

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 51

SEPTEMBER-OCTOBER, 1966

Nos. 9 and 10

THE ALKALI FELDSPAR SOLVUS IN THE SYSTEM



W. C. LUTH² AND O. F. TUTTLE,³ *Department of Geochemistry and Mineralogy, The Pennsylvania State University, University Park, Pennsylvania.*

ABSTRACT

Preliminary experiments in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ indicate that the nature of the alkali feldspar solvus is influenced by the $\text{Na}_2\text{O}+\text{K}_2\text{O}:\text{Al}_2\text{O}_3$ molar ratio in the bulk composition. The solvuses obtained by the crystallization of dehydrated gels in the presence of an aqueous vapor phase at two kilobars show significant differences which are dependent on the stoichiometry of the initial bulk composition. This feature may be a consequence of differences in thermal state in the various synthetic feldspars, or it may reflect a departure from stoichiometry. Analysis of unit cell dimensions suggest that the alkali feldspars crystallized in the presence of excess Al_2O_3 contain minor amounts of excess Al_2O_3 in crystalline solution. Unit cell dimensions of those alkali feldspars crystallized in the presence of excess $\text{Na}_2\text{O}+\text{K}_2\text{O}$ suggest that in this case a lower thermal state is obtained.

INTRODUCTION

A fundamental assumption underlying much of the recent experimental research on the synthesis, stability, and petrogenic significance of the alkali feldspars is that the 1:1:6 molar ratio of $\text{Na}_2\text{O}+\text{K}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$ is maintained. Do the analyses justify this assumption? Can all the departures from the 1:1:6 ratio be attributed to analytical uncertainty and contamination?

Calculation of the CIPW norms for alkali feldspar analyses will give directly the departure from the 1:1:6 ratio; if there is excess Al_2O_3 , corundum will appear in the norm; excess alkalis will result in acmite or alkali metasilicates in the norm; excess silica will give quartz in the norm; and with deficiency of silica nepheline will appear in the norm. If there is CaO in the feldspar, and there is not enough Al_2O_3 to form anorthite from all the CaO, the norm will show this Al_2O_3 deficiency by the appearance

¹ Contribution No. 65-5, College of Mineral Industries.

² Present Address: Department of Geology and Geophysics, Massachusetts Institute of Technology, Cambridge, Mass.

³ Present Address: Department of Geology, Stanford University, Stanford, California.

of diopside or wollastonite. Consequently, the feldspar analyses can be grouped into four categories:

(1) excess SiO_2 and excess Al_2O_3 (+Q, +C), (2) excess SiO_2 and deficiency of Al_2O_3 (+Q, -C), (3) deficiency of SiO_2 and an excess of Al_2O_3 (-Q, +C), (4) deficiency of both SiO_2 and Al_2O_3 (-Q, -C).

Deer *et al.* (1963, pp. 36-45, 110) present analytical data on 87 alkali feldspars from a wide variety of geologic environments. In terms of the four categories given above, we can construct orthogonal axes labeled $\pm Q$ and $\pm C$, and a point for each analysis can be plotted on the diagram. This has been done in Fig. 1 for 73 of the analyses given in Deer *et al.* (1963). It can readily be seen that there is a tendency for analyses to group around the stoichiometric values, but relatively large departures from the accepted stoichiometry are common. It is probable that many of these departures can be accounted for in terms of analytical difficulties, sample impurities, or a combination of both factors. However, we are inquiring as to whether or not the available analytical data indicate that stoichiometry is observed. On the basis of the data presented, it can be said that there is a tendency toward stoichiometry, but there is no evidence for exact obedience of the requirements of the stoichiometric formula.

The data obtained by Smith and Ribbe (1966) from microprobe *x*-ray-emission analysis indicates less scatter and closer agreement with the stoichiometric formula than the data obtained by classical gravimetric methods. It is possible that the reduction of scatter is due in large part to the small sample analyzed with the consequent minimization of the effects of impurities such as quartz and mica. A second reason for the closer approximation to the stoichiometric values lies in the fact that stoichiometry was in part assumed in the preparation of the calibration curves for Al and Si. Smith and Ribbe (1966) point out that systematic errors can arise if stoichiometry is not obeyed.

In a later section of this paper we will be concerned with the mol ratio $(\text{Na} + \text{K})/\text{Al}$. The analogue of this ratio in the natural feldspars is the mol ratio $(\text{Na} + \text{K} + \text{Ca} + \text{Ba} + \text{Sr})/(\text{Al} + \text{Fe}^{3+})$. In Fig. 2 this parameter is plotted against the mol per cent "An" $(\text{An} + \text{Cn} + \text{Sr} - \text{F})/(\text{Ab} + \text{Or} + \text{An} + \text{Cn} + \text{Sr} - \text{F})$ in the feldspar. The data is taken from Smith and Ribbe (1966). It is apparent, disregarding analytical precision, that 0.5 weight per cent excess Al_2O_3 in crystalline solution with the feldspars is permitted by the data. Considering only those alkali feldspars with less than 2 mol per cent "An" present, it seems possible to have alkali feldspars with either an excess or a deficiency of Al_2O_3 in amounts up to about 0.5 weight per cent. Using these two parameters, which are ratios, this value is at the margin of the precision reported by Smith and Ribbe. At the present time then, analytical techniques and problems of contamination

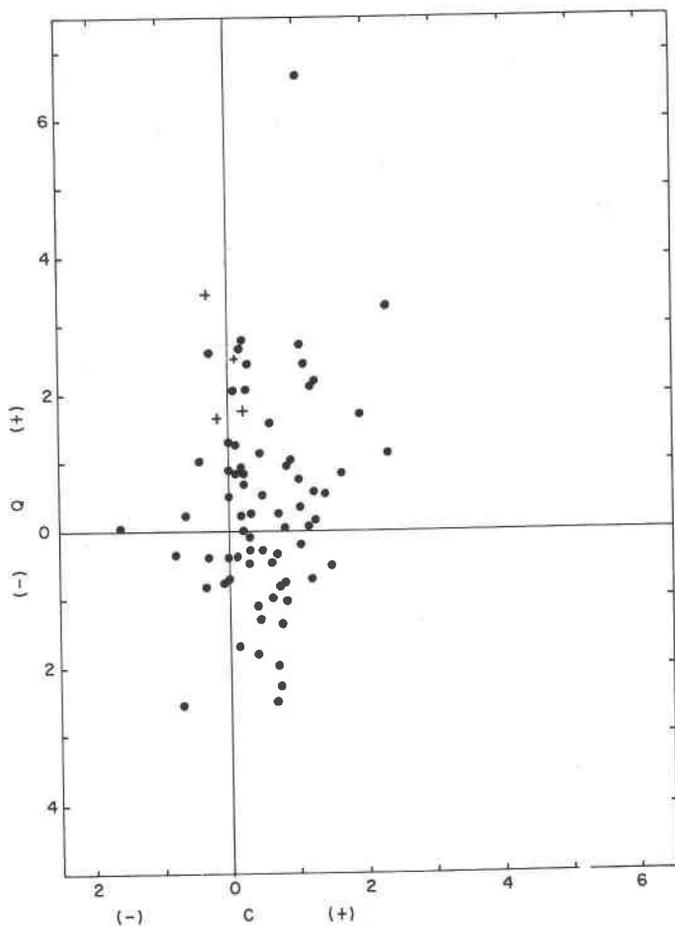


FIG. 1. Normative quartz and corundum in 73 alkali feldspar analyses (dots) from Deer *et al.* (1963, pp. 36-44, 110) and Chayes and Zies (+) (1962, p. 114). The term (-C) represents that amount of Al_2O_3 required to form albite from acmite and sodium metasilicate and to make anorthite from diopside and wollastonite. -Q is that amount of quartz required to form albite from nepheline.

do not either support or deny the possibility of non-stoichiometry at the ± 0.5 weight per cent Al_2O_3 level, and probably not the ± 1.0 weight per cent Al_2O_3 level if the assumptions made by Smith and Ribbe are considered.

The stoichiometry of the feldspars has recently been questioned by Chayes and Zies (1962) who wrote, "it seems to us that the possibility of systematic departure from the assumed 1:1:6 ratio in alkali feldspars deserves more than casual consideration." They point out that in one

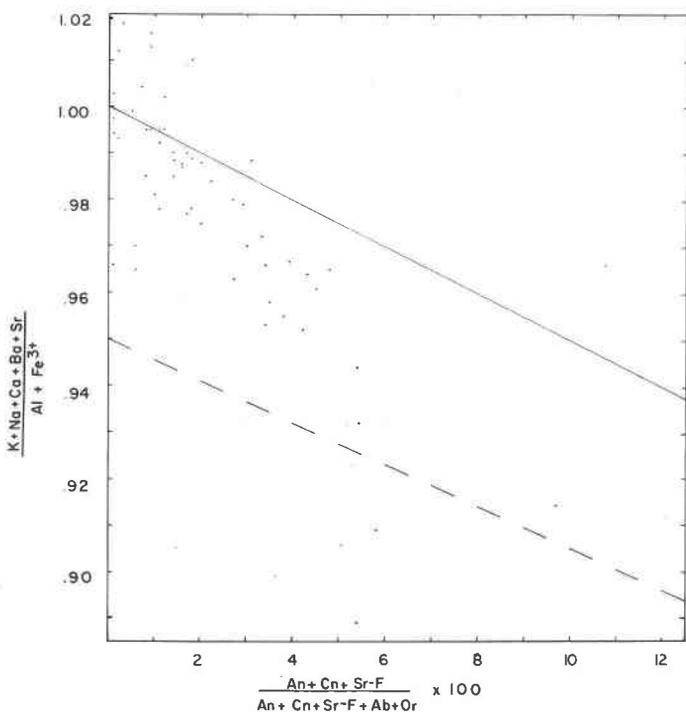


FIG. 2. The alkali/alumina mol ratio in alkali feldspars. Analytical data from Smith and Ribbe (1966). The mol ratio $K+Na+Ca+Ba+Sr:Al+Fe^{3+}$ is the ordinate and the mole per cent "An" ($An+Cn+Sr-F:An+Cn+Sr-F+Ab+Or$) is the abscissa. The line originating at 0, 1.00 terminates at 100, 0.5 and indicates exact stoichiometry, in terms of the mol ratio, for $CaAl_2Si_2O_8$, $BaAl_2Si_2O_8$, $SrAl_2Si_2O_8$, $NaAlSi_3O_8$, $KAlSi_3O_8$ and $(Na, K)FeSi_3O_8$ crystalline solutions. The line originating at 0, 0.95 indicates a hypothetical crystalline solution with 1 weight per cent Al_2O_3 in the above components.

specimen from a comendite (rhyolite) no quartz was found in the feldspar concentrate despite a careful search, yet the analysis showed 2.53 per cent excess silica.

EXPERIMENTAL STUDIES

Tuttle and Bowen (1958) have demonstrated that the nature of the alkali feldspar solvus is very sensitive to the thermal state of the feldspar. It was believed that the feldspar solvus might also be sensitive to slight variations in stoichiometry, and to check this possibility five gels were prepared having a constant ratio of Na_2O to K_2O , but with 3 weight per cent excess SiO_2 , Al_2O_3 , $NaAlSi_3O_8+KAlSi_3O_8$ and $NaSi_3O_8+K_2Si_2O_5$, in addition to the one on the $NaAlSi_3O_8-KAlSi_3O_8$ join. A second series of gels was prepared near the albite composition for unit cell determinations.

The composition of each of these eleven starting materials is given in Table 1. The gels were prepared in the manner described by Luth and Ingamells (1965).

These experiments were carried out in externally heated, cold-seal pressure vessels (Tuttle, 1949; Luth and Tuttle, 1964). The gel starting materials were placed in 2.0 mm O.D., 0.1 mm wall thickness gold capsules, together with 15 weight per cent distilled, deionized water. The capsules were run in groups of 5 or 6 in a pressure vessel so that the temperature, pressure and quenching treatment of the samples would be

TABLE 1. BULK COMPOSITIONS STUDIED

| | |
|-----|--|
| 001 | Ab ₆₀ Or ₄₀ |
| 002 | (Ab ₆₀ Or ₄₀) ₉₇ (Al ₂ O ₃) ₃ |
| 003 | Ab ₆₀ Or ₄₀) ₉₇ (Ne ₆₀ Ks ₄₀) ₃ |
| 004 | (Ab ₆₀ Or ₄₀) ₉₇ (NS ₆₀ KS ₄₀) ₃ |
| 005 | (Ab ₆₀ Or ₄₀) ₉₇ (SiO ₂) ₃ |
| 007 | Ab ₈₅ Or ₁₅ |
| 008 | (Ab ₈₅ Or ₁₅) ₉₇ (Al ₂ O ₃) ₃ |
| 009 | (Ab ₈₅ Or ₁₅) ₉₇ (NS ₈₅ KS ₁₅) ₃ |
| 010 | Ab ₉₀ Or ₁₀ |
| 011 | (Ab ₉₀ Or ₁₀) ₉₇ (Al ₂ O ₃) ₃ |
| 012 | (Ab ₉₀ Or ₁₀) ₉₇ (NS ₉₀ KS ₁₀) ₃ |
| | Ab Na ₂ O · Al ₂ O ₃ · 6SiO ₂ |
| | Or K ₂ O · Al ₂ O ₃ · 6SiO ₂ |
| | Ne Na ₂ O · Al ₂ O ₃ · 2SiO ₂ |
| | Ks K ₂ O · Al ₂ O ₃ · 2SiO ₂ |
| | NS Na ₂ O · 2SiO ₂ |
| | KS K ₂ O · 2SiO ₂ |

identical. The precision in temperature and pressure for a 30 day run is $\pm 7^\circ$ C. and ± 0.08 kb respectively. The composition of the alkali feldspars is based on the position of the 20 $\bar{1}$ reflection (Tuttle and Bowen, 1958). In connection with a related problem (Seck, Luth and Tuttle in preparation) gels were prepared on the NaAlSi₃O₈ - KAlSi₃O₈ join at two or five per cent intervals, and crystallized at low pressure and high temperature to homogeneous alkali feldspars. The absolute value of $d_{20\bar{1}}$ for these feldspars have been determined using a spinel standard supplied by Professor G. V. Gibbs. The spinel has the 111 reflection at $19.016^\circ 2\theta$ (CuK α radiation), making it very well suited for use as an internal standard both for the composition determinations, and for determination of unit cell dimensions. A working curve was prepared using the data obtained and will be presented in a later paper.

The cell constants a , b , c , α , β , γ and the unit cell volume were obtained

TABLE 2. UNIT CELL DIMENSIONS OF ALKALI FELDSPARS

| Run No. | 2θ Obs. | 2θ Calc. | No. of* lines | $a(\text{\AA})$ | $b(\text{\AA})$ | $c(\text{\AA})$ | Unit cell Volume | α ($^\circ$) | β ($^\circ$) | γ ($^\circ$) | Bulk Composition | % Or (weight) |
|---------|----------------|-----------------|---------------|-----------------|-----------------|-----------------|------------------|-----------------------|----------------------|-----------------------|------------------|---------------|
| 1192 | 21.561 | 21.544 | 14 | 8.354 .009** | 12.999 .005 | 7.167 .004 | 699.20 | 90.00 | 116.05 .06 | 90.00 | 2 | 39 |
| 1232 | 21.510 | 21.521 | 14 | 8.363 .005 | 12.984 .003 | 7.164 .003 | 698.66 | 90.00 | 116.09 .03 | 90.00 | 1 | 42 |
| 1233 | 21.550 | 21.552 | 14 | 8.350 .004 | 12.988 .003 | 7.162 .002 | 697.70 | 90.00 | 116.08 .03 | 90.00 | 2 | 40 |
| 1235 | 21.520 | 21.542 | 14 | 8.354 .007 | 12.978 .005 | 7.154 .004 | 696.43 | 90.00 | 116.12 .05 | 90.00 | 4 | 42 |
| 1407 | 21.856 | 21.865 | 12 | 8.214 .006 | 12.913 .005 | 7.148 .005 | 677.94 | 92.55 .11 | 116.44 .06 | 90.22 .10 | 7 | 16 |
| 1408 | 21.903 | 21.913 | 8 | 8.198 .003 | 12.915 .010 | 7.137 .002 | 676.01 | 92.86 .05 | 116.33 .06 | 90.29 .10 | 8 | 13 |
| 1409 | 21.912 | 21.907 | 10 | 8.198 .006 | 12.892 .006 | 7.134 .004 | 674.04 | 92.41 .09 | 116.47 .07 | 90.37 .09 | 9 | 13 |
| 1410 | 21.972 | 21.985 | 19 | 8.172 .007 | 12.877 .008 | 7.127 .006 | 671.32 | 93.26 .11 | 116.24 .07 | 89.99 .10 | 10 | 5 |
| 1411 | 21.994 | 21.974 | 17 | 8.174 .006 | 12.900 .006 | 7.134 .005 | 672.65 | 93.38 .10 | 116.33 .05 | 90.17 .08 | 11 | 3 |
| 1412 | 21.985 | 21.967 | 13 | 8.176 .006 | 12.849 .006 | 7.125 .004 | 688.99 | 93.32 .05 | 116.42 .05 | 89.83 .04 | 12 | 4 |
| 1273 | 21.313 | 21.317 | 11 | 8.449 .005 | 13.000 .003 | 7.177 .003 | 707.94 | 90.00 | 116.10 .04 | 90.00 | 1 | 60 |
| 1274 | 21.372 | 21.381 | 12 | 8.421 .06 | 13.010 .005 | 7.179 .004 | 706.27 | 90.00 | 116.11 .06 | 90.00 | 2 | 55 |
| 1276 | 21.293 | 21.283 | 17 | 8.462 .003 | 13.006 .003 | 7.175 .002 | 708.71 | 90.00 | 116.18 .03 | 90.00 | 4 | 62 |
| 1279 | 21.238 | 21.239 | 21 | 8.484 .003 | 13.015 .003 | 7.175 .002 | 711.36 | 90.00 | 116.11 .02 | 90.00 | 1 | 68 |
| 1280 | 21.243 | 21.238 | 16 | 8.479 .004 | 13.019 .004 | 7.180 .003 | 711.11 | 90.00 | 116.20 .04 | 90.00 | 2 | 67 |
| 1282 | 21.206 | 21.204 | 19 | 8.498 .003 | 13.008 .003 | 7.186 .003 | 713.42 | 90.00 | 116.08 .04 | 90.00 | 4 | 71 |
| 1248 | 21.208 | 21.220 | 13 | 8.494 .006 | 13.019 .004 | 7.172 .004 | 712.53 | 90.00 | 116.05 .05 | 90.00 | 1 | 71 |
| 1249 | 21.246 | 21.260 | 10 | 8.481 .007 | 13.012 .012 | 7.167 .003 | 711.48 | 90.00 | 115.90 .06 | 90.00 | 2 | 67 |
| 1251 | 21.168 | 21.171 | 12 | 8.513 .003 | 13.007 .002 | 7.173 .002 | 712.86 | 90.00 | 116.17 .03 | 90.00 | 4 | 76 |
| 1226 | 21.298 | 21.293 | 11 | 8.460 .005 | 13.007 .003 | 7.174 .003 | 708.71 | 90.00 | 116.13 .04 | 90.00 | 1 | 62 |
| 1227 | 21.340 | 21.356 | 10 | 8.430 .006 | 13.018 .006 | 7.182 .005 | 707.35 | 90.00 | 116.17 .06 | 90.00 | 2 | 58 |
| 1229 | 21.264 | 21.265 | 16 | 8.472 .003 | 13.011 .002 | 7.171 .002 | 709.73 | 90.00 | 116.13 .03 | 90.00 | 4 | 65 |
| 1255 | 21.358 | 21.359 | 12 | 8.430 .003 | 13.000 .003 | 7.175 .002 | 705.60 | 90.00 | 116.17 .03 | 90.00 | 1 | 56 |
| 1256 | 21.416 | 21.430 | 10 | 8.399 .010 | 13.008 .009 | 7.180 .008 | 703.64 | 90.00 | 116.17 .10 | 90.00 | 2 | 51 |
| 1258 | 21.346 | 21.343 | 14 | 8.438 .005 | 13.001 .003 | 7.173 .003 | 706.43 | 90.00 | 116.14 .04 | 90.00 | 4 | 57 |

* Number of lines used in refinement.

** Standard error.

for twenty-five of the alkali feldspars synthesized in connection with this study. A FORTRAN II program for the IBM 7074 at the Pennsylvania State University Computation Center was prepared by Professor G. V. Gibbs and Dr. C. M. Smith, Jr. based on an ALGOL program developed by Evans *et al.* (1962), of the U.S. Geological Survey for least squares refinement of cell constants from powder diffraction data. We would like to acknowledge the contribution made by Gibbs and Smith in preparing this program, and thank Dr. D. E. Appleman for supplying the ALGOL version.

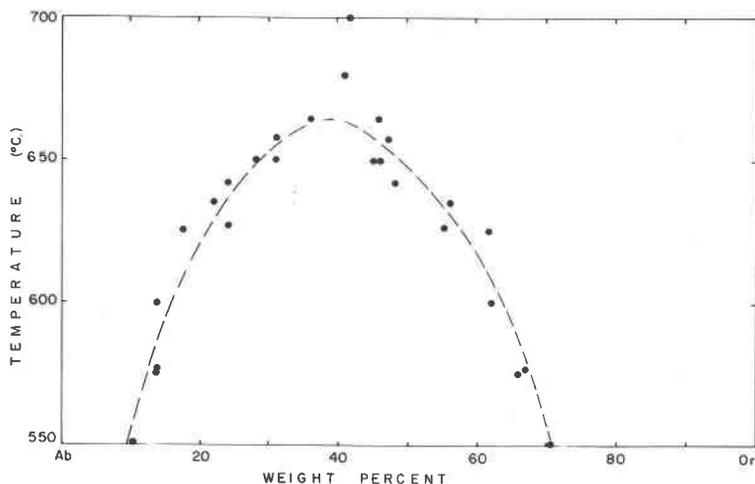


FIG. 3. Alkali feldspar solvus determined on material crystallized from a dehydrated gel of the composition $Ab_{60}Or_{40}$ at various temperatures at 2 Kb pressure. The maximum error in determining the position of the $20\bar{1}$ is ± 2 weight per cent Or and the temperature uncertainty is $\pm 10^\circ\text{C}$.

The Norelco High Angle Spectrometer with nickel filtered copper (40kv, 15ma) radiation was used for both the $20\bar{1}$ and cell constant determinations. In the determination of $20\bar{1}$ four oscillations over the range of $18-22.5^\circ 2\theta$ were completed at a scanning speed of $\frac{1}{4}^\circ 2\theta$ per minute (chart speed of one inch per minute), and the resultant value of 2θ ($20\bar{1}_{\text{feldspar}} - 111_{\text{spinel}}$) added to the $19.016^\circ 2\theta$ value for the spinel. For the determination of cell constants the following is pertinent: four oscillations; $\frac{1}{4}^\circ 2\theta$ /minute scanning speed; 1° /minute chart speed; $12-55^\circ 2\theta$ range; 1° scatter and divergence slits; 0.003 inch or 0.006 inch receiving slit; geiger sensing element; time constant 4 or 2 seconds; scale factor 0.8 or 1.0; multiplier 4 or 8. The data obtained by the least squares refinement of the powder diffraction data are presented in Table 2.

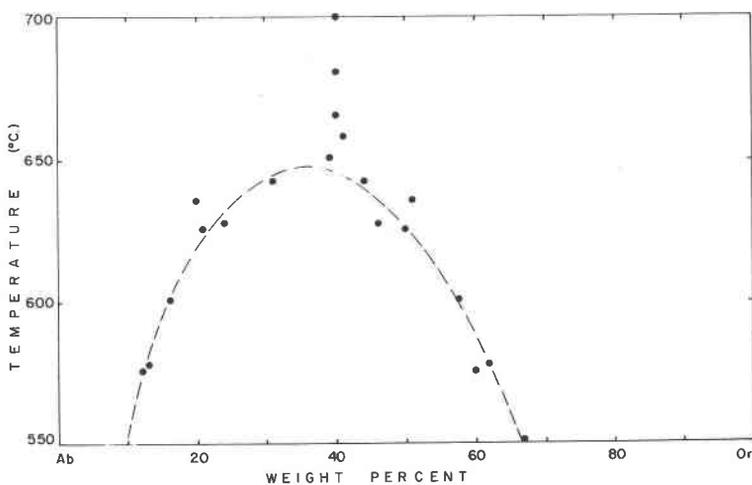


FIG. 4. Alkali feldspar solvus determined on material crystallized from a dehydrated gel of the composition $[Ab_{60}Or_{40}]_{97}[Al_2O_3]_3$ at various temperatures at 2 Kb pressure.

RESULTS

The runs reported on here are all crystallization runs in which gels are crystallized at constant pressure and temperature. Several attempts were made to approach the solvus from two directions, but the unmixing process is so slow that after 30 days equilibrium was not obtained.

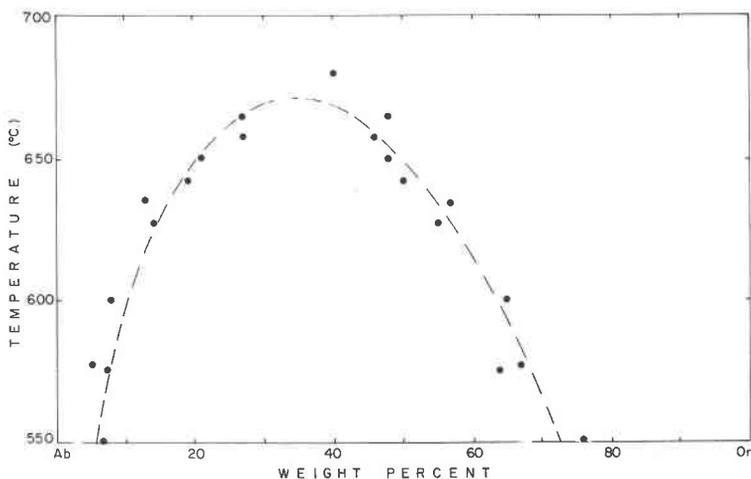


FIG. 5. Alkali feldspar solvus determined on material crystallized from a dehydrated gel of the composition $[Ab_{60}Or_{40}]_{97}[(Na_2O \cdot 2SiO_2)_{60}(K_2O \cdot 2SiO_2)_{40}]_3$ at various temperatures at 2 Kb pressure.

The results of the synthesis experiments are presented in graphic form in Figs. 3, 4, 5 and 6. The data have been compiled in tabular form and are available from either of the authors. In Figs. 3, 4, 5 and 6 best fit curves have been estimated for the position of the solvus, as determined in the synthesis runs. This is meant to indicate the best fit obtained when possible errors in temperature and composition are considered. In all probability the "true" solvus lies somewhat outside the indicated curve for each of the figures, since it would be expected that the synthesized feldspar lies somewhere between the binodal and spinodal.

There is a significant and reproducible difference between the solvus

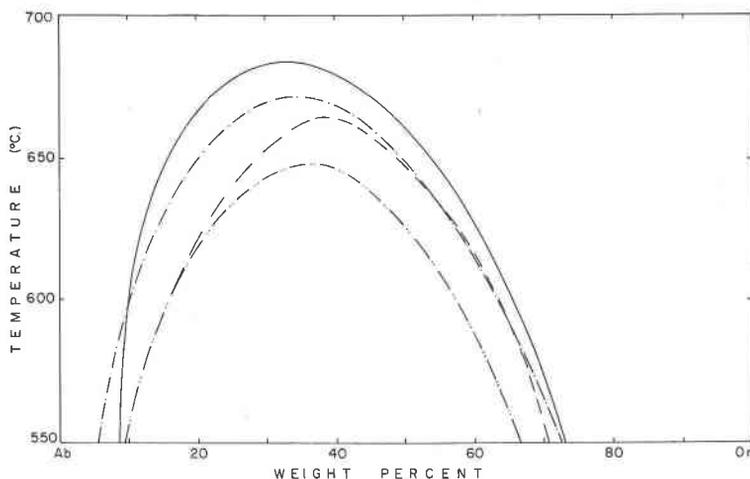


FIG. 6. Composite diagram showing the three solvuses of Figs. 2, 3 and 4 together with the solvus determined by Orville (1963).

determined in this way from gels containing excess alkalis and excess alumina and those on the join. The stoichiometric composition gives a solvus that approaches the solvus determined at 1 kb by Tuttle and Bowen (1950). The solvus determined by crystallization of the gels containing excess alkalis is similar to that determined by Orville (1963) where excess alkali was also present, as NaCl+KCl. The solvus determined in the presence of excess Al_2O_3 is different from either of the other two. These differences may be explained by differences in thermal state of the synthesized alkali feldspars, or by small departures from stoichiometry. Reversal experiments in which the postulated solvus was approached from both lower and higher temperatures might indicate which, if either, of these two cases is more plausible. The results of one such set of experiments are given in Table 3. If equilibrium had been obtained in

all three cases, the end products obtained in all three experiments would be the same. The three cases considered are:

1. direct synthesis from the gel; 2. production of the two coexisting alkali feldspars from an initially homogeneous single phase; and 3. production of the two coexisting alkali feldspars from an initial assemblage in which the Ab rich solid solution contains more Ab than the equilibrium value and the Or rich solid solution contains more Or than the equilibrium value.

The data given in Table 3 indicate that the equilibrium was not obtained in this set of reversal experiments. However, the data do show that, for each of the three bulk compositions considered here, the synthesis points

TABLE 3. REVERSAL EXPERIMENTS AT 2 KB

| | | |
|--|--|-------------------------------------|
| Set 1. Direct Synthesis: 625°, 696 hours | | |
| Composition 1 | (On Ab-Or join) | Or ₂₄ , Or ₅₅ |
| Composition 2 | (with excess Al ₂ O ₃) | Or ₂₄ , Or ₄₆ |
| Composition 4 | (with excess (K,Na) ₂ O · 2SiO ₂) | Or ₁₄ , Or ₅₆ |
| Set 2. Synthesis: 700° C, 240 hours, temperature reduced to 625° C, 624 hours | | |
| | 700° | 625° |
| Composition 1 | Or ₄₂ | Or ₃₀ , Or ₄₈ |
| Composition 2 | Or ₄₀ | Or ₂₇ , Or ₄₂ |
| Composition 4 | Or ₄₂ | Or ₂₁ , Or ₅₉ |
| Set 3. Synthesis: 550° C., 240 hours, temperature increased to 625°, 624 hours | | |
| | 550° | 625° |
| Composition 1 | Or ₁₀ , Or ₇₁ | Or ₁₄ , Or ₅₉ |
| Composition 2 | Or ₁₀ , Or ₆₇ | Or ₁₃ , Or ₅₄ |
| Composition 4 | Or ₇ , Or ₇₆ | Or ₇ , Or ₅₈ |

are intermediate to the reversal points. An unexplained exception is the Or-rich solid solution crystallized in the presence of excess alkali. It is probably more significant that the overall pattern is the same in the reversal experiments as in the direct synthesis. Thus the albite rich solid solutions crystallized in the presence of excess alkali are consistently more Ab rich than those crystallized from either a bulk composition of the Ab-Or join, or crystallized in the presence of excess alumina. Further, the Or rich solid solutions crystallized in the presence of excess alumina are consistently richer in Ab than those crystallized from bulk compositions either on the Ab-Or join, or rich in alkali. Those results do not indicate whether the differences in the solvuses as determined by direct synthesis are a consequence of different thermal states, or of non-stoichiometry in the feldspars. However, the data are not consistent with a postulated role of excess alumina as a "reaction inhibitor." That is, a closer approxima-

tion to equilibrium would be obtained in the presence of excess alkali than from stoichiometric compositions, which in turn would be closer to an equilibrium value than compositions which contain excess alumina.

It was believed analysis of the unit cell dimensions might provide some indication as to whether the differences in the solvuses is due to non-stoichiometry of the feldspars, or difference in thermal state. Figure 7 is

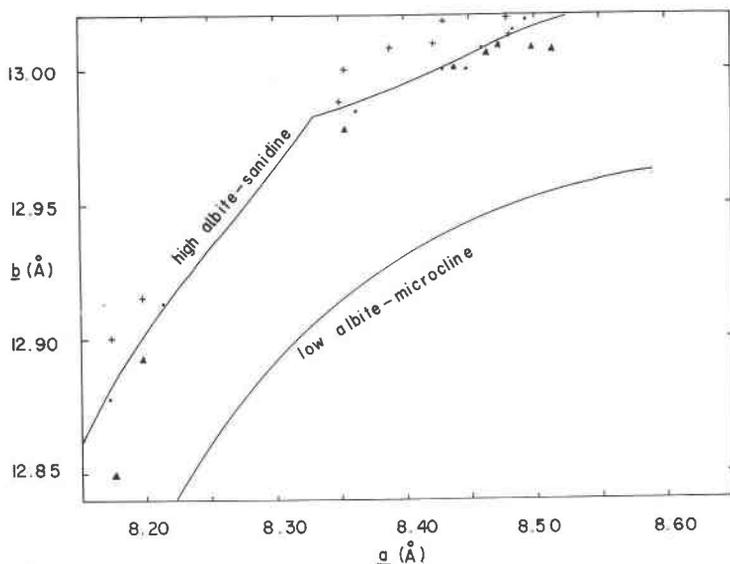


FIG. 7. a and b cell dimensions of alkali feldspars synthesized in this study. The solid line represents the a and b cell dimensions of the sanidine-high albite series as determined by Orville (1966). The dashed line indicates the a and b cell dimensions for a microcline-low albite exchange series, also from Orville (1966). Filled circles indicate cell dimensions of feldspars crystallized from a bulk composition on the Ab-Or join. Plus symbols indicate cell dimensions of feldspars crystallized in the presence of excess Al_2O_3 . Triangles give the cell dimensions of feldspars crystallized in the presence of excess alkali. Standard error of a and b is given in Table 2.

a plot of the a and b cell dimensions obtained from least squares refinement of the x -ray powder diffraction data for feldspars synthesized in connection with this study. Professor P. M. Orville (in press) has kindly provided us with the results of least square analysis of cell dimensions from the sanidine-high albite series, and from the microcline-low albite series (exchanges in alkali halide melts). The curves for the two series are also presented in Fig. 7. It can readily be seen that the data obtained for alkali feldspars crystallized from stoichiometric bulk compositions are entirely consistent with Orville's data for the sanidine-high albite series.

TABLE 4. RESULTS OF EXPERIMENTS IN THE SYSTEM $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$

| Run No. | Composition | Temp. (°C) | Pressure (Kb) | Time (hours) | 2 θ (CuK α) | | Or Content |
|---------|-------------|------------|---------------|--------------|----------------------------|--------|---|
| 1248 | 001 | 550 | 2 | 288 | 21.208 | 21.909 | Or ₁₀ Or ₇₁ |
| 1196 | 001 | 575 | 2 | 240 | 21.255 | 21.870 | Or ₁₄ Or ₆₈ |
| 1339 | 001 | 577 | 2 | 686 | 21.246 | 21.873 | Or ₁₄ Or ₆₇ |
| 1226 | 001 | 600 | 2 | 265 | 21.298 | 21.872 | Or ₁₄ Or ₆₂ |
| 1208 | 001 | 625 | 2 | 288 | 21.298 | 21.836 | Or ₁₈ Or ₆₂ |
| 1333 | 001 | 627 | 2 | 696 | 21.366 | 21.758 | Or ₂₄ Or ₆₈ |
| 1255 | 001 | 635 | 2 | 288 | 21.358 | 21.781 | Or ₂₂ Or ₆₆ |
| 1327 | 001 | 642 | 2 | 624 | 21.446 | 21.756 | Or ₂₄ Or ₄₈ |
| 1191 | 001 | 650 | 2 | 532 | 21.475 | 21.675 | Or ₃₁₋₄ Or _{46 ± 4v poor} |
| 1202 | 001 | 650 | 2 | 265 | 21.480 | 21.707 | Or ₂₈ Or ₄₆ |
| 1316 | 001 | 658 | 2 | 672 | 21.456 | 21.676 | Or ₃₁ Or ₄₇ |
| 1261 | 001 | 665 | 2 | 289 | 21.470 | 21.595 | Or ₂₆ Or ₄₆ |
| 1309 | 001 | 680 | 2 | 672 | 21.528 | | Or ₄₁ |
| 1232 | 001 | 700 | 2 | 240 | 21.515 | | Or ₄₂ |
| 1273 | 001 | 650 | 5 | 216 | 21.313 | 21.855 | Or ₁₆ Or ₆₀ |
| 1279 | 001 | 650 | 10 | 168 | 21.238 | 21.965 | Or ₆ Or ₆₈ |
| 1407 | 007 | 645 | 2 | 288 | 21.856 | | Or ₁₆ |
| 1410 | 010 | 645 | 2 | 288 | 21.972 | | Or ₅ |
| 1249 | 002 | 550 | 2 | 288 | 21.246 | 21.924 | Or ₁₀ Or ₆₇ |
| 1197 | 002 | 575 | 2 | 240 | 21.317 | 21.895 | Or ₁₂ Or ₆₀ |
| 1340 | 002 | 577 | 2 | 686 | 21.294 | 21.884 | Or ₁₃ Or ₆₂ |
| 1227 | 002 | 600 | 2 | 265 | 21.340 | 21.850 | Or ₁₆ Or ₆₈ |
| 1209 | 002 | 625 | 2 | 288 | 21.425 | 21.795 | Or ₂₁ Or ₆₀ |
| 1334 | 002 | 627 | 2 | 696 | 21.448 | 21.756 | Or ₂₄ Or ₄₆ |
| 1256 | 002 | 635 | 2 | 288 | 21.416 | 21.801 | Or ₂₀ Or ₅₁ |
| 1328 | 002 | 642 | 2 | 624 | 21.506 | 21.671 | Or ₃₁ Or ₄₄ |
| 1192 | 002 | 650 | 2 | 532 | 21.561 | | Or ₃₉ |
| 1203 | 002 | 650 | 2 | 265 | 21.560 | | Or ₃₉ |
| 1315 | 002 | 658 | 2 | 672 | 21.526 | | Or ₄₁ |
| 1262 | 002 | 665 | 2 | 289 | 21.545 | | Or ₄₀ |
| 1310 | 002 | 680 | 2 | 672 | 21.541 | | Or ₄₀ |
| 1233 | 002 | 700 | 2 | 240 | 21.549 | | Or ₄₀ |
| 1274 | 002 | 650 | 5 | 216 | 21.372 | 21.875 | Or ₁₄ Or ₆₆ |
| 1280 | 002 | 650 | 10 | 168 | 21.238 | 21.955 | Or ₇ Or ₆₇ |
| 1408 | 008 | 645 | 2 | 288 | 21.902 | | Or ₁₃ |
| 1411 | 011 | 645 | 2 | 288 | 21.933 | | Or ₃ |
| 1251 | 004 | 550 | 2 | 288 | 21.168 | 21.949 | Or ₇ Or ₇₆ |
| 1199 | 004 | 575 | 2 | 240 | 21.270 | 21.947 | Or ₈ Or ₆₄ |
| 1342 | 004 | 577 | 2 | 686 | 21.241 | 21.978 | Or ₆ Or ₆₇ |
| 1229 | 004 | 600 | 2 | 265 | 21.264 | 21.946 | Or ₈ Or ₆₆ |
| 1212 | 004 | 625 | 2 | 288 | 21.395 | 21.825 | Or ₁₉ Or ₅₄ |
| 1336 | 004 | 627 | 2 | 696 | 21.376 | 21.865 | Or ₁₄ Or ₆₆ |
| 1258 | 004 | 635 | 2 | 288 | 21.346 | 21.895 | Or ₁₃ Or ₅₇ |
| 1330 | 004 | 642 | 2 | 624 | 21.428 | 21.816 | Or ₁₉ Or ₅₀ |
| 1205 | 004 | 650 | 2 | 265 | 21.445 | 21.790 | Or ₂₁ Or ₄₈ |
| 1318 | 004 | 658 | 2 | 672 | 21.476 | 21.726 | Or ₂₇ Or ₄₆ |
| 1204 | 004 | 665 | 2 | 289 | 21.445 | 21.725 | Or ₂₇ Or ₄₈ |
| 1312 | 004 | 680 | 2 | 672 | 21.538 | | Or ₄₁ |
| 1235 | 004 | 700 | 2 | 240 | 21.517 | | Or ₄₂ |
| 1276 | 004 | 650 | 5 | 216 | 21.293 | 21.920 | Or ₁₀ Or ₆₂ |
| 1282 | 004 | 650 | 10 | 168 | 21.206 | 21.985 | Or ₄ Or ₇₁ |
| 1409 | 009 | 645 | 2 | 288 | 21.906 | | Or ₁₃ |
| 1412 | 012 | 645 | 2 | 288 | 21.984 | | Or ₄ |

On the other hand, those feldspars crystallized in the presence of excess alkali appear to lie between the curves for the two series. This suggests that those feldspars are of intermediate thermal state. This suggestion is consistent with the nature of the solvus as determined in the presence of excess alkali. Tuttle and Bowen (1958) show that the alkali feldspar solvus for the orthoclase-low albite series falls outside the solvus for the sanidine-high albite series. Consequently it is suggested that the differences in the solvus as determined in the presence of excess alkali and from stoichiometric bulk compositions is a reflection of differences in thermal

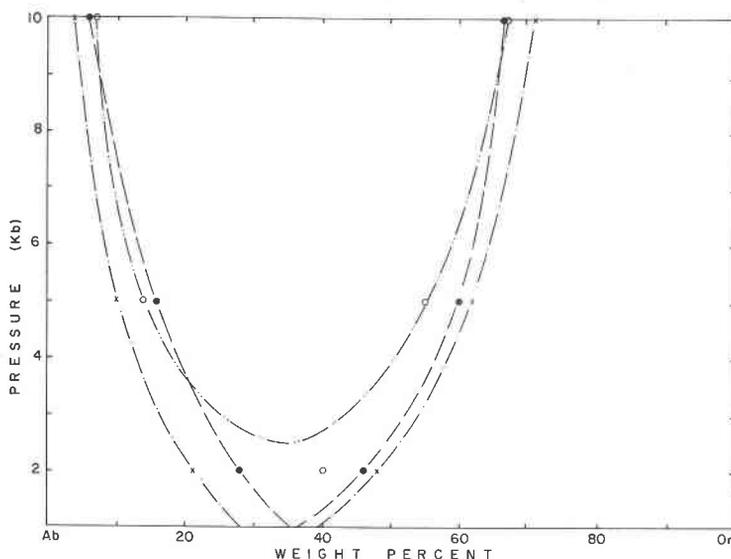


FIG. 8. Alkali feldspar solvuses as a function of pressure at 650° C., for the composition (dashed curve) on the Ab—Or join, in the presence of excess alkali (dash-dot curve), and in the presence of excess Al_2O_3 (dash double dot curve).

state of the alkali feldspars. However, the cell dimension for the alkali feldspars crystallized in the presence of excess alumina fall consistently above the curve for the high albite-sanidine series. That is, they lie beyond the region enclosed by the curves for the high albite-sanidine series, and the microcline exchange series. For a given a cell dimension, the b cell dimension is consistently larger for alkali feldspars crystallized in the presence of excess alumina than would be indicated by the high albite-sanidine series. Although the figure is not included, the unit cell volumes for alkali feldspars crystallized in the presence of excess alumina are consistently larger than would be indicated by the high albite-sanidine series. Consideration of the nature of the solvus, as determined by direct synthesis from gels in the presence of an aqueous vapor phase, and the unit

cell dimensions strongly suggests that alkali feldspars can be synthesized (either stably or metastably) which contain excess alumina over the stoichiometric value. Excess Al in the alkali feldspar structure may be accounted for if an oxonium feldspar ($H_3OAlSi_3O_8$) end member in the crystalline solution series is postulated (as suggested by Professor J. B. Thompson, pers. comm., 1965). Smith and Ribbe (1966, pp. 201, 214) also suggest that the alkali structural site may be partially occupied by $(H_3O)^+$ ions. Since the alkali feldspars crystallized in the presence of excess alumina always show either an alumino-silicate (typically mulite), corundum, or mica present in the products of the run, any solid solution postulated must be less than 3 weight per cent alumina. We would tentatively estimate 1 per cent as the maximum value at this pressure over the temperature range considered.

EFFECT OF PRESSURE ON THE SOLVUS

A number of runs was made to determine the effect of pressure on the solvus. The results are shown as a polybaric, isothermal diagram ($650^\circ C.$) in Fig. 8. It is obvious that there is a drastic pressure effect on all three solvuses.

CONCLUSIONS

These preliminary studies on the alkali feldspar studies in the system $Na_2O-K_2O-Al_2O_3-SiO_2-H_2O$ indicate that the nature of the solvus is influenced by the molar ratio of $Na_2O+K_2O:Al_2O_3$ in the bulk composition from which the feldspar is crystallized. Different solvuses are obtained depending on whether the molar ratio is less than, equal to, or greater than unity. The results of this study are not of sufficient detail to conclude that non-stoichiometry in the alkali feldspars has been demonstrated. However, the nature of the solvuses obtained by direct crystallization, and the analysis of unit cell dimensions, *suggest* that when the alkali:alumina molar ratio is less than unity, excess alumina may enter in crystalline solution in the alkali feldspars. The same lines of evidence *suggest* that when the alkali:alumina molar ratio in the bulk composition is greater than one, alkali feldspars of lower thermal state than the sanidine-high albite series are produced. It is possible that when this molar ratio is greater than one, non-stoichiometric alkali feldspars may be produced; however, the bulk of the evidence seems to point toward a lower thermal state.

ACKNOWLEDGEMENTS

We would like to acknowledge financial support provided by the National Science Foundation. F. M. Gross and R. Z. Small provided very capable assistance in the maintenance of the high pressure facilities.

We would also like to thank Professor P. M. Orville, Yale University, Dr. D. B. Stewart, U.S. Geological Survey, and D. R. Waldbaum, Harvard University, for making available their data on alkali feldspars prior to publication.

REFERENCES

- CHAYES, F. AND E. G. ZIES (1962) *Ann. Rept. Director Geophys. Lab. Carnegie Inst Washington Yearbook* **61**.
- DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1963) *Rock Forming Silicates*, v. 4. John Wiley & Sons, Inc., New York.
- EVANS, H. T., JR., D. E. APPLEMAN AND D. S. HANDWERKER (1963) The least squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing methods (abs.). *Program, Ann. Meet., Am. Cryst. Assoc., March 28, 1963, Cambridge, Mass.*, p. 42-43.
- LUTH, W. C. AND C. O. INGAMELLS (1965) Gel preparation of starting materials for hydrothermal experimentation. *Am. Mineral.*, **50**, 255-258.
- AND O. F. TUTTLE (1964) Externally heated cold-seal pressure vessels for use to 10,000 bars and 750°C. *Am. Mineral.*, **48**, 1401-1403.
- ORVILLE, P. M. (1963) Alkali ion exchange between vapor and feldspar phases. *Am. Jour. Sci.*, **261**, 201-237.
- (1966) Unit-cell parameters of the micro-cline-low albite and the sanidine-high albite solid solution series (in press).
- SECK, H., W. C. LUTH AND O. F. TUTTLE (1966) The system $\text{NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8\text{-H}_2\text{O}$ (in preparation).
- SMITH, J. V. AND P. H. RIBBE (1966) X-ray emission microanalysis of rock-forming minerals III. Alkali feldspars. *Jour. Geol.* **74**, 197-216.
- TUTTLE, O. F. (1949) Two pressure vessels for silicate-water studies. *Geol. Soc. Am. Bull.* **60**, 1727-1729.
- (1952) Optical studies on alkali feldspars. *Am. Jour. Sci., Bowen Vol.*, 553-568.
- AND N. L. BOWEN (1950) High temperature albite and contiguous feldspars. *Jour. Geol.* **58**, 572-583.
- AND N. L. BOWEN (1958) Origin of granite in the light of experimental studies in the system $\text{NaAlSi}_2\text{O}_4\text{-KAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$. *Geol. Soc. Am. Mem.* **74**.

Manuscript received, September 20, 1965; accepted for publication, June 5, 1966.