Ternary feldspars: two-feldspar assemblages at $P(H_2O) = 5\,kbar$

RHIAN H. JONES*

Department of Geology, University of Manchester, Manchester

Abstract

In a study of the liquidus surface in the silica-undersaturated part of the system Q–An–Ne–Ks at $P(H_2O) = 5\,kbar$, several two-feldspar plus liquid assemblages were obtained. The compositions of the feldspars were determined by electron microprobe analysis. The products of short runs (one or two days) consisted of fine intergrowths of two feldspars which may have crystallized during the heating period, or in the early stages of the run. Runs of four days were of sufficient length to coarsen these intergrowths such that individual euhedral crystals could be observed. However, analyses of the feldspar crystals from the longer runs showed a greater amount of ternary solid solution than expected. This may be attributed to the persistence of a small quantity of the second feldspar intergrown in the crystals. The slope of the tie-line joining one of the inferred pairs has been shown to be reproducible for gel and crystalline starting materials, hence the slopes of the tie-lines are believed to represent their equilibrium slopes.

KEYWORDS: feldspars, two-feldspar assemblages, crystallization.

Introduction

THE ternary feldspar system has been the subject of many experimental studies, because of the potential use of naturally occurring two-feldspar assemblages as a geothermometer. The reliability of two-feldspar geothermometers based on experimental phase synthesis data such as those of Seck (1971a, b) (e.g. Ghiorsio, 1984) is dependent on the reliability of the experimental data. Criticism of experimental data is largely concerned with uncertainties as to whether they represent equilibrium assemblages. Johannes (1979) believes that equilibrium could not have been achieved by Seck (1971a, b) using gel starting materials, under the conditions of his experiments. However, although Johannes (1979) claimed that, in his experiments, run times of 20 days were sufficient to reach equilibrium at 650 °C and 1 kbar in the system Or–Ab–An–H_2O, using crystalline starting materials, this claim has been disputed by Brown and Parsons (1981). Thus there is no agreement on accurate phase synthesis data on which a two-feldspar geothermometer may be based.

Most of the experimental data concerning two-feldspar pairs have been obtained using bulk compositions which themselves have ternary feldspar

* Present address: Institute of Meteoritics, Department of Geology, University of New Mexico, Albuquerque, New Mexico 87131, USA.

compositions. In this paper data are reported giving the compositions of two-feldspar pairs which were obtained in a study of liquidus phase relationships in the silica-undersaturated part of the system Q–An–Ne–Ks (Jones, 1986). Assemblages containing two feldspars plus a liquid resulted when the liquid lay on the two-feldspar liquidus surface in this quaternary system. Although the bulk compositions and the liquids coexisting with the feldspar pairs were all silica-undersaturated with respect to the ternary feldspar plane, this should not affect either the compositions of equilibrium feldspar pairs, or the limits of ternary solid solution, which are fixed for a given pressure and temperature, provided the feldspars are stoichiometric. Feldspar crystals were large enough to be analysed using an electron microprobe, allowing inferences concerning the crystallization behaviour of the two feldspars to be made.

Experimental techniques

All runs were carried out in an internally heated pressure vessel, at a pressure of water of 5 kbar ± 0.2 kbar. Pressure was measured with a manganin cell, and temperature with two Pt/Pt 13% Rh thermocouples situated at either end of the sample holder. Charges were sealed in platinum capsules, with sufficient deionized water added so that the system was water-saturated ($>12\,wt.\%\,H_2O$).

Gels were used as starting materials in most of the experiments. A separate gel was made up for each starting composition in weight percent proportions, according to the method described by Hamilton and Henderson (1968). Crystalline material of composition A5 which was used in a comparative run was prepared by heating the gel at 600 °C and at $P(H_2O) = 1$ kbar for 24 hrs in a cold seal pressure vessel. Glass starting materials were prepared by melting the gels above their liquidus temperatures at $P(H_2O) = 5$ kbar for at least 24 hrs. The compositions of the starting materials, given in terms of the quaternary system Q–An–Ne–Ks, are given in Table 1.

Table 1: Bulk compositions of gel starting materials (wt%).

Bulk composition	Q	An	Ne	Ks
A3	31.5	10.0	27.0	31.5
A4	31.5	10.0	18.0	40.5
A5	31.5	10.0	9.0	49.5
C4	22.5	10.0	22.5	45.0
C5	22.5	10.0	13.5	54.0

Run products were examined optically, and analysed by electron diffraction, using Cu-$K\alpha$ radiation. Electron microprobe analysis was performed on a Cameca Camebax microprobe, at an accelerating voltage of 15 kV, and using an energy-dispersive spectrometer with Link Systems computational instrumentation. Back-scattered electron imaging was used to locate the electron beam on individual crystals and on the glass.

TEM of feldspar intergrowths. Ion-thinned samples of the feldspar intergrowths were studied in a JEOL 2000 FX analytical transmission electron microscope operating at 200 kV. X-ray mapping of crystals of feldspar was carried out in the TEM using a Tracor Northern TN 5500 energy dispersive X-ray analysis system. X-ray images of feldspar were acquired for Ca-$K\alpha$ and K-$K\alpha$ radiation using a Tracor Northern image analysis program. Under digital beam control, X-rays were collected for 1.0 second on each pixel of a 64 pixel grid in scanning mode using an electron beam diameter of ~20 Å. This combination was found to produce reasonable X-ray intensities in the image with sufficiently high spatial resolution to resolve relatively fine-scale intergrowth features between 0.5 and 1 μm in size. Despite the extended periods of time required for the image acquisition (1 hour in this case) long term sample

drift was not found to be a problem. A scanning electron image of the region of interest was collected simultaneously with the X-ray images. Due to the relatively low X-ray intensities produced by the thin samples the images were processed in order to enhance the contrast. A simple smoothing of the digitized image was found to produce a marked improvement in contrast and enabled features to be easily resolved.

Results

Effect of increasing run time. Two-feldspar plus liquid assemblages were obtained from several bulk compositions, over a range of temperatures, and in runs of one to four days' duration. Fig. 1 shows the X-ray diffraction patterns obtained from charges of bulk compositions A4, after a one-day run at 725 °C, and a four-day run at 730 °C (Fig. 1a); and A5, after runs of one day at 810 °C, two days at 780 °C and four days at 770 °C (Fig. 1b).

The two XRD patterns for bulk compositions A4 (Fig. 1a) are broadly similar. These two charges (run at similar temperatures) appear to be comparable, suggesting that the difference in run times has little effect on the run product.

For bulk composition A5 (Fig. 1b) the XRD patterns show variation with both temperature and time. After one day at 810 °C and after four days at 770 °C, both plagioclase and alkali feldspar are present, but after two days at 780 °C no peaks are visible. This variation can be explained as follows. From reversal runs carried out in the liquidus study in the quaternary system Q–An–Ne–Ks, it was determined that runs of four days' duration were necessary to attain equilibrium run products (Jones and MacKenzie, in press), and that the liquidus temperature of bulk composition A5 was 795 °C. (The liquidus temperature of bulk composition A4 was above 770 °C.) The one-day run at 810 °C for this composition which yielded two feldspar phases was therefore above the liquidus temperature, and these phases were not stable under the conditions of the run. The XRD pattern of the two-day run, at 780 °C and thus below the liquidus, shows no discernible peaks, whereas in fact the run product did contain optically visible feldspar crystals. This observation illustrates the insensitivity of XRD to the presence of a low percentage of a crystal phase in a charge consisting mainly of glass. For the four-day run at 770 °C, bulk composition A5 shows clear peaks for both plagioclase and alkali feldspar: these phases are believed to represent the equilibrium assemblage at this temperature.

Electron microprobe analyses of the feldspar
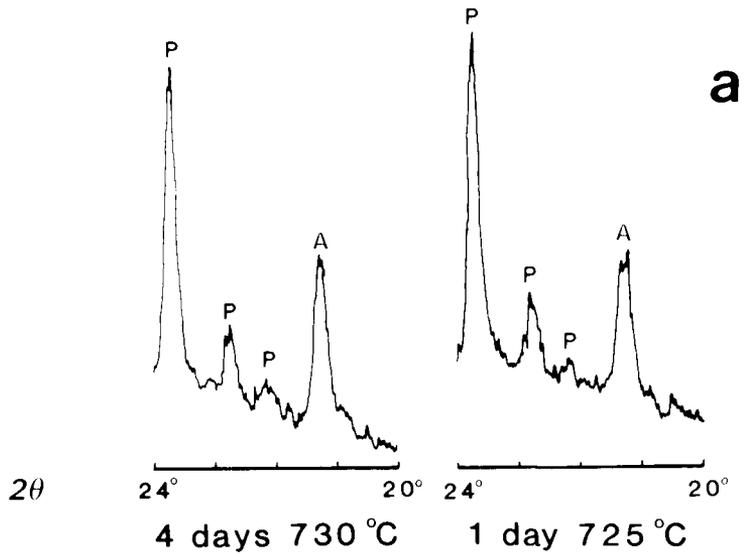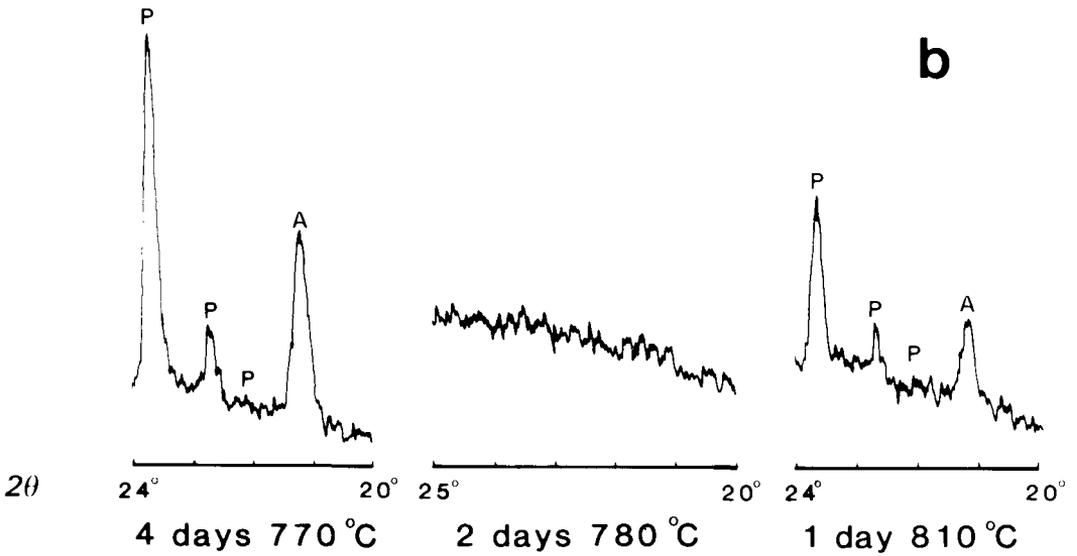
FIG. 1. Effect of run time on X-ray diffraction patterns of two-feldspar pairs. A = alkali feldspar; P = plagioclase.
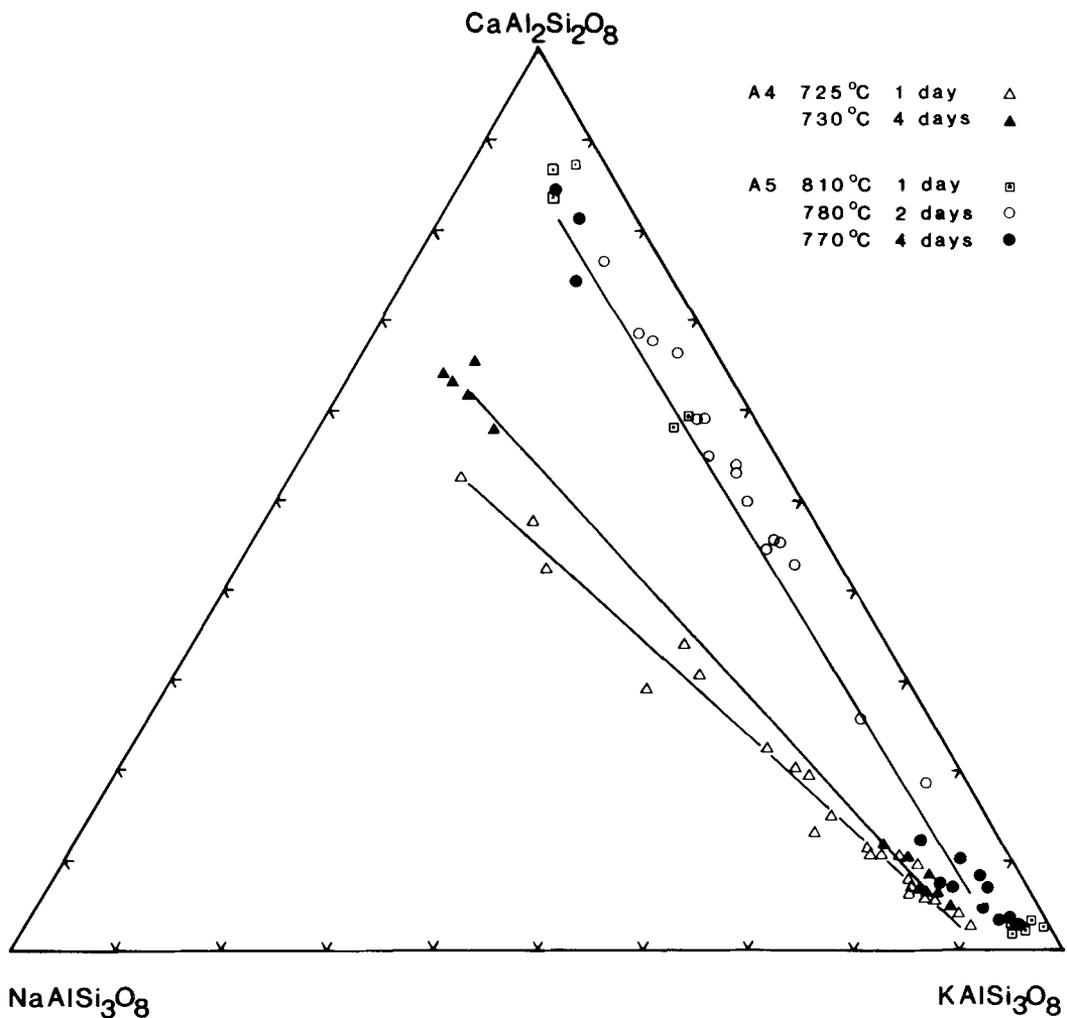
FIG. 2. Effect of run time on feldspar compositions determined by microprobe analysis. Each data point represents a feldspar analysis showing good stoichiometry and a good analysis total. $P(H_2O) = 5$ kbar.

run products showed an effect which was undetectable from XRD analysis alone. This is illustrated in Fig. 2 for the charges whose XRD patterns are shown in Fig. 1. Analyses of the feldspar grains obtained in one and two-day runs gave a large range of compositions. This range could be observed within individual feldspar grains, from points as close together as 3 μm. These grains showed irregular morphologies, and sometimes a patchy appearance in the back-scattered electron image. The scatter of compositions obtained for each charge lies approximately along the length of a mixing line joining a plagioclase to

an alkali feldspar composition, as indicated for bulk composition A4.

The morphologies of the mixed feldspar regions in bulk composition C5 (685 °C, 1 day) were studied by analytical electron microscopy. It was found that the mixed regions of feldspar show no difference in diffraction contrast from homogeneous feldspar, so that such regions could not be identified by conventional imaging techniques alone. Areas of feldspar with intermediate compositions were therefore initially identified using X-ray microanalysis and were subsequently studied in more detail by X-ray mapping of individual
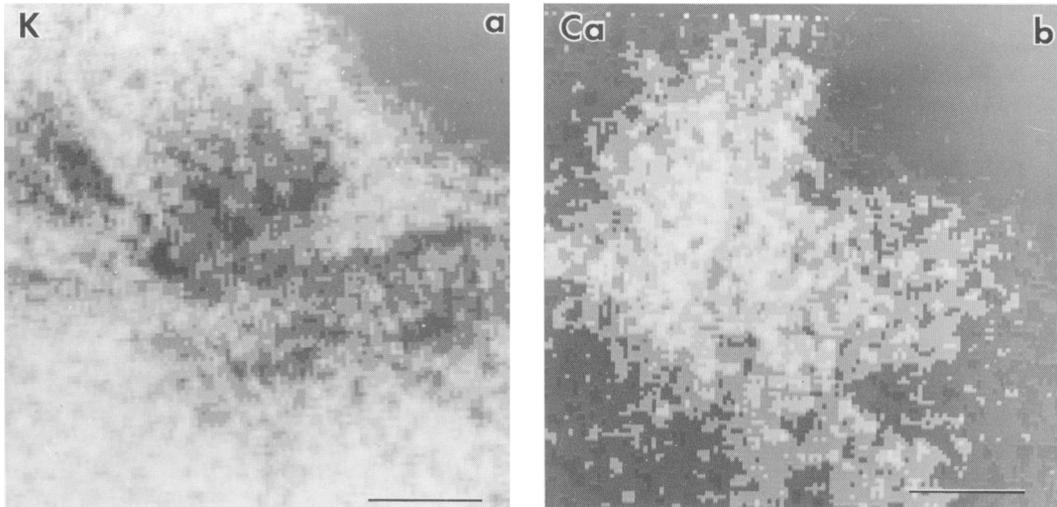
FIG. 3. K-$K\alpha$ (*a*) and Ca-$K\alpha$ (*b*) X-ray radiation maps showing the morphology of the feldspar intergrowths in C5 (685 °C, one day). Lighter shades correspond to higher concentrations for both elements. Irregular regions with enhanced Ca concentrations are included within a K-feldspar host. The images were obtained using a digital beam control on a scanning transmission electron microscope and have been smoothed using an image analysis program to enhance the contrast. Scale bars, 5 μm.

crystals as outlined earlier. Fig. 3 shows smoothed X-ray images of a typical feldspar intergrowth showing the distribution of K and Ca within the feldspar. The intergrowths are observed to be regions with highly irregular morphology, including reentrant features which are typically up to 25 μm across. Fig. 3 illustrates an example of areas showing significant enhancements in Ca concentrations included within a K-rich host.

The effect of increasing the run time to four days was to resolve this spread of analyses into two relatively distinct feldspar compositions (Fig. 2). Individual feldspar grains were euhedral and consistently gave either plagioclase or alkali feldspar compositions. Mixing lines are drawn to join the average compositions of plagioclase and alkali feldspars of the four-day runs. For bulk composition A4 this line is clearly not identical to that drawn for the one-day run. Feldspar compositions from four-day runs display a tendency to extend along the mixing line in the direction of the other feldspar composition.

Compositions of distinct feldspar pairs. In Fig. 4 eight two-feldspar pairs which were obtained in four-day runs, at temperatures of 730–785 °C, are plotted in the system An–Ab–Or. The average compositions of these feldspars are given in Table 2, with the standard deviations for each of the feldspar components, and the liquid composition in the system Q–An–Ne–Ks which coexisted with

each pair. The higher standard deviations for the An and Or components than for the Ab component reflect a small spread about the average composition along the mixing line joining the two feldspars, whilst analyses are well defined in their Ab/An and Ab/Or ratios.

The data in Table 2 are given in both weight percent and mole percent proportions, although for Ab-poor compositions in the ternary feldspar system these values are very similar. Fig. 4 is plotted in mole percent, in order that a direct comparison with previously published data may be made.

Data from two comparative runs, for bulk composition A5 at 685 °C, are included in Table 2. The compositions of the two-feldspar pairs and liquid phases are those obtained either from gel or from crystalline starting materials; the latter was prepared from the gel as described above (Experimental techniques) and consisted of plagioclase, alkali feldspar, nepheline and leucite. These comparative data are plotted in Fig. 5. There is close agreement between the feldspar compositions obtained from the two types of starting material, which illustrates reversibility of the results, hence that the data are those of feldspar pairs close to exchange equilibrium.

Discussion

Feldspar intergrowths. The presence of two identifiable feldspars in the XRD patterns of the

Table 2: Two-feldspar pairs.

Bulk comp.	Temp. (°C)	No. of analyses	An	1σ	Ab	1σ wt%	Or	1σ	An	Ab mole%	Or	Q[1]	An	Ne	Ks wt%
A3	735	7	49.6	3.9	39.7	2.2	10.7	2.6	48.5	41.1	10.4	33.2	7.6	27.8	31.4
		3	2.3	0.8	11.7	1.4	86.0	1.6	2.3	12.3	85.4				
A3	770	5	49.0	2.5	37.8	2.2	13.2	3.8	47.9	39.2	12.9	32.9	7.8	27.8	31.5
		3	6.2	3.5	13.9	2.2	79.9	5.8	6.1	14.6	79.3				
A4	730	5	62.4	2.7	25.8	1.3	11.8	2.8	61.5	26.9	11.6	27.4	8.2	27.8	36.6
		8	7.6	2.3	10.2	1.2	82.2	2.8	7.6	10.8	81.6				
A4	770	5	68.5	4.3	18.5	0.8	13.0	4.6	67.7	19.4	12.9	28.8	8.8	24.2	38.2
		6	5.5	2.6	10.8	2.6	83.7	4.6	5.5	11.4	83.1				
A5	735	1	82.1		9.5		8.4		81.6	10.0	8.4	27.3	7.9	15.7	49.1
		4	6.0	2.2	5.9	1.5	88.1	1.3	6.0	6.2	87.8				
A5	770	3	80.4	4.7	7.4	1.8	12.2	3.3	80.1	7.8	12.1	25.8	8.9	16.1	49.2
		10	6.7	3.1	5.4	1.7	87.9	4.3	6.7	5.7	87.6				
A5	785	4	79.9	3.9	8.1	0.8	12.0	4.1	79.5	8.6	11.9	27.1	9.4	14.3	49.2
		8	4.7	2.7	3.1	2.4	92.2	4.0	4.7	3.3	92.0				
A5[2]	785	4	80.8	4.5	9.5	2.8	9.7	2.7	80.4	10.0	9.6	28.3	6.9	16.7	48.1
		8	3.1	1.0	4.9	0.8	92.0	1.4	3.1	5.2	91.7				
C4	730	3	79.5	2.1	13.5	0.9	7.0	2.2	78.9	14.2	6.9	23.6	5.5	24.1	46.8
		4	2.7	0.6	5.1	1.5	92.2	1.7	2.7	5.4	91.9				

[1] composition of coexisting liquid (Q-An-Ne-Ks)
[2] crystalline starting material.
P(H$_2$O) = 5kb.

one-day runs (Fig. 1), the scatter of feldspar compositions from charges of one and two-day runs along a specific mixing line in the ternary feldspar system (Fig. 2) and the TEM results (Fig. 3) show that the feldspar grains observed in the shorter runs consist of a fine intergrowth of two stoichiometric feldspar compositions. Increasing the run time to four days largely resolves the two feldspar components, although the range of feldspar compositions which extends in the direction of the two-feldspar mixing line shows that a small amount of the second feldspar phase probably remains intergrown with each of the feldspar phases after this time.

Similar results were obtained from glass as well as gel starting materials in short runs. The feldspar run products from the crystalline starting material of bulk composition A5, run at 785 °C (Fig. 5), also showed compositional limits which suggest that small quantities of intergrown phases are still present in each feldspar after a four-day run (see below). Intergrowth textures might therefore also be expected to be present in shorter runs using crystalline starting materials.

Similar intergrowth textures and microprobe results were described by Lofgren and Gooley (1977) for feldspars grown from ternary feldspar bulk compositions in dynamic crystallization experiments, in which the intergrowths grew from a melt phase. It is possible that the intergrown

phases obtained in the study reported in this paper also grew from a melt phase, although in the case of gel starting materials they may also have crystallized during the heating period of the runs. Petersen and Lofgren (1986) also noted a significant coarsening of patchy intergrowths during similar dynamic crystallization experiments as crystallization proceeds. Morse and Lofgren (1978) discussed the arguments for the formation of intergrowths by simultaneous crystallization versus exsolution for the results reported by Lofgren and Gooley (1977). The presence of the intergrowths described in this paper in shorter runs only, and the coarsening observed with time, supports the conclusion of Morse and Lofgren (1978) that simultaneous crystallization of two feldspars in a fine intergrowth texture may take place.

Distinct two-feldspar pairs. The two-feldspar assemblages obtained in four-day runs may be compared with previously published data in two respects: the limits of ternary solid solution (i.e. of An in alkali feldspar, and Or in plagioclase), and the orientation of the tie-lines joining the two-feldspar pairs.

Fig. 4. shows the limits of ternary solid solution at 750 °C, 1 kbar, and 650 °C, 5 kbar, defined by Seck (1971a, b respectively) and selected two-feldspar tie-lines determined by Seck (1971b) at 650 °C, 5 kbar. The average feldspar compo-
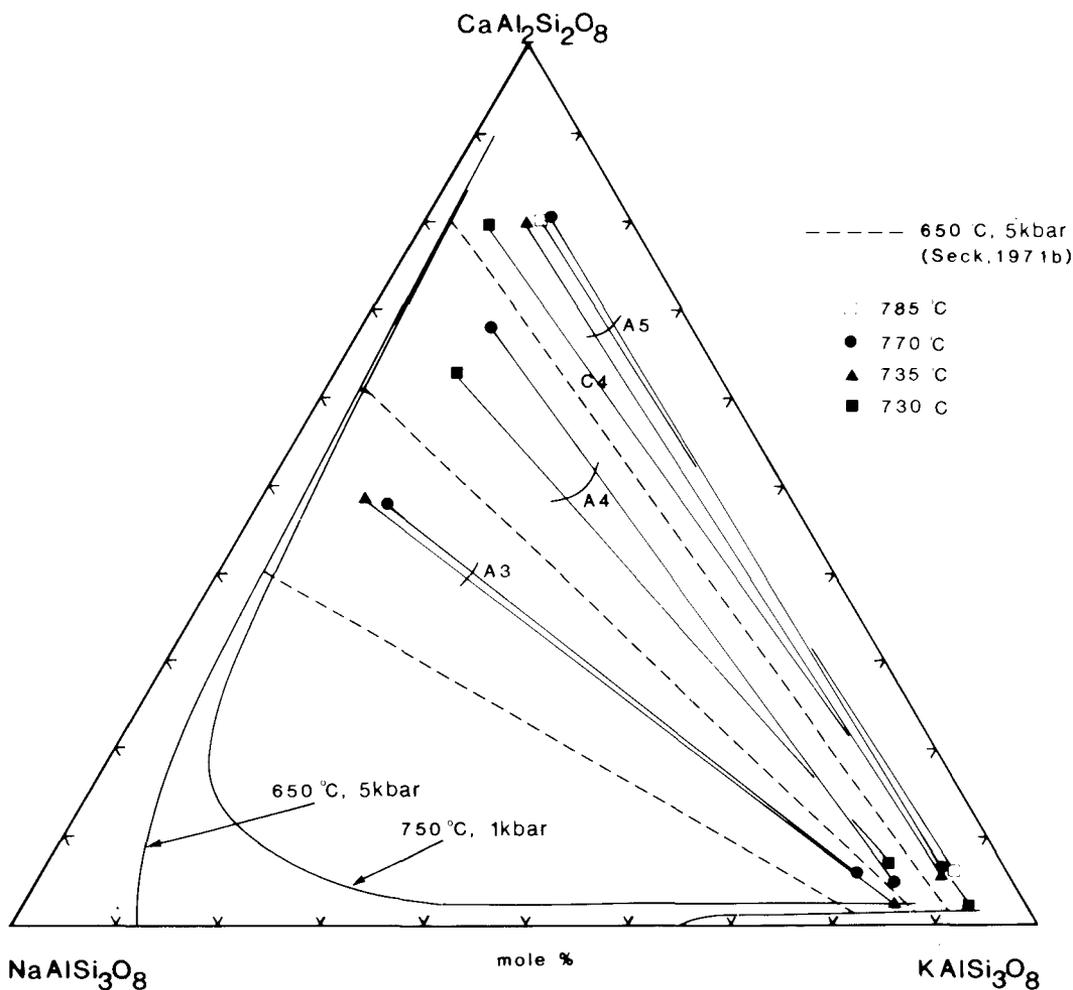
FIG. 4. Two-feldspar assemblages obtained from four-day runs, $P(H_2O) = 5$ kbar. See also Table 2. Included for comparison are the limits of solid solution of ternary feldspars at 750 °C, 1 kbar and 650 °C, 5 kbar (Seck, 1971a, b) and selected two-feldspar tie-lines determined by Seck (1971b) at 650 °C, 5 kbar.

sitions found in this study, of up to 13 wt.% Or in plagioclase and up to 8 wt.% An in alkali feldspar (Table 2), are considerably higher than the limits of solid solution given by Seck, of approximately 4 and 2 wt.% respectively. It is suggested that the data reported here still contain a small quantity of the second feldspar in an intergrowth texture after a four-day run. However, as the compositions of both feldspars of each pair are well defined in the albite component (Table 2) and show reversibility, demonstrating that they are exchange equilibrium compositions (Fig. 5), it is proposed that the slope of the tie-line for each pair is its equilibrium slope. The true equilibrium

compositions of the phases would be defined if the tie-line for each pair were extended to intersect the curve describing the limit of solid solution at the relevant temperature and pressure. The position of this curve is not known accurately for the conditions at which these two-feldspar data were obtained.

From Fig. 4 it can be seen that the orientations of the tie-lines obtained in this study correlate well with the 650 °C, 5 kbar, tie-lines defined by Seck (1971b), in that none of the tie-lines intersect. The effects of increases in pressure and temperature on the slopes of the tie-lines are to decrease and increase the slopes relative to the
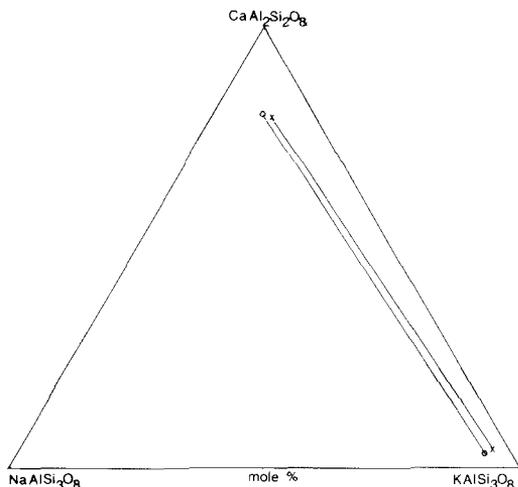
FIG. 5. Comparison of feldspar compositions obtained from gel (x) and crystalline (o) starting materials; bulk composition A5, 785 °C, $P(H_2O) = 5$ kbar, four-day runs.

Ab–Or join respectively, as illustrated in Fig. 6. For a pressure increase of 4 kbar (at 650 °C) this effect is less pronounced than for the temperature increase of 100 °C (at 1 kbar). It would therefore be expected that the tie-lines of this study would correlate better with the set at 750 °C, 1 kbar, than that at 650 °C, 5 kbar. This is not the case, although an increase in pressure on the 750 °C, 1 kbar, set of lines would bring about the appropriate decrease in slope.

Essentially, the tie-lines obtained in this study show an increase in the albite component of plagioclase, and an increase in the orthoclase component of the alkali feldspar, compared with the tie-lines determined by Seck (1971a, b). A similar rotation in comparison with Seck's data was observed by Johannes (1979) for his mix II feldspars, at 650 °C and 800 °C and at 1 kbar.

It is contended that the orientations of the two-feldspar tie-lines reported in this paper, which were obtained from gel starting materials in four-day runs, represent their equilibrium orientation. Johannes (1979) objected to the use of gels as the starting materials in Seck's experiments on the grounds that he believed that metastable feldspar phases crystallized from a gel during the heating period of the run, which are not easily equilibrated in the subsequent run, particularly in the case of anorthite-rich plagioclase. However, the microprobe data reported in this paper suggest that, in the presence of liquid and vapour, any metastable crystals growing in this manner do not persist after a period of around four days.

The metastable (or possibly stable) phases observed after short runs are present as small grains, intergrown on a fine scale, which coarsen within a few days to develop as euhedral, largely homogeneous, equilibrium feldspar crystals.

Conclusions

The spread of feldspar compositions observed in runs of one and two days' duration in the experiments conducted in this study represent a mixture of two individual feldspar phases which are intergrown on a scale too fine to be resolved by microprobe analysis. Coarsening of these intergrowths, resulting in more distinct compositions and euhedral crystals, takes place over a time interval of about four days, at 5 kbar and 700–800 °C. The compositions of the feldspars reported after four-day runs do not give an accurate determination of the limits of ternary solid solution in the feldspar system, but represent the exchange equilibrium orientations of the tie-lines between coexisting feldspar pairs. The slopes of these tie-lines are apparently not as steep as the slopes which would be predicted at 5 kbar and around 750 °C from the data of Seck (1971a, b), although it is not possible to make a direct comparison between the two sets of data. This conclusion is consistent with the results obtained by Johannes (1979) at 650 °C and 800 °C, and 1 kbar.

Acknowledgements

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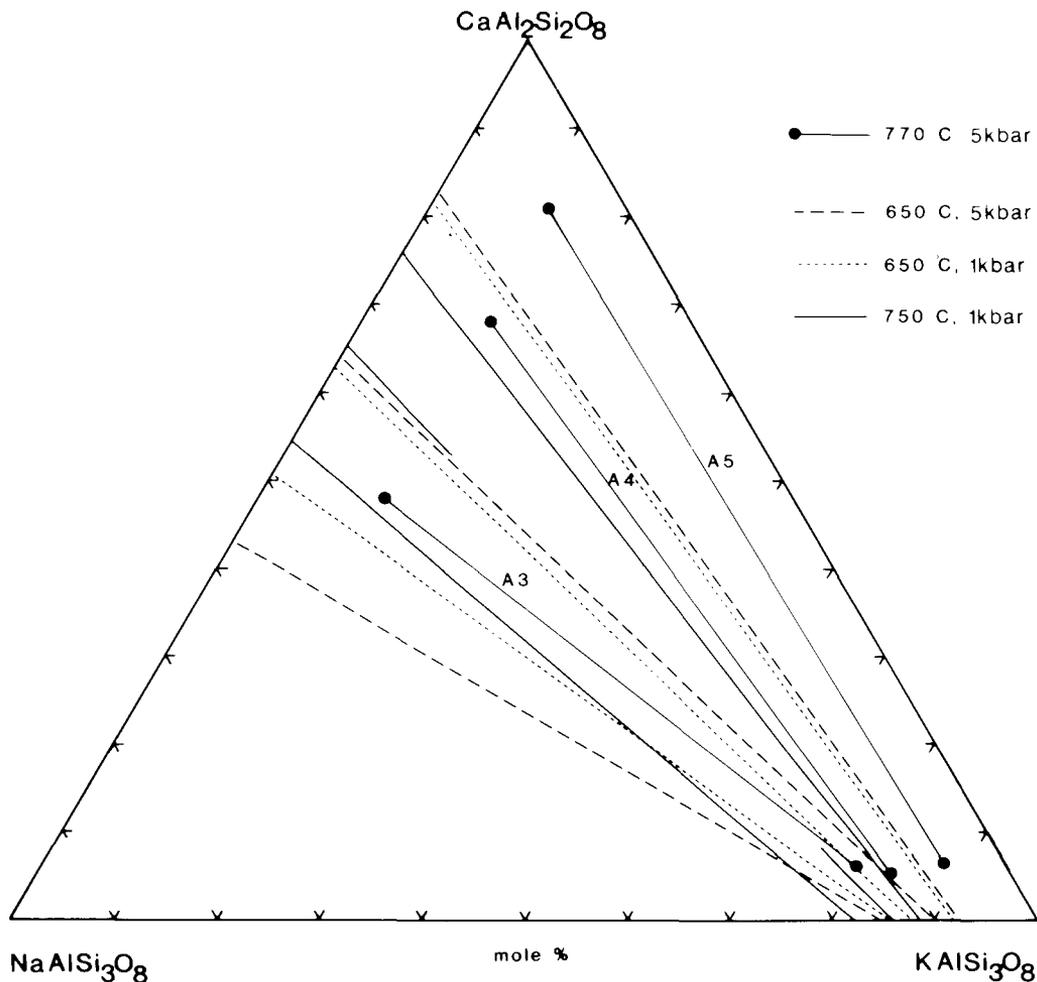
——and MacKenzie, W. S. Liquidus phase relation-

FIG. 6. Comparison of slopes of two-feldspar tie-lines for varying *P–T* conditions. Tie-lines obtained at 770 °C, 5 kbar, from this study are compared with those at 650 °C, 1 and 5 kbar, and 750 °C, 1 kbar, taken from Seck (1971*a*, *b*). Limits of solid solution are ignored.

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