°	"	$Or_{49.5}$	0.93	1.40	−0.47
29	36	35	$NaFeSi_2O_6$	760°	"	$Or_{70.5}$	1.47	3.42	−1.95
12	53	35	$NaFeSi_2O_6$	810°	"	$Or_{89.5}$	4.22	12.20	−7.98
0	65	35	$NaFeSi_2O_6$	860°	"	$Or_{97.5}$	15.57	55.83	−40.26
67	10	23	$NaFeSi_2O_6$	830°	"	Or_3	0.20	0.04	+0.16
55	22	23	$NaFeSi_2O_6$	795°	"	Or_3	0.52	0.04	+0.48
44	33	23	$NaFeSi_2O_6$	790°	"	$Or_{42.5}$	0.95	1.06	−0.11
34	43	23	$NaFeSi_2O_6$	810°	"	Or_{75}	1.54	4.29	−2.75
70	20	10	$NaFeSi_2O_6$	847°	"	Or_{11}	0.38	0.18	+0.20
60	30	10	$NaFeSi_2O_6$	820°	"	$Or_{25.5}$	0.65	0.49	+0.16
50	40	10	$NaFeSi_2O_6$	840°	"	$Or_{58.5}$	1.02	2.02	−1.00
					Join C				
55	0	45	K_2SiO_3	772°	Quartz				
37	18	45	K_2SiO_3	760°	"				
0	55	45	K_2SiO_3	812°	Feldspar				
65	0	35	K_2SiO_3	738°	"	$Or_{7.5}$	0.42	0.12	+0.30
55	10	35	K_2SiO_3	725°	"	$Or_{22.5}$	0.76	0.42	+0.34
45	20	35	K_2SiO_3	736°	"	Or_{67}	1.24	2.91	−1.67
37	28	35	K_2SiO_3	745°	"	Or_{78}	1.82	5.08	−3.26
29	36	35	K_2SiO_3	777°	"	Or_{87}	2.71	9.58	−6.87
12	53	35	K_2SiO_3	835°	"	$Or_{94.5}$	8.59	24.60	−16.01
67	10	23	K_2SiO_3	775°	"	$Or_{20.5}$	0.62	0.37	+0.25
55	22	23	K_2SiO_3	790°	"	$Or_{58.5}$	1.07	2.02	−0.95
44	33	23	K_2SiO_3	838°	"	Or_{80}	1.69	5.73	−4.04
34	43	23	K_2SiO_3	855°	"	Or_{89}	2.61	11.58	−8.97
70	20	10	K_2SiO_3	815°	"	$Or_{48.5}$	0.80	1.35	−0.55
60	30	10	K_2SiO_3	850°	"	$Or_{71.5}$	1.17	3.59	−2.42
50	40	10	K_2SiO_3	865°	"	$Or_{77.5}$	1.69	4.93	−3.24
					Join D				
55	0	45	$NaKSiO_3$	785°	Quartz				
37	18	45	$NaKSiO_3$	770°	"				
0	55	45	$NaKSiO_3$	775°	Feldspar				
46	14	40	$NaKSiO_3$	718°	Quartz				
65	0	35	$NaKSiO_3$	780°	Feldspar	$Or_{2.5}$	0.20	0.04	+0.16
55	10	35	$NaKSiO_3$	748°	"	$Or_{8.5}$	0.45	0.13	+0.32
45	20	35	$NaKSiO_3$	705°	Feldspar + quartz	Or_{41}	0.80	1.00	−0.20
37	28	35	$NaKSiO_3$	746°	Feldspar	$Or_{72.5}$	1.18	3.77	−2.59
29	36	35	$NaKSiO_3$	763°	"	$Or_{82.5}$	1.71	6.75	−5.04
12	53	35	$NaKSiO_3$	823°	"	Or_{94}	4.14	22.43	−18.29
0	65	35	$NaKSiO_3$	845°	"	$Or_{97.5}$	10.84	55.83	−44.99
67	10	23	$NaKSiO_3$	788°	"	$Or_{10.5}$	0.38	0.17	+0.21
55	22	23	$NaKSiO_3$	783°	"	$Or_{36.5}$	0.72	0.82	−0.10
44	33	23	$NaKSiO_3$	805°	"	$Or_{70.5}$	1.16	3.42	−2.26
34	43	23	$NaKSiO_3$	832°	"	Or_{81}	1.74	6.10	−4.36
22	55	23	$NaKSiO_3$	855°	"	Or_{90}	2.94	12.88	−9.94
70	20	10	$NaKSiO_3$	815°	"	$Or_{23.5}$	0.55	0.44	+0.11
60	30	10	$NaKSiO_3$	835°	"	$Or_{60.5}$	0.83	2.24	−1.41
50	40	10	$NaKSiO_3$	845°	"	Or_{73}	1.21	3.87	−2.66

* + Magnetite in most cases.

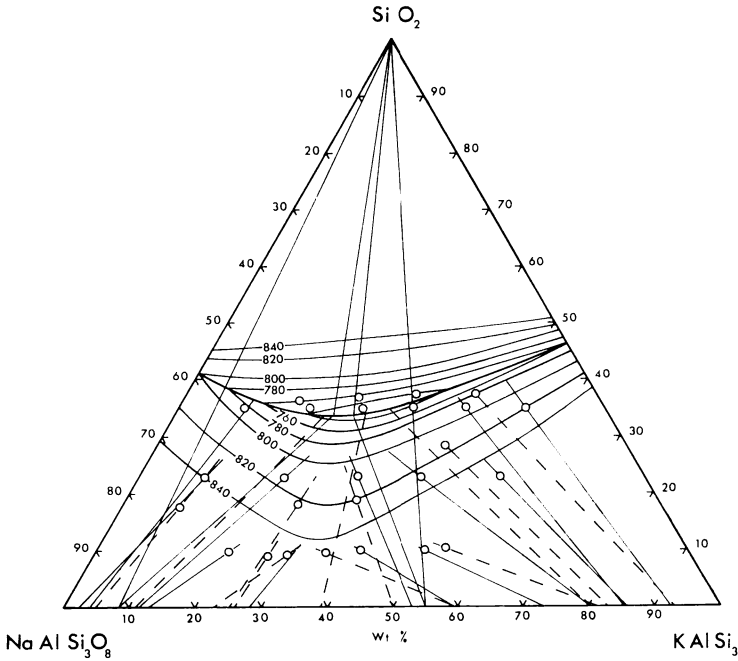

Fig. 1. Isobaric projection (P_{H_2O} = 1000 bars) onto the plane $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 of the liquidus surface in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O. The isotherms and position of the quartz-feldspar field boundary are from Carmichael and MacKenzie (1963). Feldspar-liquid tie lines determined in the present study are shown as solid lines; those given by Tuttle and Bowen (1958) are shown dashed.

Figure 2 shows the isobaric (P_{H_2O} = 1000 bars) liquidus surface and feldspar-liquid tie lines for the join. As Bailey and Schairer (1966, p. 123) have pointed out, the isotherms in a pseudoternary join of this type are merely the intersection of the join with the isothermal shells within primary phase volumes. In the present instance they serve as a convenient way of illustrating liquidus data and as intercepts of the isothermal shells in part of the quaternary condensed system SiO_2–Al_2O_3–Na_2O–K_2O. However, it should be stressed that liquid paths cannot directly be deduced from them. The liquid ends of the feldspar-liquid tie lines lie slightly outside the join, because about 10 percent feldspar must crystallize before its composition may be determined by the $\bar{2}01$ method.

The general level of liquidus temperatures is distinctly lower in join A than in Ab–Or–Qz, whatever thermocouple arrangements are used. One must not, of course, directly compare the melting temperatures of specific pairs of points in figures 1 and 2, because they do *not* have the same compositions, and the comparison is meaningless. However, a broad region of low temperatures on the liquidus (compare, Tuttle and Bowen's (1958) "thermal valley") lies between the quartz-feldspar field boundary and the baseline of the diagram in much the same apparent

position as the thermal valley in Ab–Or–Qz. In figures 1 and 2, the distribution of feldspar-liquid tie lines is remarkably similar. However, if reference is made to table 1, where the data on which figure 2 is constructed are given, the actual alkali ratios of the liquids and feldspars are to be found. From these it may be seen that the larger part of the added sodium has entered the liquids, lowering their K_2O:Na_2O ratios considerably, while the K_2O: Na_2O ratios of the feldspars are changed less.

A further point to emphasize is that the apex of join A is not quartz but quartz plus 5 percent *ns*. This means that the apparent position of the quartz-feldspar field boundary in this join is deceptive, as may be illustrated by considering the position of the minimum on the liquidus in Ab–Or–Qz and Carmichael and MacKenzie's joins. In the diagram showing these (1963, fig. 4) the minimum appears to migrate slightly toward the quartz apex. In fact the SiO_2 contents of the three minima *decrease* with increasing peralkalinity: the figures being 78.6 percent for Ab–Or–Qz, 76.8 percent for the 4.5 *ac* /4.5 *ns* join, and 75.2 percent for the 8.3 *ac*/8.3 *ns* join.

As Bailey and Schairer (1964) have noted, calculation of the excess sodium as metasilicate exaggerates the potential free silica in the ex-

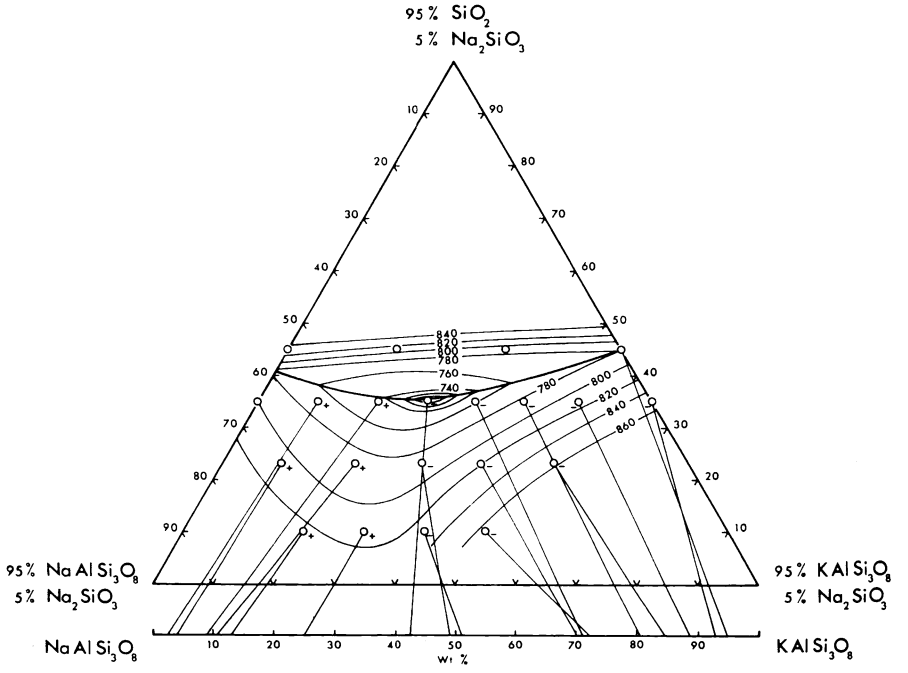

Fig. 2. Liquidus diagram for pseudoternary join A at P_{H_2O} = 1000 bars. Compositions in this join were made up in Ab–Or–Qz, with 5 percent Na_2SiO_3 added to them. The compositions of the primary feldspars lie outside this plane and are represented on a separate base-line $NaAlSi_3O_8$–$KAlSi_3O_8$. The plus or minus signs beside bulk compositions give the sign of the figure found by subtracting the K_2O:Na_2O ratio of the primary feldspar from that of the liquid. The actual figures are in table 1.

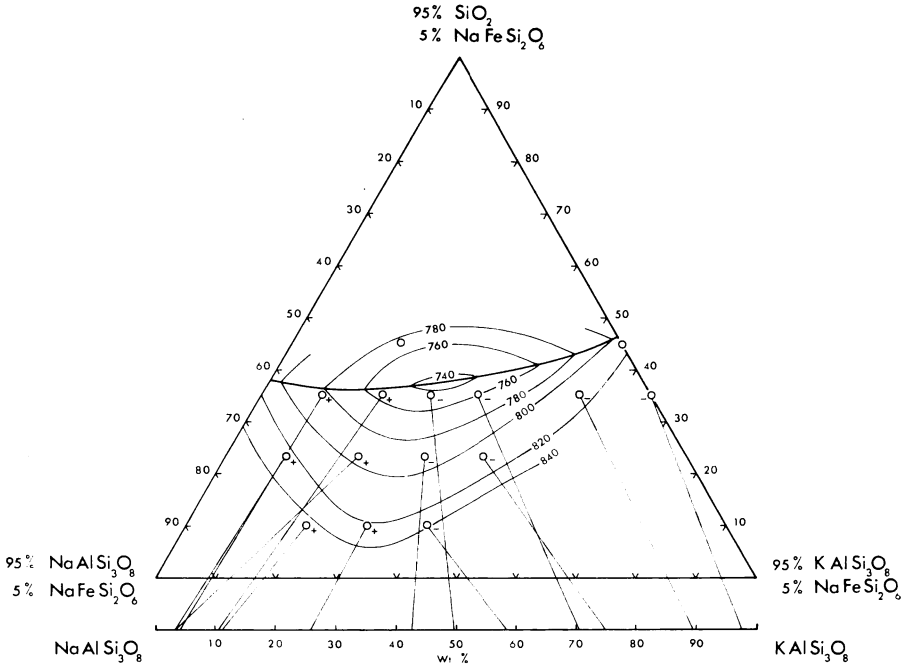

Fig. 3. "Liquidus" diagram for pseudoternary join B at P_{H_2O} = 1000 bars. Compositions in this join were made in Ab–Or–Qz, with 5 percent $NaFeSi_2O_6$ added to them. The diagram is drawn using the same conventions as figure 2. Note that this "liquidus surface" applies only to quartz and feldspar, as small amounts of magnetite remain in most of the glasses.

perimental liquids, because it is clear from their studies that the excess sodium in a peralkaline acid liquid will actually be in the form of potential sodium disilicate. Although this complication could easily have been avoided on the present work by using a sodium disilicate additive or by recalculating the figures given here, this would introduce the serious practical problem that all rock analyses calculated into C.I.P.W. norms would have to be recalculated before they could be compared in any way with the experimental results. It would also *not* remove the distortion of the position of the quartz-feldspar field boundary mentioned above, although it would lessen it.

Join B.—The 15 compositions used to determine this join were made up in Ab–Or–Qz with 5 percent acmite added to them. This introduced iron, one of the important components of peralkaline acid rocks, into the system. Figure 3 shows the isobaric (P_{H_2O} = 1000 bars) "liquidus surface"[2] and feldspar-liquid tie lines for this join. Table 1 shows the data used for constructing this diagram, together with alkali ratios of liquids and primary feldspars. The general level of liquidus temperatures in

[2] It is not a true liquidus surface, because magnetite remained in most of the quartzo-feldspathic glasses, due to the incongruent melting of acmite (Nolan, 1966).

join B is intermediate between those of join A and Ab–Or–Qz. This may reflect the smaller amount of Na_2O added in 5 percent acmite (0.67 percent) than in 5 percent sodium metasilicate (2.54 percent). The distribution of liquid-feldspar tie lines and the apparent position of the "thermal valley" are also broadly similar to those of join A. Thus it seems reasonable to suggest that the introduction of a further component, iron (in fact Fe_2O_3 and FeO) in small amounts, does not seriously affect equilibria in quartzo-feldspathic compositions treated as in the quaternary condensed system SiO_2–Al_2O_3–Na_2O–K_2O (see below).

Join C.—The 16 compositions used to study this join were made up in Ab–Or–Qz, with 5 percent potassium metasilicate added to them. It is harder to understand this join in relation to naturally occurring rocks than A and B, because if a rock were to contain a small amount of "excess potassium", this would, in the C.I.P.W. norm procedure, be allocated to orthoclase molecules, and the excess expressed as sodium. Figure 4 shows the isobaric (P_{H_2O} = 1000 bars) liquidus surface and feldspar-liquid tie lines for join C. The general level of liquidus temperatures is the same as in A, but this is not immediately apparent because the position of the "thermal valley" and distribution of feldspar-liquid tie lines are entirely different from that in the three joins previously discussed. Table

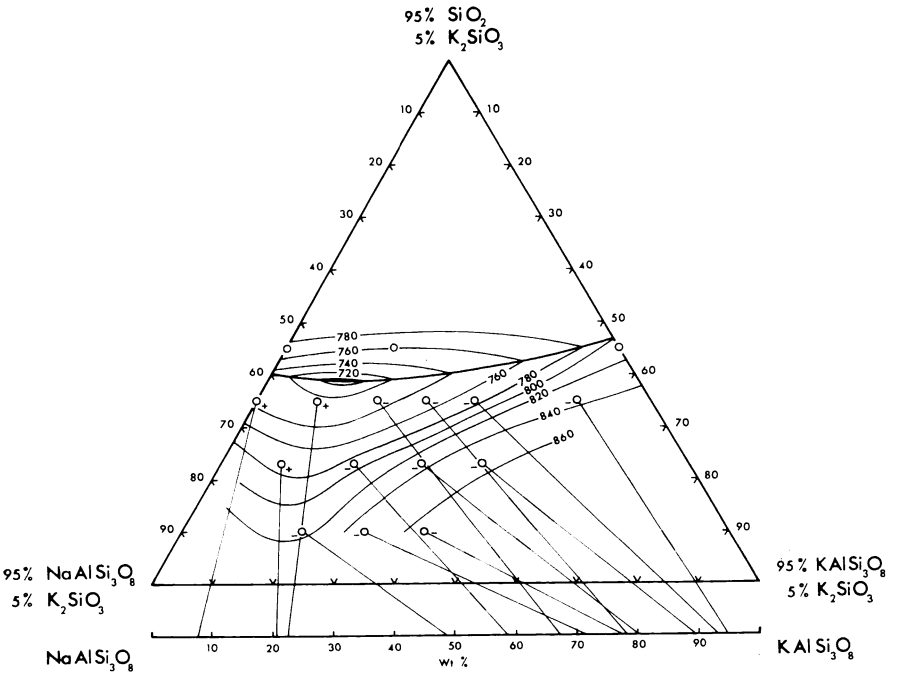

Fig. 4. Liquidus diagram for pseudoternary join C at P_{H_2O} = 1000 bars. Compositions in this join were made up in Ab–Or–Qz, with 5 percent K_2SiO_3 added to them. The diagram is drawn using the same conventions as figure 2.

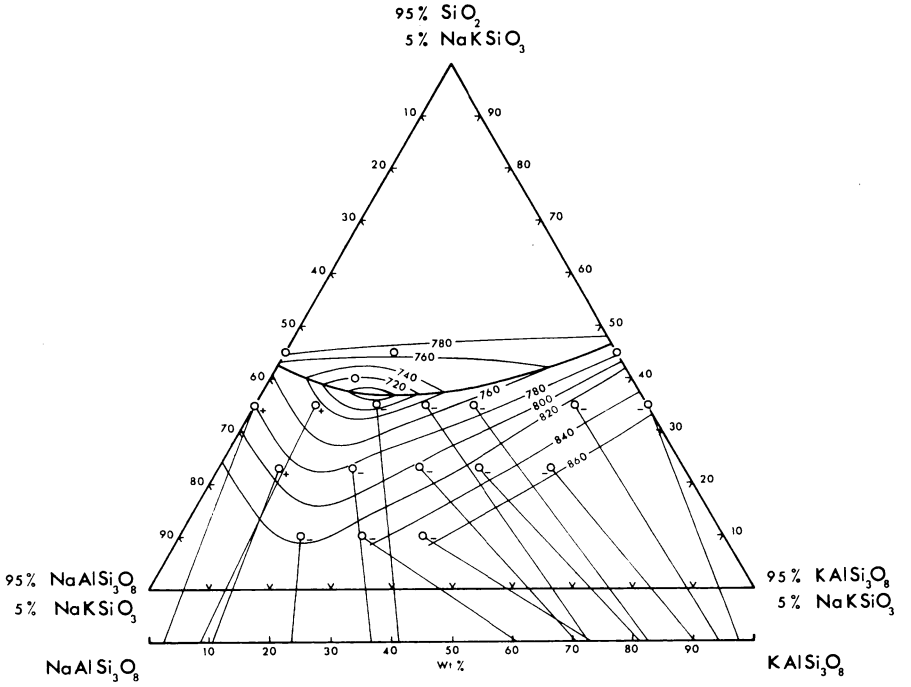

Fig. 5. Liquidus diagram for pseudoternary join D at P_{H_2O} = 1000 bars. Compositions in this join were made up in Ab–Or–Qz, with 5 percent $NaKSiO_3$ added to them. The diagram is drawn using the same conventions as figure 2.

1 summarizes the data from which figure 4 was constructed together with alkali ratios of liquids and feldspars. From these it may be seen that, although the K_2O:Na_2O ratios of both liquids and feldspars have increased, the feldspars are relatively more potassic for all compositions than in Ab–Or–Qz. In a sense, most of the added potassium has entered the feldspars.

Join D.—The 19 compositions used to determine this join were made up in Ab–Or–Qz with 5 percent of a 1:1 molecular mixture of sodium and potassium metasilicate added to them. This is the equivalent of adding 2.2 weight percent *ns* and 2.8 weight percent *ks*. The object in determining this join was to add equal numbers of excess atoms of sodium and potassium to compositions in Ab–Or–Qz and obtain a clear view of the extent of preferential incorporation of excess potassium into feldspars and sodium into liquids which is apparent in joins A and C. Chayes (1964) suggested that the excess alkalis in peralkaline rocks might be calculated in a similar way, into equimolar amounts of sodium and potassium metasilicates. The example he gave of a pantellerite may be compared with the experimental data in join D.

Figure 5 shows the isobaric (P_{H_2O} = 1000 bars) liquidus surface for this join, together with feldspar-liquid tie lines. The data from which

these were constructed are to be found in table 1, along with alkali ratios of liquids and feldspars. It should be remembered that even in this join the alkali ratios of liquids are different from those of "corresponding" liquids in Ab–Or–Qz, and figures 1 and 5 cannot be compared visually. The striking feature of join D is that it resembles join C more closely than any of the others.

DISCUSSION OF EXPERIMENTAL RESULTS

The system SiO_2–Al_2O_3–Na_2O–K_2O–H_2O.—The quaternary condensed part of this system is of fundamental importance in understanding the magmatic evolution of felsic igneous rocks. Doubtless the component H_2O cannot be ignored at low temperatures, when hydrated and highly soluble phases might appear. The only joins in this system for which liquidus surfaces have so far been determined at $P_{H_2O} = 1000$ bars are $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_3 and part of SiO_2–Al_2O_3–K_2O (Tuttle and Bowen, 1958). The positions of joins A, C, and D in SiO_2–Al_2O_3–Na_2O–K_2O may be seen in perspective in figure 6. This diagram also shows that these three joins are *approximately* three different views of a single surface in the tetrahedron: the join 95 percent Ab + 5 percent Na_2SiO_3–95 percent Or + 5 percent K_2SiO_3–95 percent Qz + 5 percent $NaKSiO_3$. The differing appearances of joins A, C, and D are less a matter of different composition fields than of three different views of the same one.

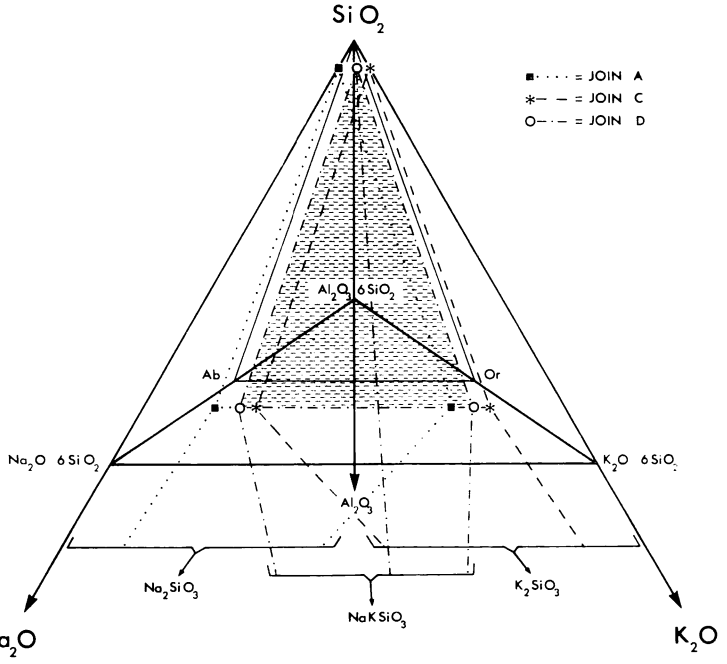

Fig. 6. Perspective diagram of the siliceous part of the tetrahedron SiO_2–Al_2O_3–Na_2O–K_2O. The relative positions of joins A, C, D, and Ab–Or–Qz are shown.

Thus any point in the more potassic parts of join A has a roughly equivalent point in join C, which may be found by recalculating the excess alkali from *ns* into *ks*.

It is clear from figure 6 that join D gives the best view of this 5 percent metasilicate plane, because the distortions in it are of a symmetrical kind. Similarly Chayes' (1964) method of recalculating analytical data would seem to be the most satisfactory, although again in projection, distortions are merely symmetrical and *not* eliminated. The "thermal valley" and minimum on the liquidus in join D are considerably displaced toward the Ab–Qz (plus metasilicate) sideline, relative to the valley and minimum in Ab–Or–Qz. Like the isotherms delineating it, this valley in the liquidus of join D does not have the same significance as that in Ab–Or–Qz. Liquids do not tend along or toward it but *through* it in the third dimension, because the quartz and feldspar crystallizing from them are not coplanar with their bulk compositions. It is merely the intercept of the chosen plane with a "low temperature zone" in the feldspar phase volume of the acid part of the condensed system SiO_2–Al_2O_3–Na_2O–K_2O. This zone is the extension of the "thermal valley" in Ab–Or–Qz into the space of the tetrahedron.

The new data show clearly that, within the small part of the system SiO_2–Al_2O_3–Na_2O–K_2O between join D and Ab–Or–Qz, the axis of this zone is inclined quite steeply toward the plane Si_2O–Al_2O_3–Na_2O (see fig. 6). If the iron contents of the joins determined by Carmichael and MacKenzie (1963) may be neglected for present purposes (see join B above), their results indicate that this shift of the zone toward SiO_2–Al_2O_3–Na_2O continues progressively with more peralkaline compositions. This may be illustrated by considering the K_2O/Na_2O ratios of the minimum melting compositions in their joins. The K_2O/Na_2O ratios of the "ternary" minimum composition in Ab–Or–Qz (Carmichael and MacKenzie, 1963, table 3) is 0.98; for their 4.5 percent *ac* + 4.5 percent *ns* join it is 0.77, and for their 8.3 percent *ac* + 8.3 percent *ns* join it is 0.62. It should perhaps be pointed out that this trend is in the opposite direction from that apparent in the projections used by Chayes and Zies (1962) and Carmichael and MacKenzie (1963).

Feldspar-liquid tie lines and the fractional crystallization curves derived from them are given by Tuttle and Bowen (1958, figs. 23 and 30) for the join Ab–Or–Qz at $P_{H_2O} = 1000$ bars. If figure 1 is compared with figures 2, 3, 4, and 5, it will be seen that the distribution of feldspar-liquid tie lines in relation to the "thermal valley" in joins A, B, C, and D is essentially the same as in Ab–Or–Qz. Therefore it would appear that isobaric fractional crystallization curves in the part of SiO_2–Al_2O_3–Na_2O–K_2O with which we are concerned are probably similarly shaped to those in Ab–Or–Qz although of course *at an angle to that plane.* In the feldspar phase volume in the tetrahedron these curves will originate in the feldspar join, the groups of curves will be convex toward each other, with the axis of the low temperature zone probably at their surface of meeting. Curves near the Ab–Or join will run at a very low angle to it,

until they approach the low temperature zone. Here they will turn sharply and run almost parallel to the axial surface of the zone, toward the quartz-feldspar boundary surface.

As this concept of the relation of fractionation curves to the axial plane of the low temperature zone in part of SiO_2–Al_2O_3–Na_2O–K_2O is based on Tuttle and Bowen's deductions for Ab–Or–Qz, there is no more (or less) evidence for it in the "quaternary" than in the "ternary" system. However, it appears to be the picture that best fits the evidence of all the feldspar-liquid equilibria so far determined in both systems. It is therefore important to see whether this concept of a low temperature zone, into which liquids are channeled by the changing composition of the precipitating feldspar, may be applied to what is already known of feldspar-liquid relations in natural and synthetic peralkaline acid systems.

The "orthoclase effect".—Bailey and Schairer (1964) emphasized two points in their discussion of the data on peralkaline systems available to them:

1. In a system that is deficient in alumina with respect to alkalis, the separation of *any* feldspar molecule, not necessarily anorthite, will accentuate this deficiency in the residual liquid.

2. In most of the natural and synthetic peralkaline liquid-feldspar pairs whose chemical compositions are known, the feldspar has a higher K_2O/Na_2O ratio than the liquid.

It was to cover these two points that Bailey and Schairer suggested the term "orthoclase effect". In their words (1964, abs.), it "means that separation of alkali feldspars from a slightly alumina-deficient liquid will fractionate alumina, and eventually potash, leading to strongly peralkaline and sodic residual liquids".

It will be shown below that this statement is amplified and clarified rather than contradicted by the new experimental data and by the concept of a low temperature zone in the feldspar volume in SiO_2–Al_2O_3–Na_2O–K_2O. Before doing so, it is appropriate to recall Tuttle and Bowen's (1958, p. 64-66) discussion of fractional crystallization in Ab–Or–Qz. These authors distinguished three main areas within the field of primary feldspar in this system. All bulk compositions falling on the sodic side of the *axis* of the "thermal valley" precipitate a feldspar that is constantly more sodic than the residual liquid. The minimum to which this liquid trends is more potassic than any bulk composition in this first area. In a second large area on the potassic side of the thermal valley, all bulk compositions precipitate relatively potassic feldspars and fractionate toward a relatively sodic minimum melting composition. There is a third area, along the Ab–Or join and in the "thermal valley" on the potassic side of its *axis,* where fractionation is complex. The separating feldspar is usually at first more potassic than the residual liquid but later *always* becomes more sodic than it. The minimum may be more or less sodic than the original composition, depending on the position of this in the third area.

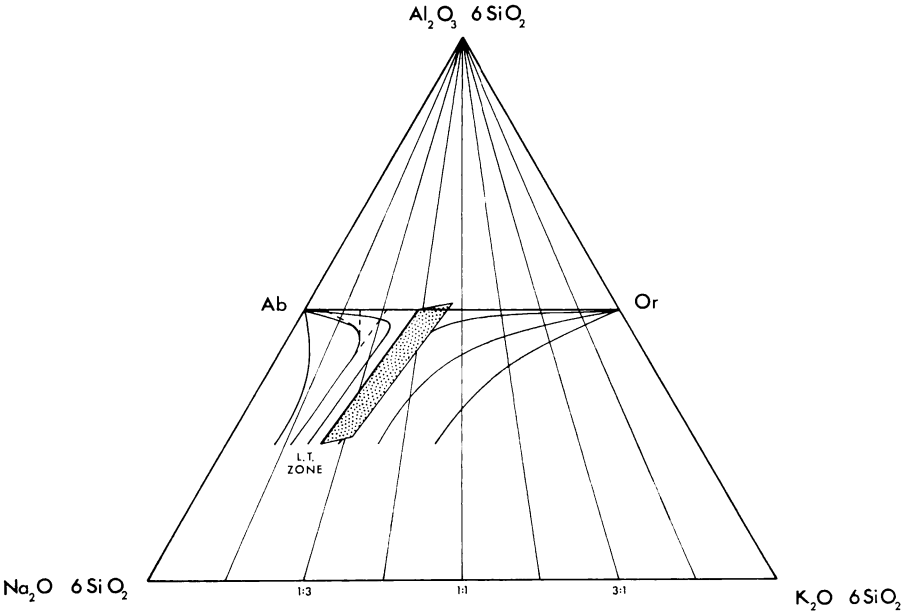

Fig. 7. Postulated fractionation relations in the primary feldspar volume in the acid quaternary condensed part of the system SiO_2–Al_2O_3–Na_2O–K_2O–H_2O, projected from SiO_2 onto the plane Al_2O_3 · $6SiO_2$–Na_2O · $6SiO_2$–K_2O · $6SiO_2$. This plane is marked on figure 6. The axial surface (stippled) of the low temperature zone is shown in perspective, as it is not radial to SiO_2 in the tetrahedron. Projected hypothetical fractionation curves are shown as full lines; projected feldspar-liquid tie lines as dashed lines. Lines radiating from Al_2O_3. $6SiO_2$ are the traces of planes of equal K_2O/Na_2O ratio in the tetrahedron.

Bailey and Schairer's contention is that among peralkaline acid rocks feldspars are usually more potassic than their parent liquids. This contrasts with other acid rocks, a considerable proportion of which contain relatively sodic feldspars. In joins A-D of the present synthetic study all compositions on the sodic sides of the axes of the "thermal valleys", located by means of liquidus temperatures, precipitate relatively sodic feldspars, as they would if in Ab–Or–Qz. This point has been made as clear as possible by marking plus and minus signs against the compositions with determined primary feldspars in figures 2 to 5. These symbols give the sign of the difference between the alkali ratios of liquid and feldspar (K_2O/Na_2O in liquid less K_2O/Na_2O in feldspar) as detailed in table 1. If this figure is positive, the feldspar is more sodic than its parent liquid, and *vice versa*. In the two synthetic joins determined by Carmichael and MacKenzie (1963) there are several compositions lying on the sodic sides of the axes of the "thermal valleys" that precipitate relatively potassic feldspars. There are also compositions further into the sodic field that precipitate relatively sodic feldspars.

Figure 7 is designed to clarify these diverse feldspar-liquid equilibria and the concept of the "orthoclase effect" by considering the rela-

tionship of the low temperature zone, as previously envisaged, to planes of equal K_2O/Na_2O ratio in SiO_2–Al_2O_3–Na_2O–K_2O. This schematic diagram is drawn as a projection from the SiO_2 apex onto the plane $Al_2O_3 \cdot 6SiO_2$–$Na_2O \cdot 6SiO_2$–$K_2O \cdot 6SiO_2$. The join Ab–Or is a line on this plane. The axial surface of the low temperature zone is shown in perspective (tilted to the right), because it is not radial to the SiO_2 apex and projects as an area rather than a line (see, for instance, fig. 2). Lines of equal K_2O/Na_2O ratio radiating from $Al_2O \cdot 6SiO_2$ are marked on the diagram, and the axis of the low temperature zone is shown crossing these lines toward the sodic side-line. This is in accordance with the marked preferential incorporation of potassium into feldspars seen in the experimental studies.

The traces of schematic fractionation curves are shown, although there can be no knowing as yet how they terminate toward the alkali silicate side-line when other phases appear. If this diagram is a correct representation of fractionation in the peralkaline acid part of SiO_2–Al_2O_3–Na_2O–K_2O it shows the following features:

1. Liquids lying on the subparallel bunch of fractionation curves in the low temperature zone all precipitate feldspars with higher K_2O/Na_2O ratios than their bulk compositions. In contrast, liquids lying in the "thermal valley" in Ab–Or–Qz all precipitate relatively sodic feldspars.

2. All liquids on the potassic side of the axial surface of the zone precipitate relatively potassic feldspars. Fractionation curves running from Or near the Ab–Or join presumably still have an inflection in them, as in Ab–Or–Qz, when they turn sharply into the low temperature zone. However, it appears that the effects of this inflection (reversed zoning of separating feldspar) are counteracted by the entire low temperature zone migrating quickly toward the SiO_2–Al_2O_3–Na_2O plane.

3. Extremely sodic liquids, to the left of the low temperature zone, at first precipitate relatively sodic feldspars, while the liquid becomes more potassic. However, as fractionation proceeds and the liquid approaches the low temperature zone a reversal takes place, so that the separating feldspar becomes relatively potassic and the residual liquid progressively more sodic. Three dashed hypothetical feldspar-liquid tie-lines have been drawn tangential to one of the fractionation curves in order to emphasize the point. This inflection in fractionation curves, which would be indicated by a reversal of zoning in natural feldspar phenocrysts, is analogous to that described by Tuttle and Bowen (1958) in Ab–Or–Qz, except that it occurs in liquids on the *sodic* side of the low temperature zone as they move *away* from the plane Ab–Or–Qz. It is consistent with the experimental data in the sodic parts of joins A-D and those determined by Carmichael and MacKenzie (1963), if the iron contents of these may be ignored in this instance. It further provides a simple model to explain why some liquids on the sodic side of the "thermal valleys" in Carmichael and MacKenzie's joins precipitate relatively potassic feldspars.

4. The eventual minimum or eutectic in SiO_2–Al_2O_3–Na_2O–K_2O toward which peralkaline acid liquids fractionate is extremely rich in Na_2O. It is certainly more sodic than most conceivable mildly peralkaline acid natural liquids at the beginning of fractionation sequences.

The concept of fractionation in the peralkaline acid part of SiO_2–Al_2O_3–Na_2O–K_2O which has been outlined above is of course consistent with the experimental data on which it is based. It also confirms the points stressed by Bailey and Schairer (1964), as detailed above, and clarifies them by relating them to a specific quaternary (condensed) system. Admittedly the experimental data in the peralkaline acid part of SiO_2–Al_2O_3–Na_2O–K_2O are still scanty. For instance they are only at 1000 bars P_{H_2O}. Nevertheless, it will be shown in the following section that the available experimental data correlate well with those from natural occurrences.

The purpose of the foregoing discussion has been to try to show that the "curious circumstance" (Chayes, 1964) of the "orthoclase effect" appears to signify fractionation conditions in the peralkaline part of SiO_2–Al_2O_3–Na_2O–K_2O which are not fundamentally different from those in Ab–Or–Qz but are merely an extension of the complexities on that plane into the space of the tetrahedron. Reference to figure 7 shows that in this quaternary system three situations would theoretically be possible. The trace of the axial surface of the low temperature zone could be parallel to a line of equal K_2O/Na_2O ratio (a unique case) or cross these lines toward either the potassic or sodic side-lines. With a fractionation pattern in Ab–Or–Qz as detailed by Tuttle and Bowen (1958), either of the first two alternatives would give feldspar-liquid equilibria in peralkaline acid rocks which were deceptively similar to those in Ab–Or–Qz. It is only in the third alternative, the one which in fact occurs, that feldspar-liquid relations would be radically different. For this reason the present authors are doubtful of the value of the term "orthoclase effect" as such. It links a number of related factors in the fractionation of peralkaline liquids but, by compiling them in a single "effect", might lead to misapprehension of the true nature of the differences in feldspar-liquid relations between peralkaline acid compositions and those in Ab–Or–Qz.

PETROLOGICAL DISCUSSION

The experimental results suggest that synthetic peralkaline liquids fractionating in the feldspar phase volume in SiO_2–Al_2O_3–Na_2O–K_2O will tend to move into the low temperature zone and be held in it by precipitating feldspar of a restricted composition (Or_{30-40}). The pantellerite glasses analyzed by Carmichael seem to be the best examples yet described of natural liquids lying in a multicomponent analogue of this zone. By looking at the relationships among peralkaline acid volcanic liquids in three dimensions rather than two, it is possible to see a greater variety of fractional crystallization trends than is apparent from Carmichael and MacKenzie's (1963) results. Thus, fractionation curves run into the low temperature zone from both sodic and potassic trachytes

(see fig. 7), and there is also a line of liquid descent via the "ternary" minimum region in Ab–Or–Qz and the line of minimum temperature across the feldspar-quartz field boundary surface in SiO_2–Al_2O_3–Na_2O–K_2O. Therefore, the rock types which might be parental to pantellerites and comendites are both sodic and potassic trachytes and rhyolites (and of course any other compositions actually falling in the low temperature zone). Viewing the peralkaline granites in the same way, if these are formed by crystal-liquid processes, they could be derived by fractional crystallization or melting of either granites or syenites. These parental types must be slightly peralkaline themselves or within the metaluminous range of bulk compositions that can become peralkaline through the operation of the "plagioclase effect" (Bailey and Schairer, 1964, p. 1205).

Figure 8 is designed to see whether natural peralkaline acid rocks fit the pattern of the experimental results. It is a plot of molecular

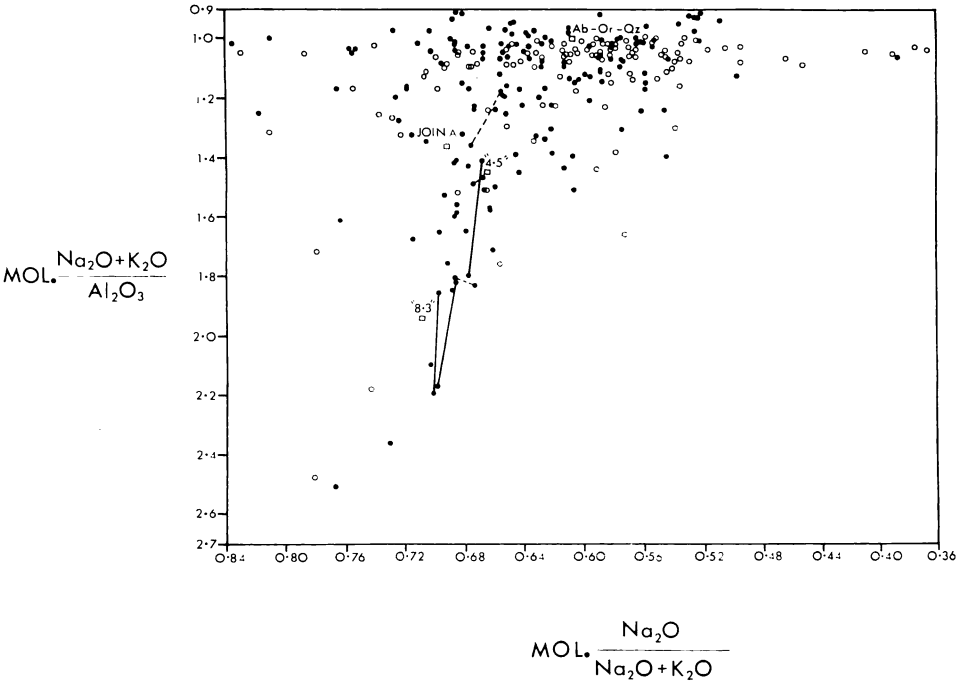

Fig. 8. Molecular ratio $(Na_2O + K_2O):Al_2O_3$ plotted against the ratio Na_2O: $(Na_2O + K_2O)$ for analyses of peralkaline acid rocks taken from the literature. Dots represent volcanic rocks; open circles plutonic rocks. Trachytes with $(Na_2O + K_2O)$: Al_2O_3 less than one, which are however closely associated with pantellerites in the field, have also been plotted. Liquidus minima for Ab–Or–Qz at $P_{H_2O} = 1000$ bars (Tuttle and Bowen, 1958), join A (this study), and the 4.5 percent *ac* + 4.5 percent *ns* and 8.3 percent *ac* + 8.3 percent *ns* joins determined by Carmichael and MacKenzie (1963) are plotted as labelled squares. Dotted lines join Zies' (1960) reanalyses with two of Washington's (1913) pantellerites. Solid lines join pantellerite whole rock-residual glass pairs analyzed by Carmichael (1962). The sources of data used for this figure are given at the end of the references (p. 733-734).

$(Na_2O + K_2O)/Al_2O_3$ (peralkalinity) against molecular $Na_2O/(Na_2O + K_2O)$ (sodicity) for analyses of these rocks from the literature. It uses the same components, Al_2O_3, Na_2O, and K_2O, as figure 7 and suffers from the same deficiency, that variations in SiO_2 content are eliminated, so that trachytes are superimposed on rhyolites. Another problem with this plot is that the scatter of points is bound to be due partially to combining the work of a large number of analysts. Zies' (1960) reanalyses of two of the pantellerites studied by Washington (1913) illustrate this. Despite these reservations, the following features are clear:

1. Alkali feldspar, with a molecular ratio $(Na_2O + K_2O)/Al_2O_3$ of one, is an important mineral in all these acid rocks. It may be reemphasized that the crystallization of any feldspar from a mildly peralkaline liquid will leave a strongly peralkaline residuum.

2. Slightly peralkaline acid rocks (and the metaluminous trachytes closely associated with pantellerites in the field) show a wide range of alkali ratios. It would be particularly interesting in the future to study the rare examples of extremely sodic mildly peralkaline acid lavas and discover whether these contain relatively sodic alkali feldspar phenocrysts, as would appear likely from the experimental results.

3. As these rocks become more peralkaline, the range of their Na_2O/K_2O ratios becomes progressively restricted, suggesting that fractional crystallization and melting processes are moving the natural liquids into a multicomponent analogue of the low temperature zone in SiO_2–Al_2O_3–Na_2O–K_2O.

4. Strongly peralkaline acid rocks show a distinct tendency to become progressively more sodic. This is best seen in Carmichael's analyses of pantellerite whole rock-residual glass pairs.

5. The progressive increase in Na_2O/K_2O ratio is of exactly the same order as one would expect from the experimental results. This is shown by marking the minimum melting compositions in Ab–Or–Qz, join A of this study, and Carmichael and MacKenzie's (1963) 4.5 percent *ac* + 4.5 percent *ns* and 8.3 percent *ac* + 8.3 percent *ns* joins on the diagram. These synthetic compositions show a progressive rise in Na_2O/K_2O ratio with increasing peralkalinity and plot very close to the natural liquids.

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