

PHASE EQUILIBRIUM INVESTIGATIONS OF TERNARY FELDSPARS

by

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Linda Tarbox Elkins

Submitted to the Department of Earth, Atmospheric and Planetary Sciences
on June 1, 1987 in partial fulfillment of the requirements for the degree of
Master of Science.

Abstract

Natural feldspars are used as starting materials for ternary feldspar equilibration experiments. The feldspars are run in water at 700 and 800° C and 2 and 3 kbars for times varying from 14 days to 119 days (17 weeks). Nine experiments were successfully completed: three at 800° C and 2 kbars, four at 700° C and 2 kbars and two at 700° C and 3 kbars. The runs are analyzed on an electron microprobe to facilitate close examination of the phase relations and controlled analysis of only the rims of the crystals. Microprobe rim analyses from each experiment cluster at one alkali feldspar and one plagioclase composition. The compositional analyses in these clusters are averaged to obtain an alkali feldspar and a plagioclase pair for each experiment. Evidence is presented for the pairs being at equilibrium. Margules parameters for the anorthite-orthoclase binary are solved for using the ternary data from this study and published Margules parameters for the orthoclase-albite and the albite-anorthite binaries.

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Chapter 1

INTRODUCTION

Feldspars are a common mineral of crustal igneous rocks and many igneous and metamorphic rocks contain two feldspars: a plagioclase feldspar which consists primarily of the components $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite) and $\text{NaAlSi}_3\text{O}_8$ (albite), and an alkali feldspar which consists primarily of KAlSi_3O_8 (orthoclase). A ternary miscibility gap is present in the feldspar system and coexisting alkali and plagioclase feldspars from different geologic settings contain differing amounts of orthoclase, albite and anorthite in solid solution. The calibration of the change in the limits of this solvus with temperature can provide a two-feldspar thermometer which could be applied to a wide variety of rocks.

This two feldspar thermometer was first proposed and empirically calibrated by Barth (1951). Barth (1951) used measurements of the distribution of albite between plagioclase and alkali feldspar in natural rocks to calibrate the two feldspar thermometer. By estimating the temperature of crystallization of these rocks from other geologic indicators he was able to calibrate temperature.

Succeeding thermodynamic models for coexisting feldspars have become more sophisticated and have been based on the experimental determination of the ternary solvus.

Previously, only Seck (1971a, 1971b) and Johannes (1979) have conducted experiments in the ternary system. They both used synthetic feldspars crystallized from gels as starting materials and analyzed their run products using x-ray techniques. Many ternary feldspar thermometers have been calibrated from Seck's data (Stormer, 1975; Powell and Powell, 1977; Whitney and Stormer, 1977; Brown and Parsons, 1981; Price, 1985; Green and Udansky, 1986a).

This study was undertaken to provide more accurate information on the position of

the ternary solvus at 700 and 800° C and 2 and 3 kbars. An electron microprobe with scanning electron microscope for compositional analysis has been used to examine the reaction textures in the run products. Recrystallization and diffusion in the feldspar system is extremely slow. Even when a partial melt is formed to speed diffusion there is little hope of generating homogeneous run products during acceptable run times. Because of this sluggishness of reaction only the outermost rims of the run products have undergone reaction and reequilibration and can be considered candidates for the equilibrium assemblage. Johannes (1979) suggested this reaction mechanism based on x-ray diffraction analysis of run products. The electron microprobe has made it possible to characterize these overgrowth rims, a necessity for an accurate assessment of equilibrium compositions. Experiments must be run for time periods which provide sufficient reaction. In this study the longest possible run times were used for the 700° C experiments. The 800° C experiments did not require such long run times. Further, natural feldspar starting materials were used. These provide results which should be more directly applicable to the interpretation of natural assemblages.

The existing published thermochemical data for the albite-orthoclase and albite-anorthite binaries are combined with the experimental data from this study and used to refine a solution model for the ternary system. The approach follows the method developed by Ghiorso (1984).

Chapter 2

STARTING MATERIALS

Five natural feldspars were used as starting materials. Their compositions are listed in table 2-I and shown in figure 2-1. The crystals used were all large and clean. The feldspars are as follows:

(1) Albite from Amelia Courthouse, Virginia. The Amelia albite is low albite, triclinic $C\bar{1}$, with Al and Si completely ordered. See Thompson et al (1973).

(2) Microcline from the Hugo pegmatite, South Dakota. The Hugo is maximum microcline, triclinic $C\bar{1}$, with Al and Si completely ordered. See Orville (1967). The sample used contains coarse exsolution lamellae of albite. Table 2-I gives the electron microprobe compositions for both phases as well as an bulk estimate based on the approximate ratio of the two phases.

(3) Bytownite from Crystal Bay, Minnesota. The Crystal Bay is an intermediate plagioclase, triclinic $I\bar{1}$. It contains submicroscopic intergrowths of bytownite and labradorite. See Wainwright (1969) and McConnell (1974).

(4) Anorthoclase from Kilbourne Hole New Mexico. The Kilbourne Hole is high temperature feldspar with almost total Al-Si disorder, rapidly cooled during eruption. See Carter (1970).

(5) Oligoclase from Lake Harbour, Baffin Island. The Lake Harbour is found in siliceous pods in marble. Slow cooling has probably made it well ordered with respect to Si and Al. See Grice and Gault (1983). This oligoclase was a gift of the Harvard Mineralogical Museum, catalogue number 119756B.

**Table 2-I: Compositions of Starting Materials
from Averaged Electron Microprobe Analyses**

Feldspar	CaO	Na ₂ O	K ₂ O	Al ₂ O ₃	SiO ₂	An	Ab	Or
Kilbourne Hole Anorthoclase	1.785	8.400	3.273	21.022	65.423	.085	.728	.187
Crystal Bay Bytownite	15.635	2.612	0.091	31.915	49.345	.764	.231	.005
Lake Harbour Oligoclase [†]	2.607	10.172	0.308	21.590	65.130	.122	.861	.017
Hugo Microcline								
----- Albite component	0.000	11.910	0.040	19.500	69.500	.000	.998	.002
Microcline component	0.000	0.510	14.700	18.930	65.180	.000	.050	.950
Bulk estimate						.005	.255	.740

[†]Gift of the Harvard Mineralogical Museum, cat. #119756B,
courtesy of Carl Francis

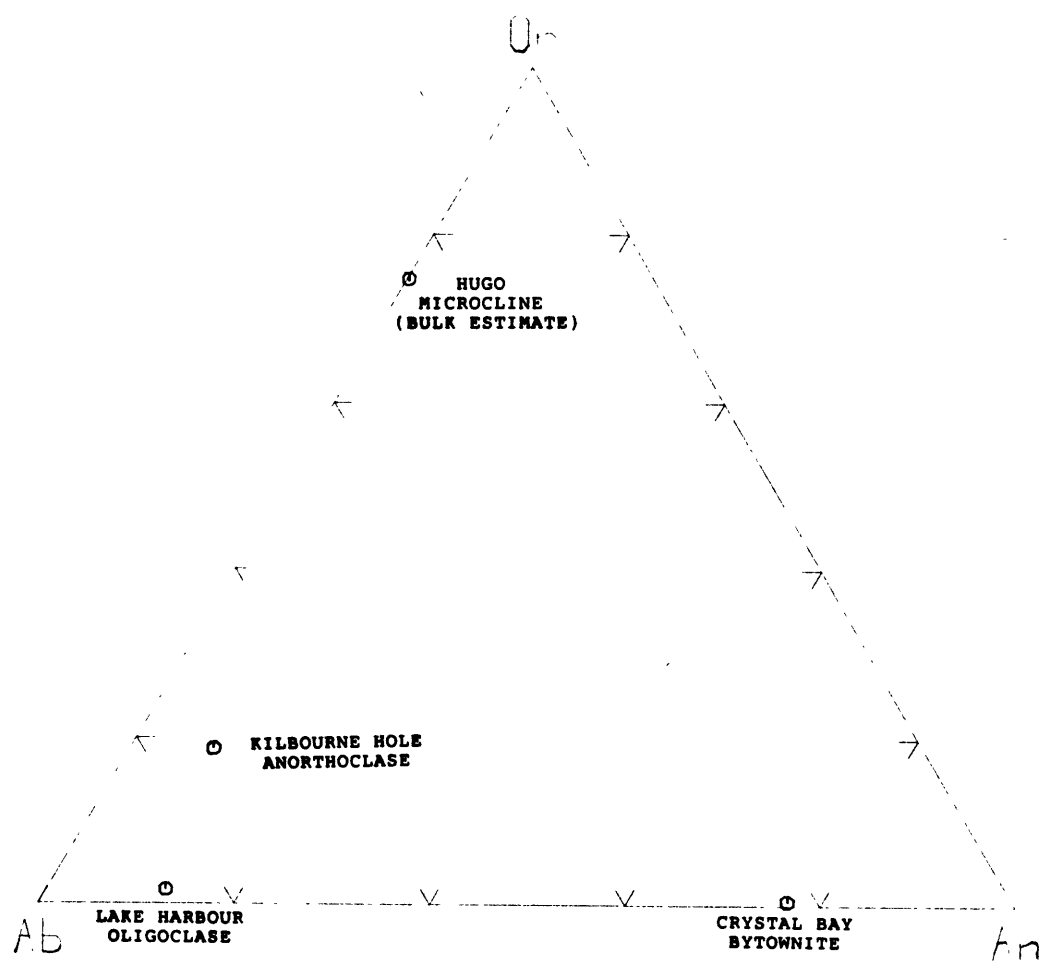


Figure 2-1: Ternary Diagram showing Starting Material Compositions from Averaged Electron Microprobe Analyses

Chapter 3

EXPERIMENTAL TECHNIQUE

Natural feldspar starting materials were ground in an agate mortar to a maximum grain size of 50 μ . The ground feldspars were then weighed and mixed to make the experimental bulk compositions.

Approximately 0.1g of the ground mixed feldspar was used for each charge. Charges were sealed in 3/4" long gold capsules with 15 μ l. of distilled water. The capsules were placed in 12" long cold seal bombs machined from Stellite (Haynes alloy #25) or Rene #6717 steel. The bombs were located in the hot spots of the furnaces such that the temperature gradient over the charge was less than $\pm 2^\circ$ C. Temperatures were measured with chromel-alumel thermocouples calibrated with a thermocouple standardized against the melting point of NaCl. Temperatures were maintained within $\pm 10^\circ$ C of the stated value. Pressures were maintained inside the bombs with an oil and water mixture. Pressures were measured with a 16" factory calibrated Heise gauge and are probably accurate to within $\pm 2\%$ of the stated value.

Runs were terminated by quenching the pressure vessel in a pressurized air stream for approximately five minutes. The runs were then allowed to cool to room temperature. Capsules were opened and the contents washed in millipore water before being mounted in epoxy. The epoxy mounts were polished starting with grit size 240 and finishing with .3 μ grit. The mounts were then cleaned in an ultrasound machine in millipore water, washed in ethyl alcohol and carbon-coated for microprobe analysis.

Charges were analyzed using a JEOL 733 Superprobe electron microprobe using on-line data reduction and the matrix correction procedures of Bence and Albee (1968) with the modifications of Albee and Ray (1970). Analysis points (thirty or more) were taken on

small crystals or crystal edges from each charge until the reaction overgrowths and compositional zoning in the run products had been established.

Chapter 4

PREVIOUS STUDIES OF FELDSPAR EQUILIBRIA

4.1 BINARY SYSTEMS

Of the feldspar binary systems, the albite-orthoclase binary has been most studied (e.g. Orville, 1963; Luth and Tuttle, 1966; Thompson and Waldbaum, 1969; Goldsmith and Newton, 1974; Hovis and Waldbaum, 1977; Lagache and Weisbrod, 1977; Thompson and Hovis, 1979; Brown and Parsons, 1981; Haselton et al, 1983).

For the anorthite-albite system, Newton et al (1980) presents the only available measurements of the excess energy terms for high structural state feldspars.

Bowen (1956) constructed an anorthite-orthoclase phase diagram based on observations of the natural system, but the binary system anorthite-orthoclase has not been studied experimentally.

4.1.1 THE ALBITE-ORTHOCLASE BINARY

Orville (1963) conducted ion-exchange experiments in the system $\text{KAlSi}_3\text{O}_8\text{-NaAlSi}_3\text{O}_8\text{-NaCl-KCl-H}_2\text{O}$ at temperatures from 350° C to 700° C, pressures of 2000 bars and total chloride concentrations of 2 Molar. Synthetic feldspars crystallized from gels were used as starting materials and run products were analyzed using the $\bar{2}01$ x-ray method. Orville demonstrated equilibrium by using starting compositions which lay on either side of the equilibrium value and which converged to an equilibrium value during the run time. When plotted on an Or vs. K plot, non-equilibrium starting assemblage tie lines with varying slopes can be seen to converge and become subparallel after being run.

Luth and Tuttle (1966) investigated the influence of $\text{Na}_2\text{O} + \text{K}_2\text{O} : \text{Al}_2\text{O}_3$ on the

shape of the solvus. They recrystallized dehydrated gels in aqueous vapor at 2 kbars and temperatures between 550° C and 700° C. Compositions of run products were obtained using the $\bar{2}01$ x-ray method. The solvii determined from gels containing excess alkalis, excess alumina and stoichiometric compositions were all significantly different. The solvii were also all more symmetrical than that derived by Orville (1963). However, Luth and Tuttle's attempts at reversals failed: their thirty-day run times were not long enough.

Thompson and Waldbaum (1969) is the third in the three-paper series on alkali feldspar equilibria. In each of these papers thermodynamic mixing parameters are calculated from previous experimental work. Part One (Thompson and Waldbaum, 1968) utilizes the ion-exchange data of Orville (1963) to calculate Margules parameters. Part Two (Waldbaum and Thompson, 1968) uses the volume data of Donnay and Donnay (1952) and Orville (1967) for this purpose. In Part Three Thompson and Waldbaum obtain Margules parameters from coexisting phases given by Luth and Tuttle (1966) and Orville (1963). Two methods are used to calculate Margules parameters. The first method is to plot appropriate functions of composition against reciprocal temperature and obtain Margules parameters by least-squares fit. The second method makes use of the near-linear relationships in the critical region between the square of the difference in composition of the two phases, the mean composition and the reciprocal temperature. The second method is preferred when the experimental runs did not reach complete equilibrium. Because of their close agreement, the results of this study were felt to confirm Orville's (1963) solvus.

Smith and Parsons (1974) crystallized feldspar pairs from stoichiometric gels at 1 kbar water pressure and temperatures from 300° C to 700° C. They note that different bulk compositions in terms of Na:K produce different feldspar pairs when crystallized at the same temperature. They bracket a solvus using these compositional differences and approaching the solvus from both directions in composition space. They analyze their data using the method of Thompson and Waldbaum (1969). After using a pressure correction on Orville's (1963) data, their solvii are very similar.

Goldsmith and Newton (1974) ran synthetic and natural feldspars at water pressures between 9 and 15 kbars and temperatures between 300° C and 600° C. They concentrate on a "rigorous demonstration of compositional equilibrium", noting that none of the direct synthesis solvii have been bracketed by reversed reactions using crystalline materials. They observed that when a feldspar moves toward the solvus by continuous crystallization the recrystallized feldspar will never overstep the solvus because that would require passing through a free energy minima, a thermodynamic impossibility. Therefore, one aims for a close bracketing of the solvus by forward and reversal experiments as is possible. Goldsmith and Newton used x-ray analysis on their run products. They found that the structural states of the run products varied from 40% ordered at 350° C to highly disordered at 600° C, but the ordered feldspars did not depart significantly from a solvus corresponding to highly disordered phases. Their solvus was approached fairly closely from both sides and agreed well with those of Orville (1963) and Thompson and Waldbaum (1969). They did not calculate Margules parameters.

Lagache and Weisbrod (1977) ran gels and synthetic feldspars in chloride solutions at temperatures from 300° C to 660° C, pressures from 0.2 to 2 kbars and total chloride concentrations from 0.05 to 0.14 moles/kg H₂O. They obtained their run product compositions using the x-ray technique of Orville (1963). No effect of pressure on the solvus could be detected. In the runs using gels, the resulting feldspars were fairly homogeneous in internal composition. The runs using synthetic feldspars had rims whose compositions were the same as the gel results. Lagache and Weisbrod had less scatter around their solvus than did Luth and Tuttle (1966). They calculated Margules parameters using the regular asymmetric solution model of Thompson and Waldbaum (1968).

Thompson and Hovis (1979) reevaluated the entropy of mixing in high-temperature feldspars using the heats of solution presented by Hovis and Waldbaum (1977) and the data of Orville (1963). They used the heats of solution to obtain the parameters for E^{ex} , V^{ex} and

H^{ex} . Using these parameters, they curve-fit to Orville's (1963) data and extracted ΔH° , ΔS° and finally G^{ex} for an asymmetric solvus. They state that their Gibbs free energy function gives a far more accurate representation of highly disordered alkali feldspars than did the formulation of Thompson and Waldbaum (1969).

Haselton et al (1983) measured the heat capacities for five highly disordered alkali feldspars by adiabatic calorimetry. They used analbite obtained by heating albite and sanidine obtained by ion-exchanging with the analbite as starting materials. They measured the deviations from a linear combination of end-member heat capacities and thereby obtained excess entropy terms. Values for the free energy of mixing parameters, B and C (Margules terms: see Thompson, 1967) are tabulated along with asymmetric excess enthalpies. They combine their symmetrical entropy and volume of mixing data with the plagioclase data of Newton et al (1980) to calibrate a two-feldspar geothermometer.

4.1.2 THE ALBITE-ANORTHITE BINARY

Orville (1972) conducted ion-exchange experiments in the system $\text{NaAlSi}_3\text{O}_8\text{-CaAl}_2\text{Si}_2\text{O}_8\text{-CaCl}_2\text{-NaCl-SiO}_2$ at 700°C , 2 kbars and total chloride concentrations from 0.2 to 2.0 normal. He used as starting materials feldspars crystallized from gels. Because of the extremely small grain size of the products x-ray powder diffraction techniques were used for analysis. As a check for internal consistency in his results, Orville required that the ion content of the feldspar, the ion content of the salt and the bulk starting composition plot on a straight line in composition space. He notes that the plagioclase binary as a whole shows positive deviations from ideality, but in modelling the activities treats the composition ranges $\text{An}_0\text{-An}_{50}$ and $\text{An}_{85}\text{-An}_{100}$ as ideal (with constant activity coefficients). Only the central compositions from disordered high albite at An_{50} to ordered anorthite at An_{85} are treated as non-ideal.

Saxena and Ribbe (1972) used Seck's (1971a, 1971b) and Orville's (1972) data to

calculate the excess Gibb's free energy in the albite- anorthite and albite-orthoclase binaries. They used Guggenheim's expression for excess free energy, which is asymmetric but does not contain higher order composition terms. They claim that their alkali feldspar excess terms, calculated solely from Seck's data, agree well with those of Thompson and Waldbaum (1969). In the plagioclase binary, the excess terms they calculated from Seck's data differ significantly from those calculated from Orville's data. This difference may be due to the ternary interaction in Seck's data. If this is the case, the alkali excess terms may also be suspect, although the ternary interaction in the alkali binary is far less significant than that in the plagioclase binary.

Newton et al (1980) measured the heats of solution for high structural state plagioclases synthesized from gels at 1200° C and 20kbars. Additional experiments were conducted using Amelia albite. From this data asymmetric excess enthalpies of solution were calculated. By combining their ΔH^{ex} expression with the entropy expression of Kerrick and Darken (1975) the free energy of mixing of Orville (1972) is reproduced well.

Blencoe et al (1982) criticized the choice of standard states and the manner in which the compositions of the phases were expressed in Saxena and Ribbe (1972) and Orville (1972). To improve the accuracy of the data, they chose undissociated solute components in an ideally dilute, aqueous vapor, assumed to be Henrian. To fulfill these requirements, they limit their investigation to Orville's data at 2 kbars, 700° C and solute concentrations less than 0.05 normal. They employ a Raultian standard state, where $\gamma \rightarrow 1$ as $\chi \rightarrow 1$. Using these different assumptions they recalculate Orville's (1972) data and present it in activity vs. composition diagrams. However, their analysis precludes asymmetric mixing behavior.

Carpenter and Ferry (1984) derive a simple mixing model for the high structural state plagioclases by taking into consideration the $\bar{C}\bar{1}/\bar{I}\bar{1}$ transformation (Al/Si order/disorder) at high temperatures. They treat the $\bar{C}\bar{1}$ solid solution as ideal except for anorthite-rich

compositions. The activity coefficient for anorthite is controlled by the free energy difference between \bar{C}_I and \bar{I}_I at the temperature of interest. Using published data for entropy and enthalpy they extract "crude estimates" for activity coefficients for anorthite. They stress that the importance of their model is its recognition of the constraints on mixing and not the accuracy of the activity coefficients derived.

4.2 TERNARY SYSTEMS

The majority of the experimental work on ternary feldspars has been done by Seck (1971a, 1971b). Starting with feldspars crystallized from gels, Seck determined the compositions of over 100 coexisting feldspar pairs recrystallized at temperatures from 650° C to 900° C and 0.5, 1, 5 and 10 kbars. Seck was the first to show that increasing pressure had an effect on the solvus opposite to that of increasing temperature. While Brown and Parsons (1981) state that "the regularity of Seck's results is consistent with a good approach to equilibrium", Seck's data may be questioned on several grounds. His run times were at all temperatures less than 45 days (run times were longer than 12 days at temperatures greater than 825° C and longer than 30 days at temperatures greater than 650° C). Due to the sluggishness of reaction in the ternary feldspars, it is doubtful that a significant depth of equilibrium recrystallization could be obtained during these run periods at any but the highest temperatures.

Johannes (1979) provides the remainder of the experimental data available for ternary feldspars. He ran two bulk compositions at 650° C and 800° C, generating four pairs of coexisting ternary feldspars. Johannes also used as starting materials feldspars crystallized from gels. These starting materials were found to have almost unordered Al/Si distribution, appropriate for the temperatures in consideration. Johannes used longer run times than Seck, but at 650° C they were still less than half what was found to be necessary in this study to produce significant reaction overgrowths. Johannes also used x-ray techniques for

compositional analysis. His techniques did not require graphing through the bulk starting composition, but they measured crystal interiors which should not necessarily be considered at equilibrium.

Chapter 5

EXPERIMENTAL RESULTS

5.1 MIXING BULK STARTING COMPOSITIONS

Data on run temperatures, pressures, durations and products is found in table 5-I.

Finely ground starting materials were mixed together in different ratios to form the bulk starting compositions of the runs. The seven "forward" runs (TFK1, TFL1, TFG3, TFG2, TFE2, TFG5 and TFA4) consisted of different proportions of Hugo microcline, Crystal Bay bytownite and Lake Harbour oligoclase. The "reversal" runs (TFI'1 and TFA''1) consisted of Kilbourne Hole anorthoclase and either Hugo microcline or Lake Harbour oligoclase. See table 5-I. The bulk starting compositions are shown in figure 5-1. They are labelled with one-letter names. The third letter in each run number is the bulk composition which was used for that run.

The proportions of the natural feldspar starting materials were varied to produce the different bulk starting compositions in specific areas on the feldspar ternary. The bulk starting compositions were chosen to give a variety of feldspar bulk compositions between An_0 and An_{50} which would react to outline the equilibrium solvus.

With the exception of K and L the bulk compositions with low An contents were chosen because most two-feldspar assemblages found in nature lie in this composition range. This was an attempt to limit the run products to this part of composition space.

Bulk starting compositions K and L were mixed specifically for the 800° C runs. Bulk compositions run at 800° C which lay closer to the plagioclase binary (compositions H, A and E; see figure 5-1) did not produce an alkali feldspar run product. Bulk compositions K and L produced both a plagioclase and alkali feldspar pair at 800° C and a limited amount of melt which increased reaction rates significantly.

Bulk compositions A and E contain considerably less of the potassium component than does composition G. This difference was created to determine whether the run products of such offset bulk compositions would contain plagioclases with similar orthoclase contents and alkali feldspars with similar albite contents, i.e., whether runs made under the same conditions but with quite different bulk starting compositions would produce run products which approach the solvus in the same way. If running a high-potassium bulk composition and a low-potassium bulk composition at the same pressure and temperature produces run products which lie on the solvus there is evidence that the run product compositions are in response to the pressure and temperature and not the bulk composition. This is a first step in evidence for equilibrium.

The "forward" runs are so-called because their bulk compositions are mixed from plagioclase starting materials which lie on or very near the binaries, and so when reacting during a run the feldspar compositions must move away from the binaries to reach the equilibrium solvus. The "reversed" runs have bulk starting compositions which are mixed from plagioclase starting materials at least one of which lies inside the solvus at the temperature and pressure of the run. Thus when reacting during the run the starting material crystal composition must move toward the binary to reach the equilibrium solvus. Since during continuous recrystallization the crystal composition can never pass through the solvus because that entails passing through a free energy minimum, one aims for a close bracketing of the solvus through forward and reversed experiments. This close bracketing or, if possible, actual delineation of one solvus with forward and reversed experiments is important evidence for equilibrium.

The bulk compositions I' and A'' were mixed using the Kilbourne Hole anorthoclase to create reversed experiments. Bulk composition A'' and bulk composition A plot in the same place on the feldspar ternary, as do bulk compositions I and I'.

Table 5-I: Data for Ternary Feldspar Runs
H=Hugo microcline, XB=Crystal Bay bytownite,
LH=Lake Harbour oligoclase,
KH=Kilbourne Hole anorthoclase.

run number	duration [days]	T [° C]	P [kb]	starting materials	Averaged PL			Averaged AF		
					An	Ab	Or	An	Ab	Or
TFK1	14	800	2	H, XB, LH	.267	.645	.087	.018	.253	.729
TFL1	14	800	2	H, XB, LH	.338	.596	.066	.017	.225	.757
TFG3	31	800	2	H, XB, LH	.325	.594	.081	.022	.234	.744
TFG2	115	700	2	H, XB, LH	.210	.732	.058	.009	.273	.719
TFE2	115	700	2	H, XB, LH	.153	.782	.064	.009	.331	.660
TFI'1	119	700	2	H, KH	.046	.736	.217	.009	.382	.609
TFA' '1	119	700	2	KH, XB	.119	.797	.084	.016	.392	.593
TFG5	102	700	3	H, XB, LH	.131	.801	.068	.010	.327	.663
TFA4	102	700	3	H, XB, LH	.152	.780	.068	.013	.320	.667
TFI1	189	600	2	H, XB, LH	NO REACTION					
TFJ1	189	600	2	H, XB, LH	NO REACTION					

5.2 DESCRIPTION OF REACTION

Because reaction rates are so slow in crystalline feldspars a major effort was made to grow reaction rims wide enough to analyze with an electron microprobe. To speed reaction rates water was added to the charges and, where the bulk starting composition allowed it, some melt was created. These partially melted experiments reacted far faster than those with only water to aid in ion diffusion.

In some initial runs a chloride solution was used instead of water with the aim of speeding up reaction times. Chloride solutions were mixed with Na:K:Ca in a 1:1:1 ratio with the bulk starting compositions of the runs. Runs at 700° C with appropriate chloride solutions produced exactly the same run products as the same bulk compositions run in water alone. The chloride solution experiments did not react significantly faster than the water experiments and so were abandoned in preference for water.

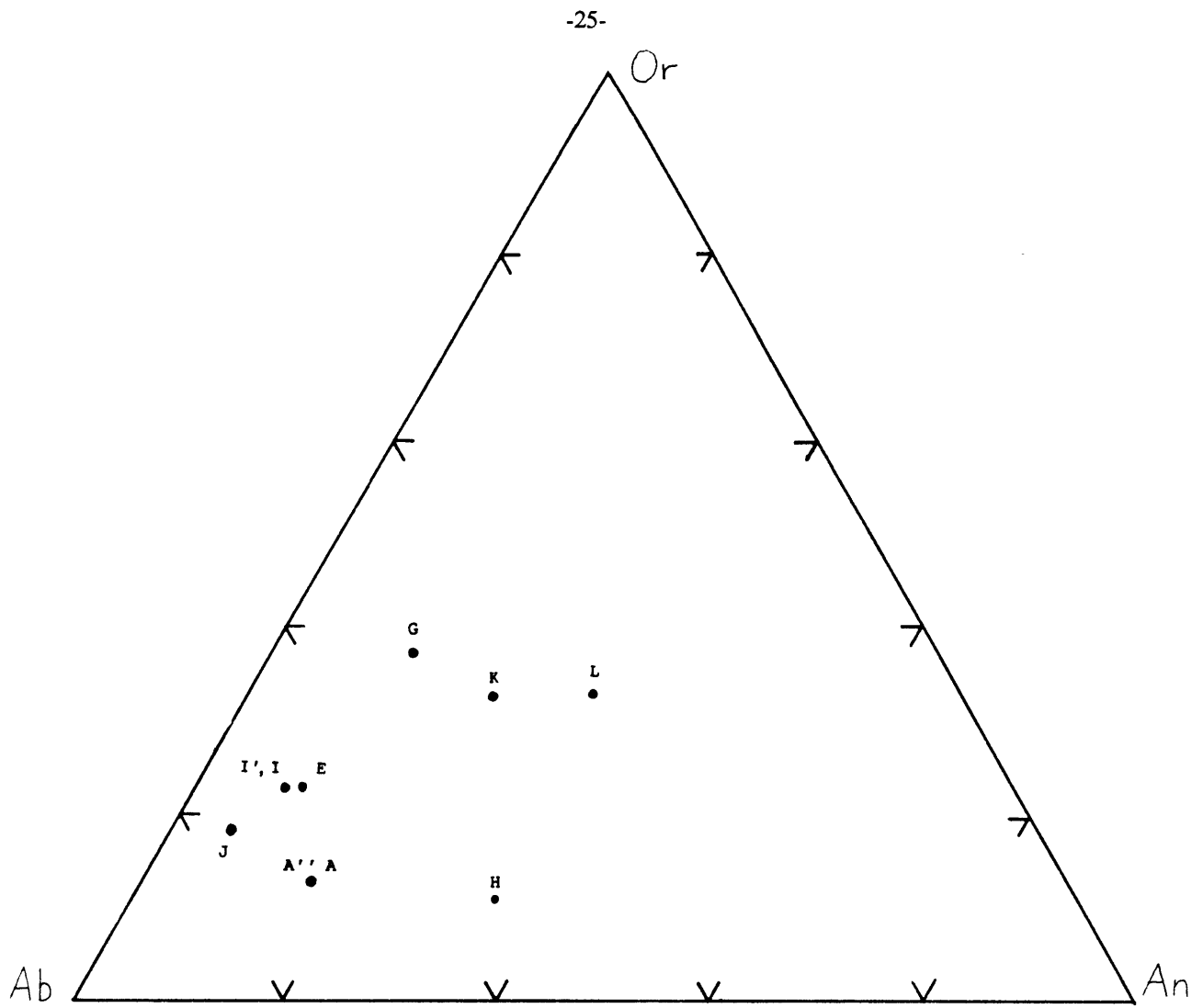


Figure 5-1: Ternary diagram showing bulk starting compositions for all runs

The scanning electron microscope on the electron microprobe enabled us to look closely at the compositional variations present in each of the run products. None of the well-reacted run products consisted of entirely homogeneous feldspar crystals. All experiments contained unreacted cores overgrown by reaction rims. These outermost reaction rims were used for analysis. In all successful experiments rims at least 5μ wide were achieved. Most runs also contained many 5μ to 15μ crystals of homogeneous composition which matched the overgrowth rims.

Few of the run products showed gradational change from the interior to the exterior of the crystals and not all showed clear step function reaction rims. Particularly in the lower temperatures morphological characteristics of the starting materials would be retained in the run products and overgrowths were almost always asymmetrical and discontinuous. Within a given experiment the relationships between the different feldspar compositions would remain consistent. At higher run temperatures the products were more homogeneous and fewer complex boundaries were found.

The Hugo microcline contains coarse exsolution lamellae of albite. The microcline and albite lamellae would anneal to a greater or lesser extent depending on the run temperature. In the 700° C runs many scattered areas of albite remain in the alkali feldspar, while in the 800° C runs the albite is reduced significantly or eliminated altogether. The alkali feldspar often contained cores of highly potassic material while the reaction rims graded to less potassic and more calcic compositions. For photomicrographs of the unannealed lamellae and unreacted cores, see figures 5-3 and 5-4. The alkali feldspar was often overgrown by plagioclase. In the 800° C runs the plagioclase overgrowth rims were less common than in the 700° C runs. Figure 5-6 shows a photomicrograph of an alkali feldspar with overgrowths.

In the 700° C runs the Crystal Bay bytownite tended to dissolve partially and then form sharp overgrowths. This may be because of the slowness of reaction caused by the

addition of a quartz molecule to each feldspar molecule when moving from anorthite toward albite. In the 800° C runs a few of these overgrowths were present.

In the 700° C runs the Lake Harbour oligoclase formed reaction rims to progressively more potassic and calcic compositions. In the 800° C runs the plagioclase phase was close to homogeneous.

The Kilbourne Hole anorthoclase was only run at 700° C. It behaved similarly to the Lake Harbour, forming reaction rims progressively in one compositional direction (the direction differed in the two runs it was used in: see figures 5-22 and 5-24).

Since only the outermost rims have undergone reaction during most of these experiments, much of the initial feldspar material from the interior of the crystals is left at varying stages of reaction. For this reason the ternary feldspar pair is influenced but not controlled by the initial bulk composition and a mass balance is never possible between the ternary pair and the bulk starting composition.

5.3 ELECTRON MICROPROBE ANALYSIS

Because of the general lack of large homogeneous, fully reacted crystals in any of the run products even after extended run times the use of the electron microprobe for analysis was absolutely required. Only the outermost rims were considered candidates for equilibrium compositions. The microprobe can obtain good analyses up to 2 μ from the edge of the crystal and this ability was found very useful. From each run product 40 to 90 individual analyses were taken from rims and plotted on a ternary diagram. The compositional variation and trends in such a diagram are a measure of the reaction processes which move the compositions of the starting materials toward equilibrium. If the run had come to complete equilibrium, all analyses would plot neatly at the equilibrium alkali feldspar and plagioclase compositions only, and all crystals would be completely homogeneous.

In the ternary plots of most run analyses a number of points could be seen trailing away from the starting materials compositions and moving toward one of the extreme ternary feldspar compositions. In the experiments which had not had sufficient run duration, rim analyses would usually plot along lines between the starting materials and some plagioclase and some alkali feldspar composition, but no significant clusters could yet be seen. In the experiments which had had a sufficient run time, a majority of points would cluster at one plagioclase and one alkali feldspar composition.

All the rim analyses for each of the runs are plotted on ternary feldspar diagrams in figures 5-8, 5-10, 5-12, 5-14, 5-16, 5-18, 5-20, 5-22 and 5-24. The analyses in the alkali feldspar and plagioclase clusters are then averaged to obtain the compositions toward which the run was moving. Deciding which rim analyses lie within the clusters is to some extent arbitrary. The densest areas are chosen in each case, and in general the boundaries to these areas are well defined.

The compositions of the averaged alkali feldspar and plagioclase for each of the runs are shown in table 5-II. Only probe points with good stoichiometry and totals were used in these averages. The oxide totals were between 98.5 and 101.5%, the 5-oxygen formula base totals between 4.98 and 5.02 and the 8-oxygen formula base totals between 7.98 and 8.02.

Analytical error ellipses around the averaged alkali feldspar and plagioclase based on a one standard deviation distribution around the average are given in figures 5-9, 5-11, 5-13, 5-15, 5-17, 5-19, 5-21, 5-23 and 5-25. These error ellipses were calculated using Monte Carlo simulation (see for example Press et al, 1986). This technique assumes that the probability distribution of the measured data is the same as the true physical parameters being measured. Using this assumption synthetic data sets with the same distribution are created. Enough random numbers are drawn from appropriate synthetic data sets to map out the probability distribution. Here the probability distribution is Gaussian and outlines a one standard deviation 68% confidence region.

The standard errors of the means for the feldspar averages are given in table 5-III. These standard errors encompass all sources of analytical error because they rely only on the standard deviations of the final averaging of microprobe analyses. In table 5-IV one standard deviation errors for unaveraged oxides based solely on electron microprobe counting statistics are given. These standard deviations are calculated with the following equation:

$$\frac{(P_C + P_B)^{.5}}{(P_C - P_B)} \times 100 = \sigma$$

where P_C equals the numbers of x-ray counts detected by the machine on the peak wavelength of the element, and P_B is the number of x-ray counts on the background. The error did not vary significantly within one phase of one experiment, so only the worst case errors for each phase in each experiment are given.

The errors for major constituents are on the order of 1 to 2% (1σ) of the amount present. The worst errors are for the trace components in the coexisting feldspars. The counting statistic error for calcium in the alkali feldspar was 8 to 12% (1σ) of the amount present. In plagioclase the counting statistic error for potassium content was 3 to 4% (1σ) of the amount present.

The standard analytical errors of the mean shown in table 5-III are very close to the electron microprobe counting statistic standard deviations shown in table 5-IV. This implies that a large percentage of the analytical error in these experiments may be attributed to the statistical counting errors of the electron microprobe analyses.

The alkali feldspar and plagioclase averages for the 700° C, 2 kbar runs are plotted in a feldspar ternary diagram with appropriate tie lines in figure 5-26. The 700° C, 3 kbar averages are plotted similarly in figure 5-27, and the 800° C, 2 kbar averages in figure 5-28.

Figures 5-29 and 5-30 show the data from this study plotted on feldspar ternary

diagrams with data from Seck's (1971b) and Johannes's (1979) ternary feldspar experiments. In figure 5-29 the data from this study at 800° C and 2 kbars is plotted with Seck's (1971b) data at 825° C and 1 kbar and Johannes's data at 800° C and 1 kbar. Note that the alkali feldspar phases at this temperature and pressure from this study contain from 5 to 8 mol% more orthoclase than do Seck's. Johannes's alkali feldspar phases contain approximately 9 mol% more orthoclase than do Seck's. The run times from this study at this temperature were 14 to 31 days. Seck's run times were 12 to 45 days.

In figure 5-30 the data from this study at 700° C and 2 kbars is plotted with Seck's (1971b) data at 750° C and 1 kbar. Because of the inverse effects of temperature and pressure on composition in the feldspars, this comparison should be roughly correct. The plagioclases from this study contain approximately 5 mol% less orthoclase and the alkali feldspars about 8 mol% more orthoclase than do Seck's phases. The run times from this study at these temperatures were 115 to 119 days. Seck's run times were 30 to 45 days.

5.4 600° C, 2 KBAR EXPERIMENTS

Run durations of 189 days failed to produce measurable reaction rims.

5.5 800° C, 2 KBAR EXPERIMENTS

Three experiments at 800° C and 2 kbars were considered successful. See figures 5-2 and 5-3 for photomicrographs of runs TFK1 and TFG3, figures 5-8, 5-10 and 5-12 for microprobe data, figures 5-9, 5-11 and 5-13 for error ellipses around the averaged alkali feldspar and plagioclase.

Initial 800° C, 2 kbar experiments were run for 4.5 weeks. The crystalline run products were fairly homogeneous and a significant amount of melt was generated. Some of the more plagioclase-rich bulk compositions melted entirely and could not be used.

There was little scatter in the rim analyses toward the starting compositions and the clusters at the compositions feldspar pairs were dense and focused. The melt increased reaction rates significantly. Further 800° C, 2 kbar experiments were run for only 2 weeks with good results. The feldspar pairs were not quite as tightly defined in the analysis and there was more scatter toward the starting compositions than in the 4.5 weeks experiments. The significant decrease in scatter in the 4.5 week runs over the 2 week runs and the 700° C runs is a further validation of this method of run analysis.

5.6 700° C, 2 KBAR EXPERIMENTS

Two experiments at 700° C and 2 kbars succeeded in producing reaction rims which clustered at a plagioclase and an alkali feldspar composition. See figure 5-4 for a photomicrograph of run TFE2, figures 5-14 and 5-16 for microprobe data, figures 5-15 and 5-17 for error ellipses around the averaged alkali feldspar and plagioclase.

Initial runs of 46 days were found to have only begun to react. Runs of 98 days produced measurable reaction rims, but the rim analyses failed to cluster at any ternary feldspar compositions. Runs times of at least 112 days are needed for a significant amount of the rim material to cluster at a ternary plagioclase and alkali feldspar composition. Even at 112 days most of the larger crystals displayed the complex, asymmetrical rims mentioned above. Each of the 112 day, 700° C experiments did achieve good focii of points around a plagioclase and an alkali feldspar but there was a significant scatter of points toward the starting materials in each case.

5.7 700° C, 3 KBAR EXPERIMENTS

Two experiments at 700° C and 3 kbars were considered successful. See figures 5-5 and 5-6 for photomicrographs of run TFA4, figures 5-18 and 5-20 for microprobe data, figures 5-19 and 5-21 for error ellipses around the averaged alkali feldspar and plagioclase.

The 700° C, 3 kbar experiments were run for 102 days. The run products looked very similar to the 700° C, 2 kbar experiments, with relatively complex zoning and asymmetric rims. These experiments achieved acceptable focii of points around a ternary plagioclase and alkali feldspar composition but did display significant scatter, particularly toward the composition of the Lake Harbour oligoclase starting material. The run products did not display more homogeneous rim compositions than the 700° C, 2 kbar experiments. In these two experiments, unlike the others, the stoichiometry of the alkali feldspars was poor and very good microprobe data was unattainable from them. The plagioclases did not suffer from this problem. For this reason these two are the least reliable of the experiments in this study.

5.8 700° C, 2 KBAR REVERSALS

Two reversals were made at 700° C and 2 kbars for 17 weeks. See figure 5-7 for a photomicrograph of run TFI'1, figures 5-22 and 5-24 for microprobe data, figures 5-23 and 5-25 for error ellipses around the averaged alkali feldspar and plagioclase. Run number TFA''1 was made of the Kilbourne Hole anorthoclase and the Crystal Bay bytownite. Run number TFI'1 was made of the Kilbourne Hole anorthoclase and the Hugo microcline. The run products of each showed significant reaction. Each displayed significant clusters at a specific alkali feldspar and a specific plagioclase composition.

The Kilbourne Hole-Crystal Bay reversal (TFA''1) was dominated by the Kilbourne Hole composition and much of the Crystal Bay did not react. An appropriate alkali feldspar

and plagioclase pair did form, but a lot of scatter toward the starting materials was found even in the outermost reaction rims. The final plagioclase composition did contain more anorthite than the Kilbourne Hole and so must have reacted with the Crystal Bay. The scatter around the plagioclase in run TFA''1 is due to the sluggishness of reaction of the particular starting materials used. Much of this sluggishness may result from the slow reaction in calcic plagioclase when moving toward more albitic compositions. The tie line from this reversal is parallel with the tie lines of the other 700° C experiments and the trends in the reactions of the starting materials are comparable. This reversal is considered successful.

The Hugo microcline-Kilbourne Hole reversal (TFI'1) produced a very focused plagioclase composition but the alkali composition was spread over a range of 6 mol% orthoclase. That this reversal was more thoroughly reacted than the other may be explained by the speed of reaction of the Hugo microcline as compared with the Crystal Bay bytownite. Both of the ternary compositions were very close to the orthoclase-albite join. Since the run temperature was well above the critical temperature for the binary solvus, this should not have been an influence. This reversal is also considered successful.

5.9 EVIDENCE FOR EQUILIBRIUM

As was described in the section above on bulk starting compositions, very different bulk compositions were run under identical conditions. These runs succeeded in producing run products which delineate a smooth solvus, which constitutes a first step toward proof of equilibrium. At 700° C in particular the data from this study delineates a smooth solvus. See figure 5-26. The 800° C and 700° C, 3 kbar data also forms smooth solvii. See figures 5-28 and 5-27.

The reversed experiments used the Kilbourne Hole anorthoclase as a starting material, compositionally inside the solvus at the run temperatures and pressures. The

starting materials did recrystallize to run product compositions which lay on the same smooth solvus as the other 700° C, 2 kbar data. See again figure 5-26. Because the solvus was approached from both compositional directions at the lowest run temperature, the feldspar pairs presented for each run are considered to be good candidates for the equilibrium compositions at their temperatures and pressures.

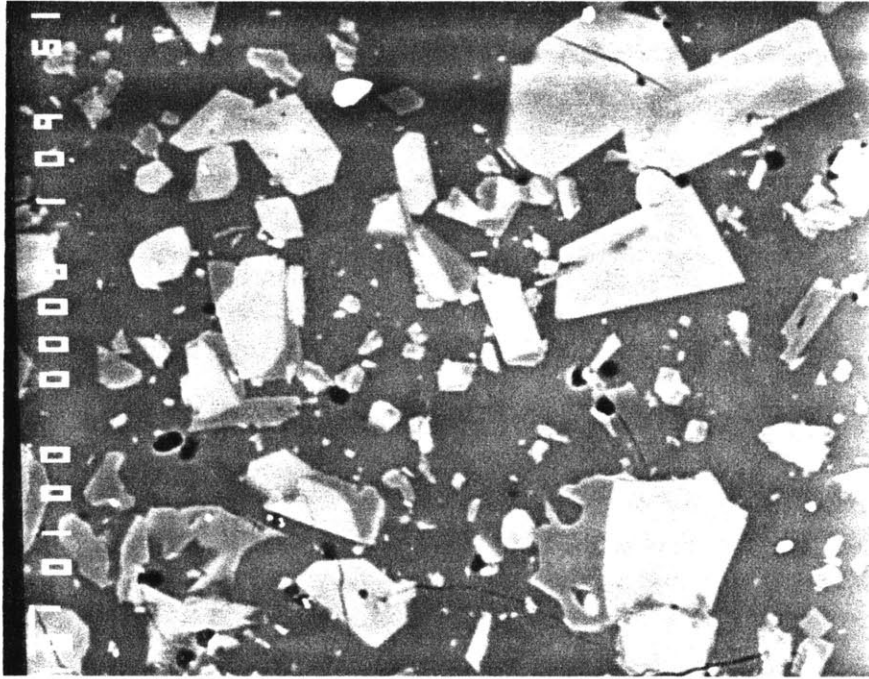


Figure 5-2: 600x photomicrograph of run number TFK1, 800° C, 2 kbars.

The light colored alkali feldspar and the dark plagioclase run products lie in a field of melt. The crystals are generally homogeneous. A few of the alkali feldspars display unreacted cores.

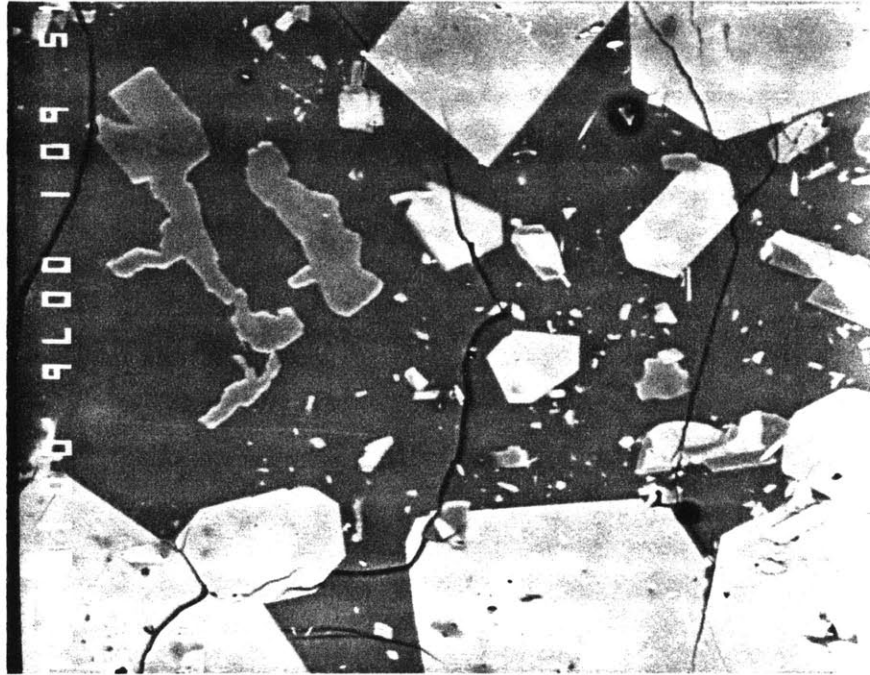


Figure 5-3: 600x photomicrograph of run number TFG3, 800° C, 2 kbars.

The light colored alkali feldspar and the dark plagioclase run products lie in a field of melt. The alkali feldspars display unreacted cores and vestiges of albite lamellae from the starting material. The plagioclase is homogeneous.

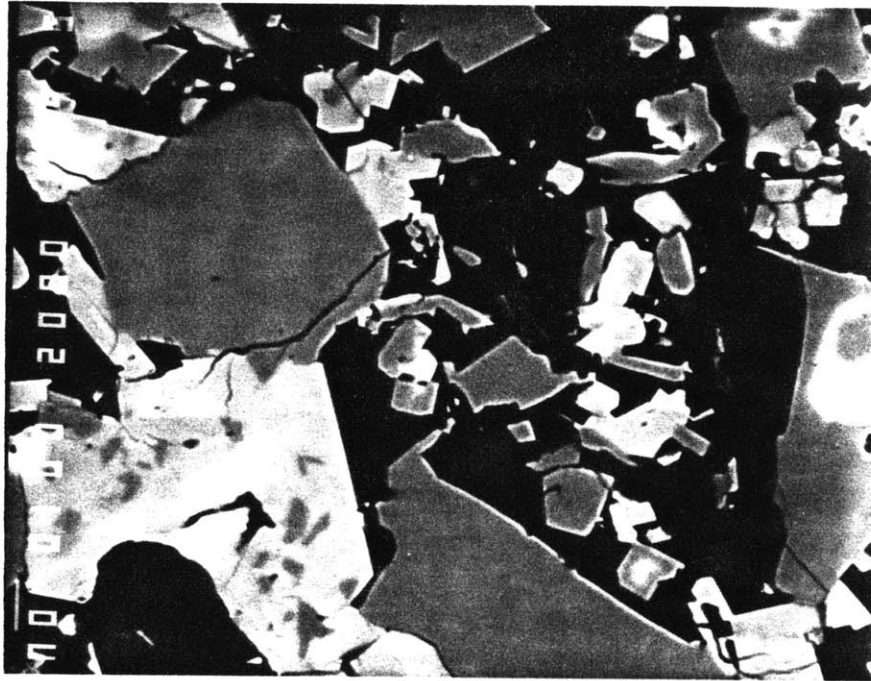


Figure 5-4: 600x photomicrograph
of run number TFE2, 700° C, 2 kbars.

The light colored alkali feldspar and the dark plagioclase are surrounded by mounting epoxy. The small crystals are homogeneous, while the alkali feldspar shows more of the unannealed albite lamellae than did the 800° C runs. Plagioclase zoning is present but not visible.

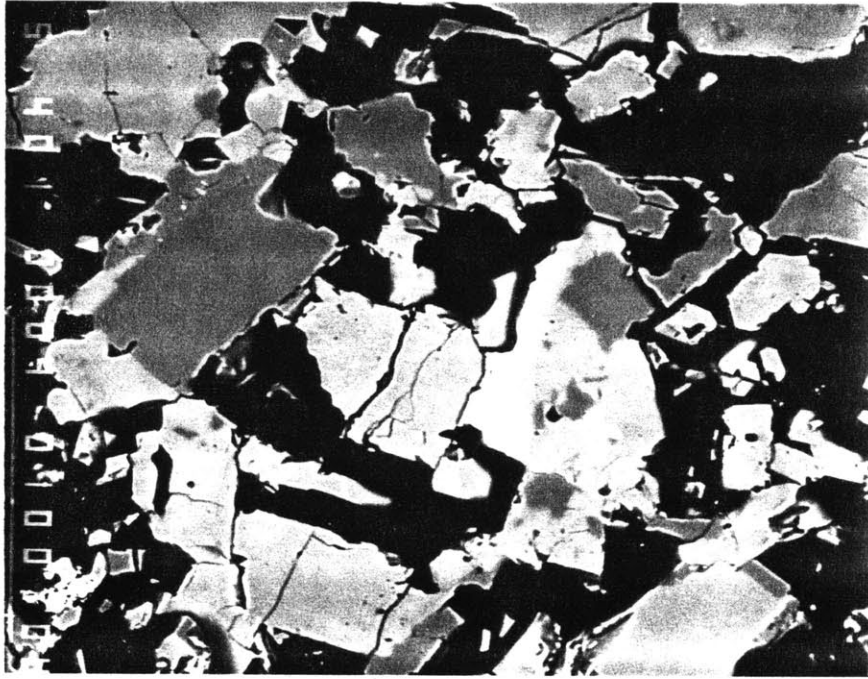


Figure 5-5: 400x photomicrograph
of run number TFA4, 700° C, 3 kbars.

The light colored alkali feldspar and the dark plagioclase are surrounded by mounting epoxy. The crystals display the rough edges and cracks typical of the 700° C runs.

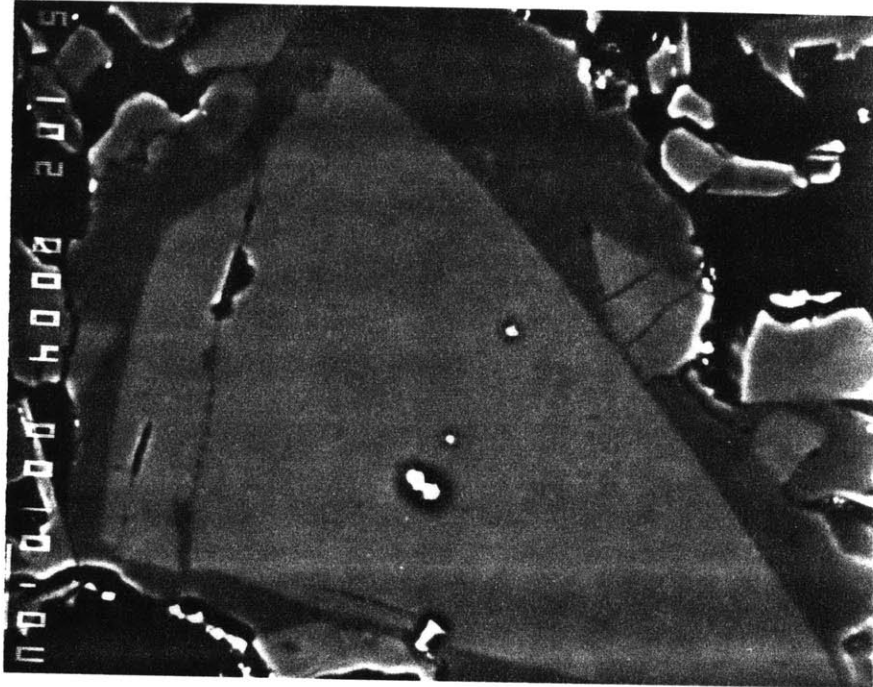


Figure 5-6: 1000x photomicrograph of run number TFA4, 700° C, 3 kbars.

The light colored alkali feldspar is overgrown by a rim of plagioclase and surrounded by mounting epoxy. The bright spot in the center of the crystal is a piece of brass from the polishing holder.

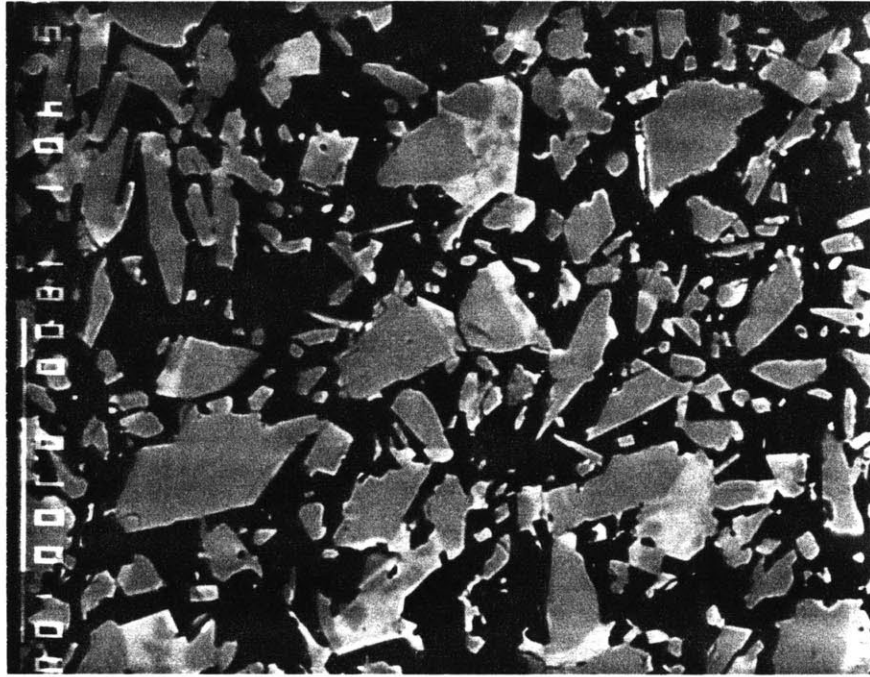


Figure 5-7: 400x photomicrograph of run number TFI'1, 700° C, 2 kbar reversal.

The dark colored plagioclase and a small amount of light alkali feldspar lie in black mounting epoxy. The alkali feldspar displays vestiges of albite lamellae and the crystals are generally jagged and not well annealed.

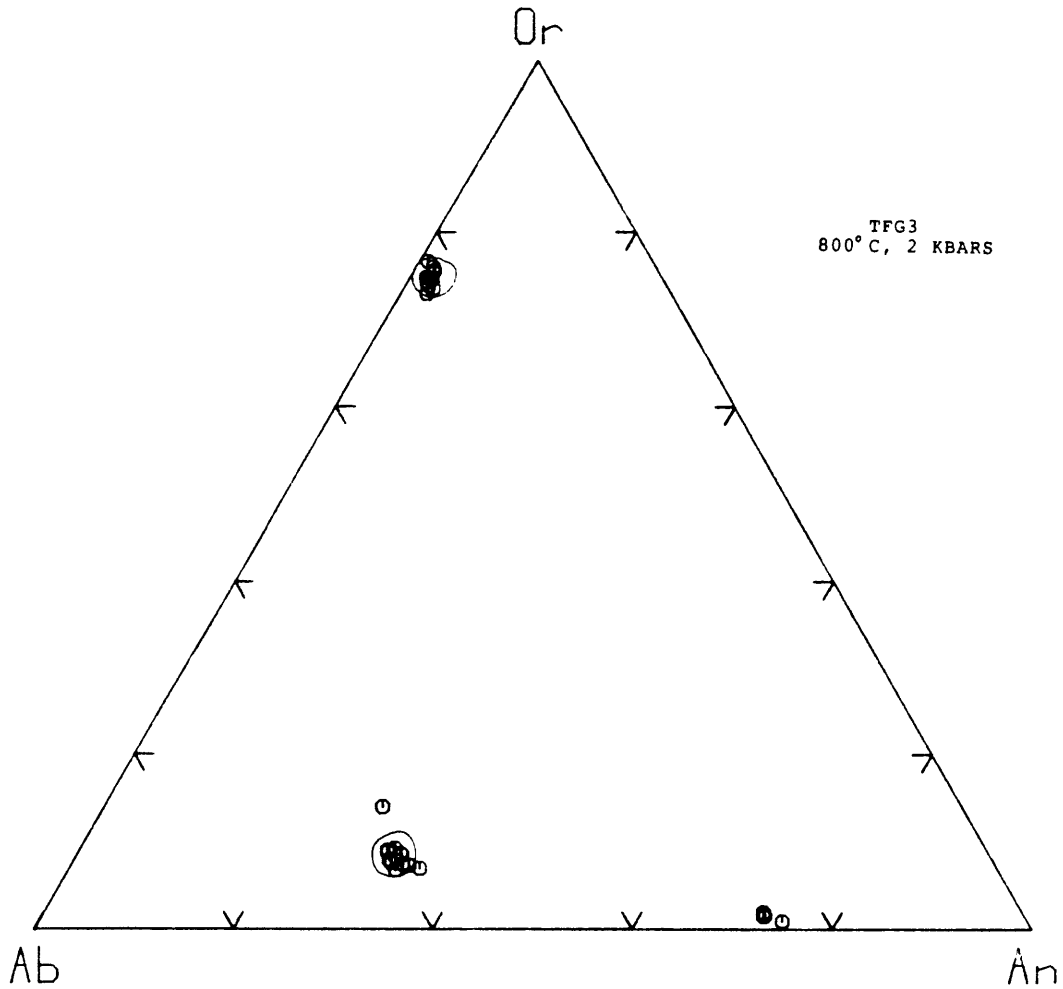


Figure 5-8: Ternary diagram for run number TFG3:
800° C, 31 days. Each point represents one
electron microprobe rim analysis.

Little scatter toward the starting materials is seen.
The analyses within the circles were averaged to find
the ternary pair.

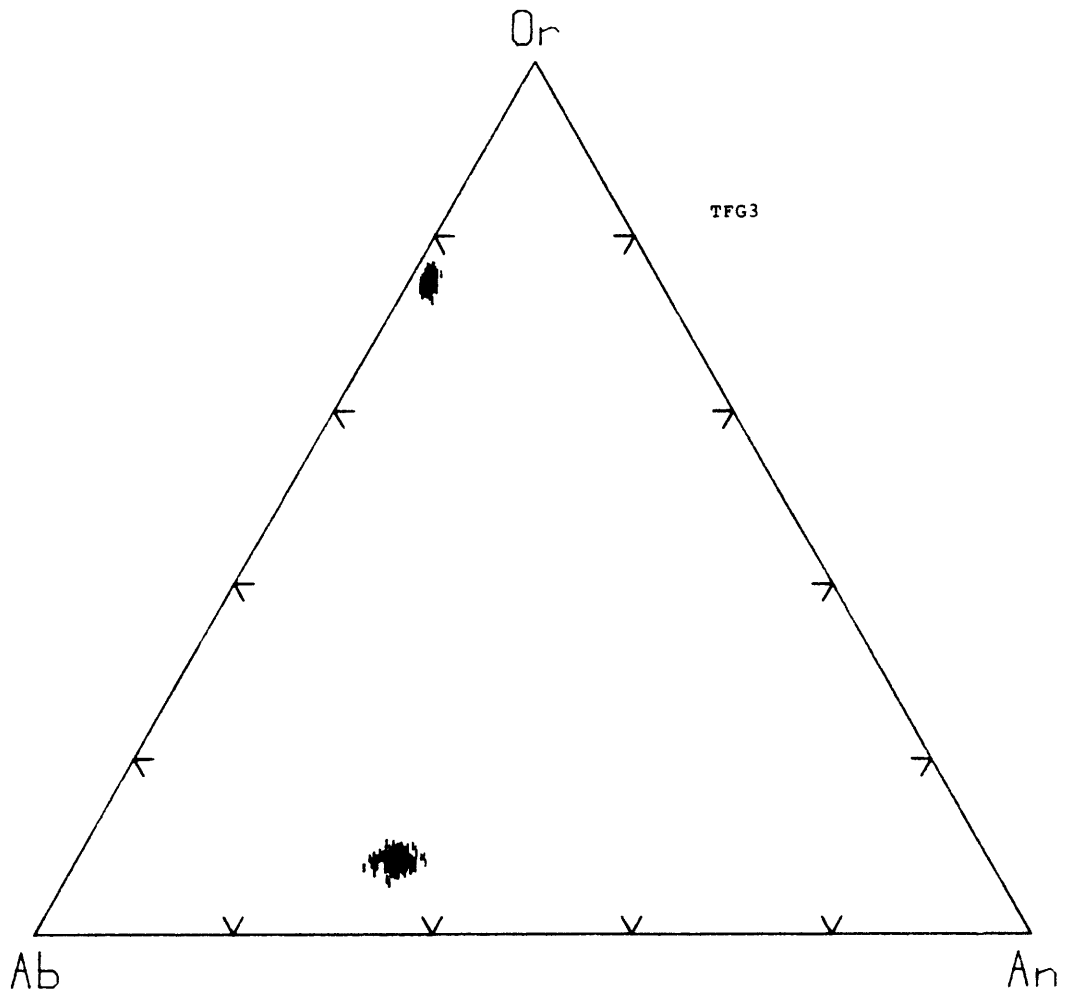
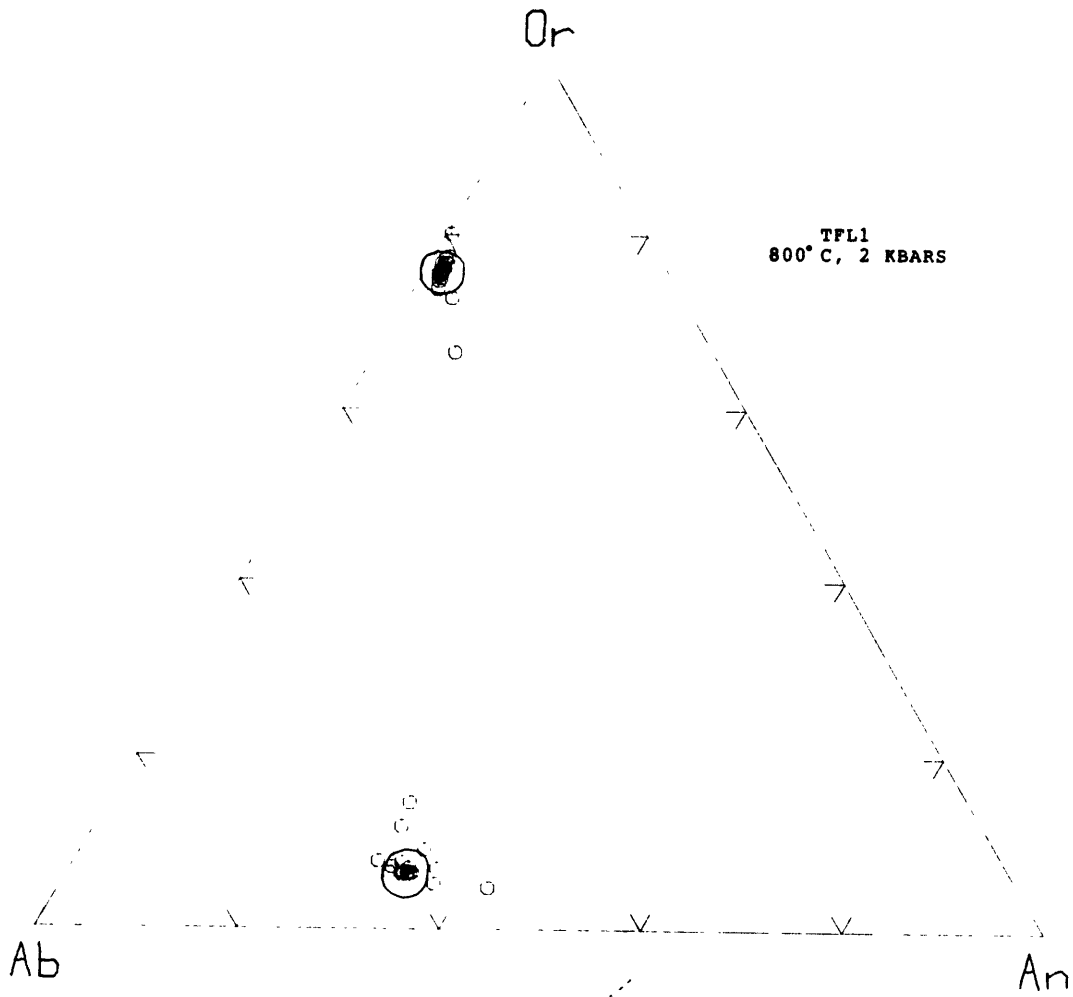


Figure 5-9: Run number TFG3: 1 σ error ellipses based on a Gaussian distribution of points around the alkali feldspar and plagioclase averages.



**Figure 5-10: Ternary diagram for run number TFL1:
800° C, 14 days. Each point represents one
electron microprobe rim analysis.**

**Some scatter is seen. The analyses within the circles
were averaged to find the ternary pair.**

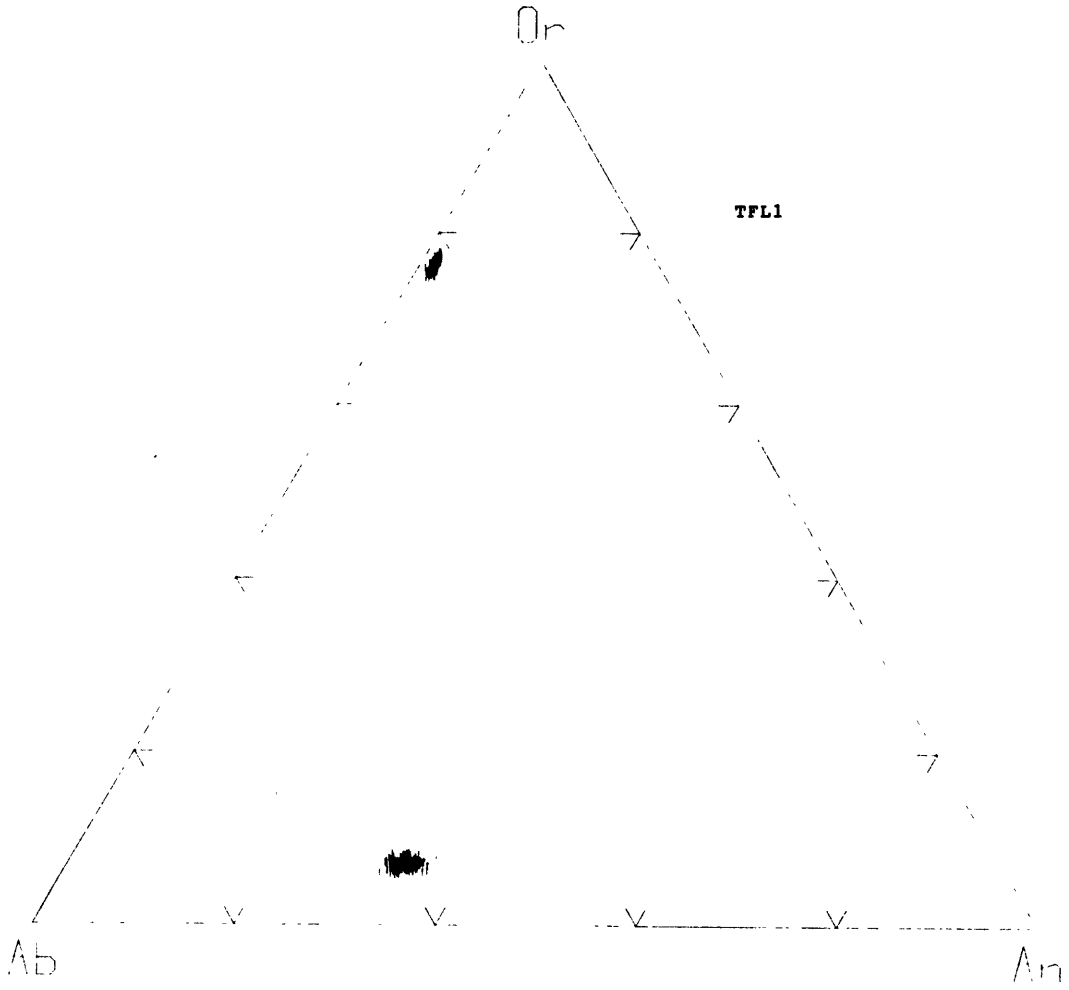


Figure 5-11: Run number TFL1: 1 σ error ellipses based on a Gaussian distribution of points around the alkali feldspar and plagioclase averages.

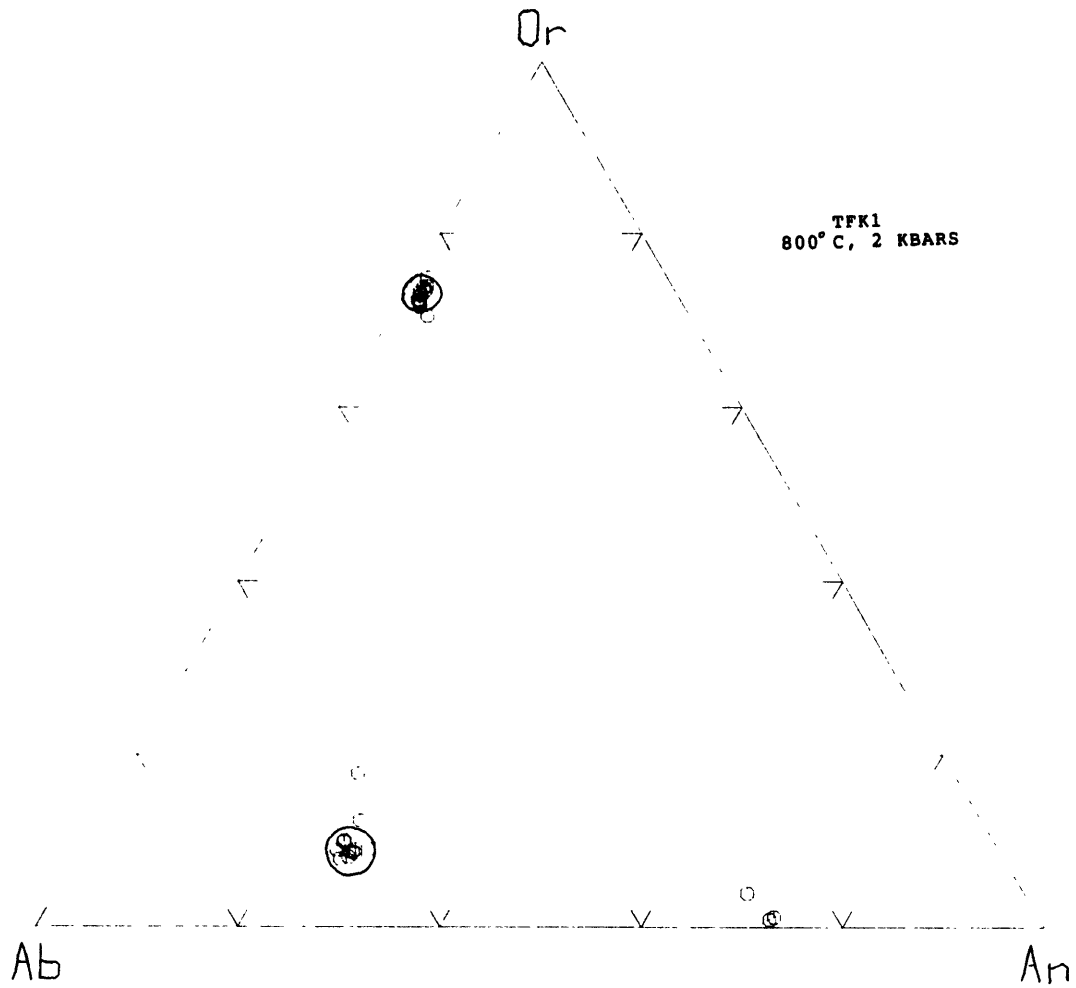


Figure 5-12: Ternary diagram for run number TFK1:
800° C, 14 days. Each point represents one
electron microprobe rim analysis.

The analyses within the circles were averaged to find
the ternary pair.

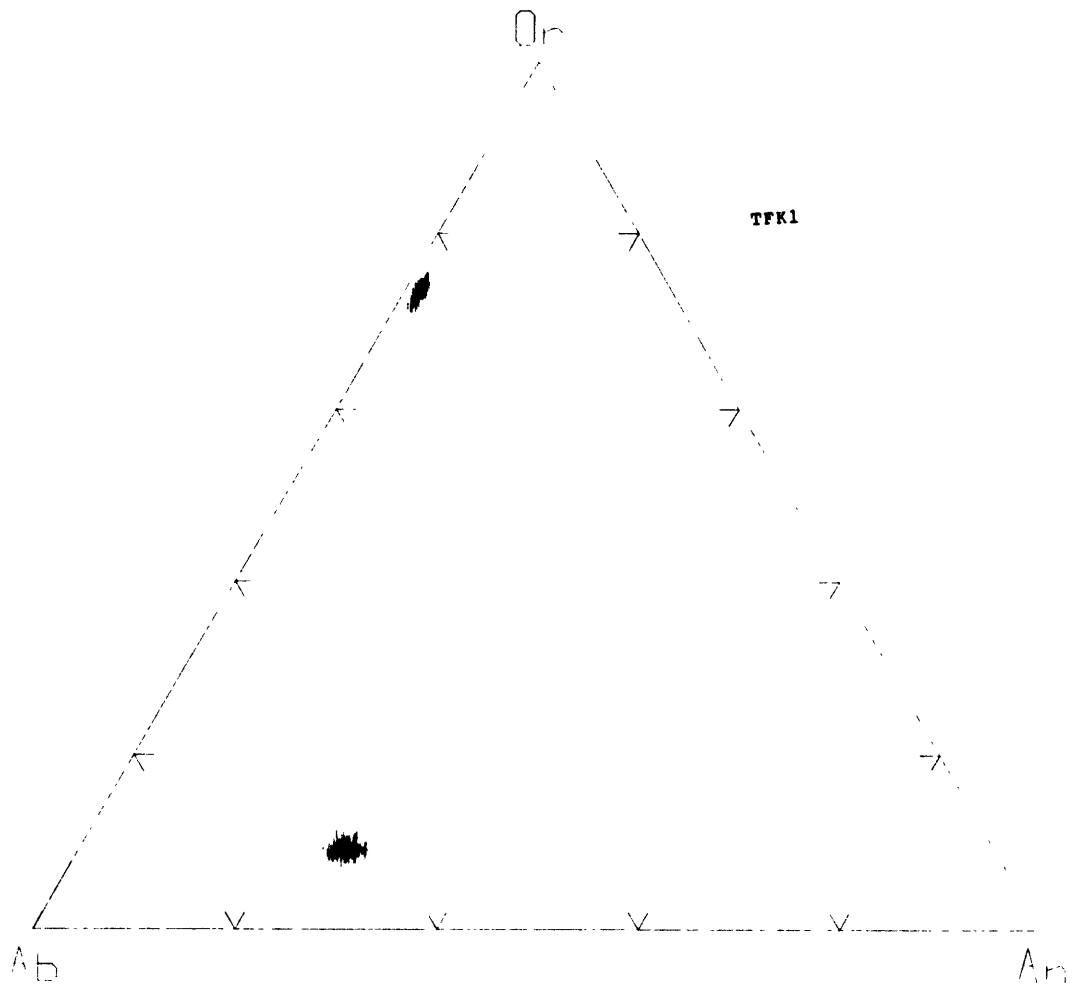


Figure 5-13: Run number TFK1: 1 σ error ellipses based on a Gaussian distribution of points around the alkali feldspar and plagioclase averages.

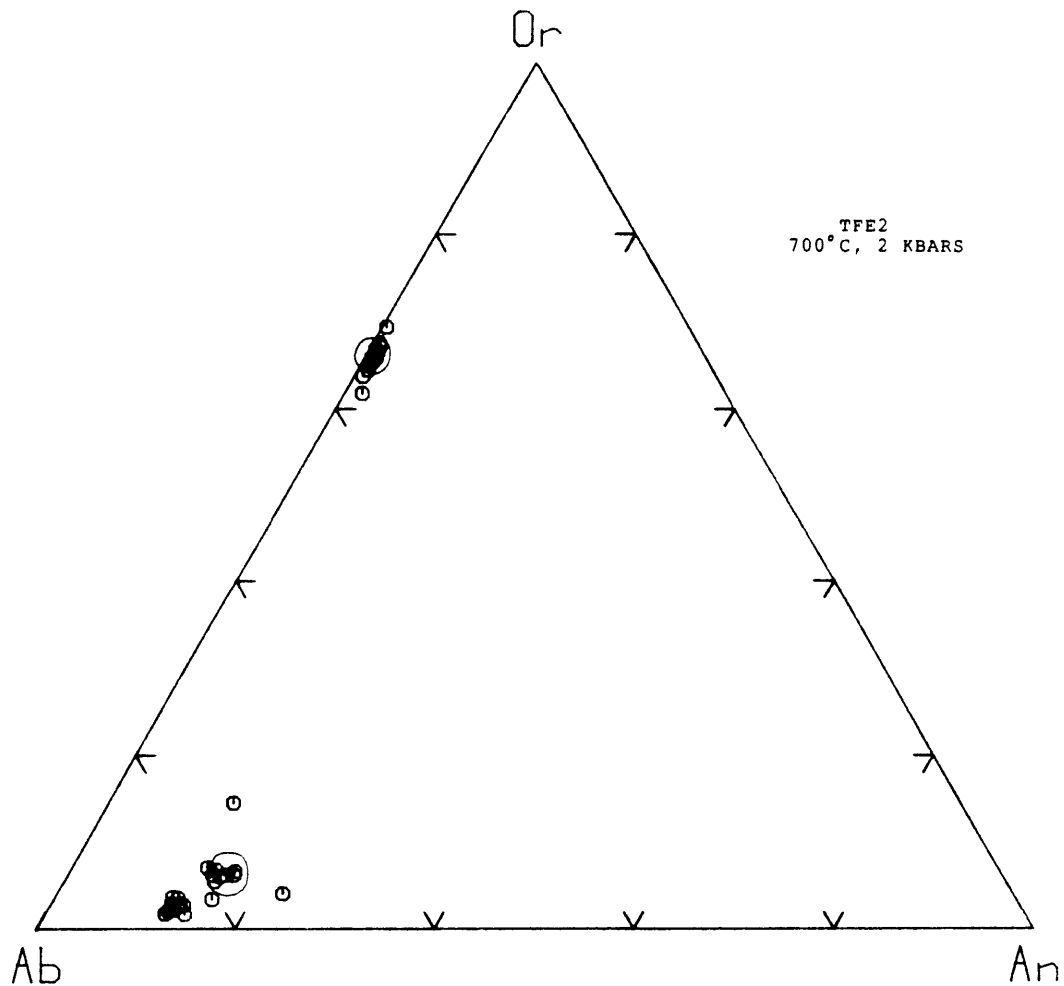


Figure 5-14: Ternary diagram for run number TFE2:
700° C, 115 days. Each point represents one
electron microprobe rim analysis.

Scatter toward the starting materials is seen. The
analyses within the circles were averaged to find the
ternary pair.

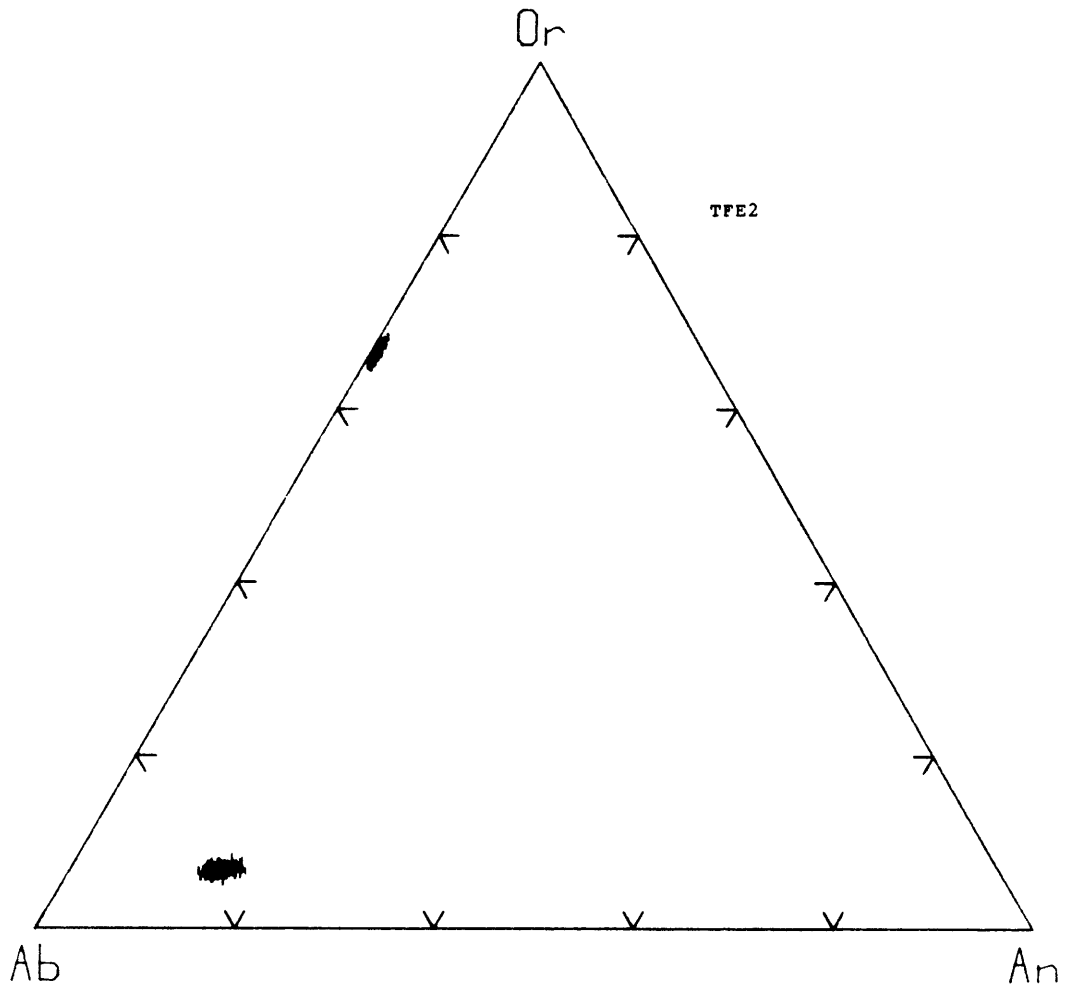


Figure 5-15: Run number TFE2: 1 σ error ellipses based on a Gaussian distribution of points around the alkali feldspar and plagioclase averages.

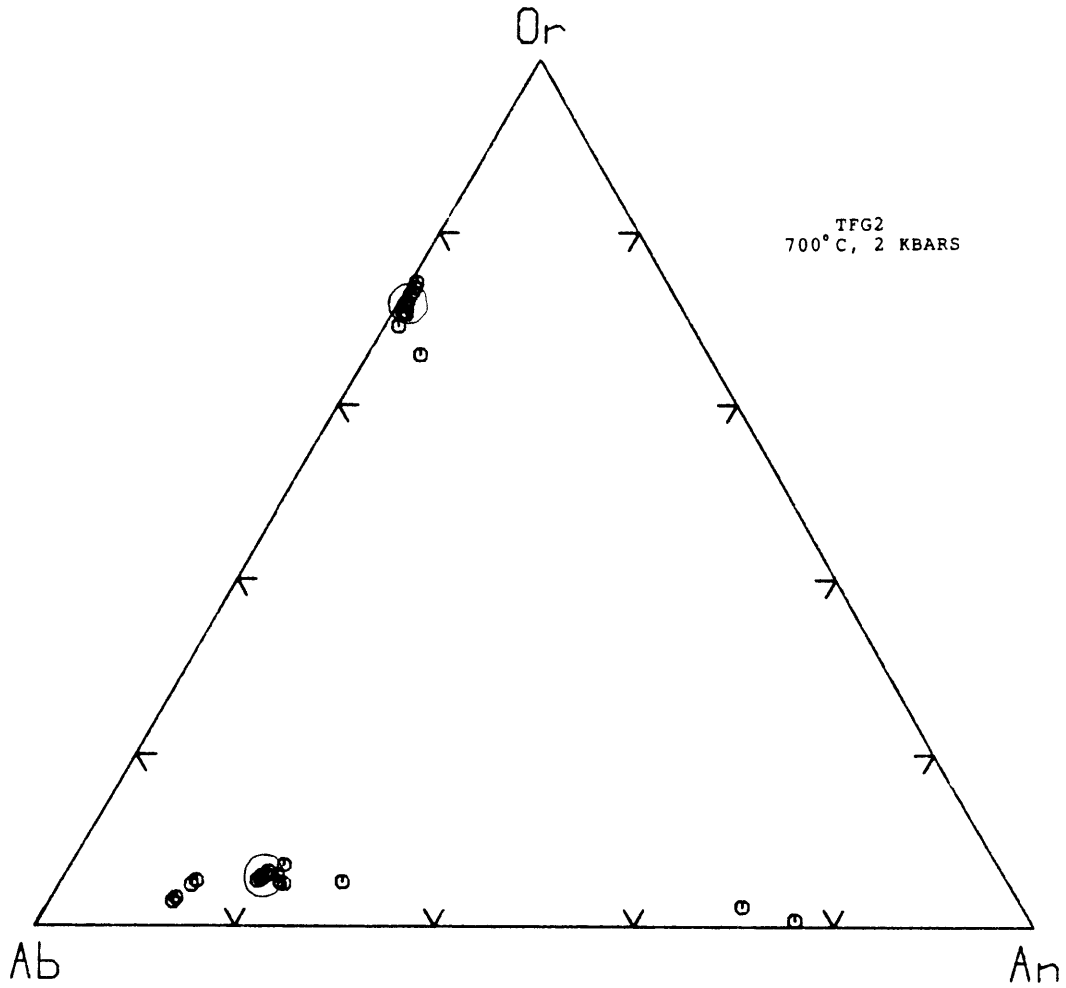


Figure 5-16: Ternary diagram for run number TFG2:
700° C, 115 days. Each point represents one
electron microprobe rim analysis.

Scatter toward the starting materials is seen. The
analyses within the circles were averaged to find the
ternary pair.

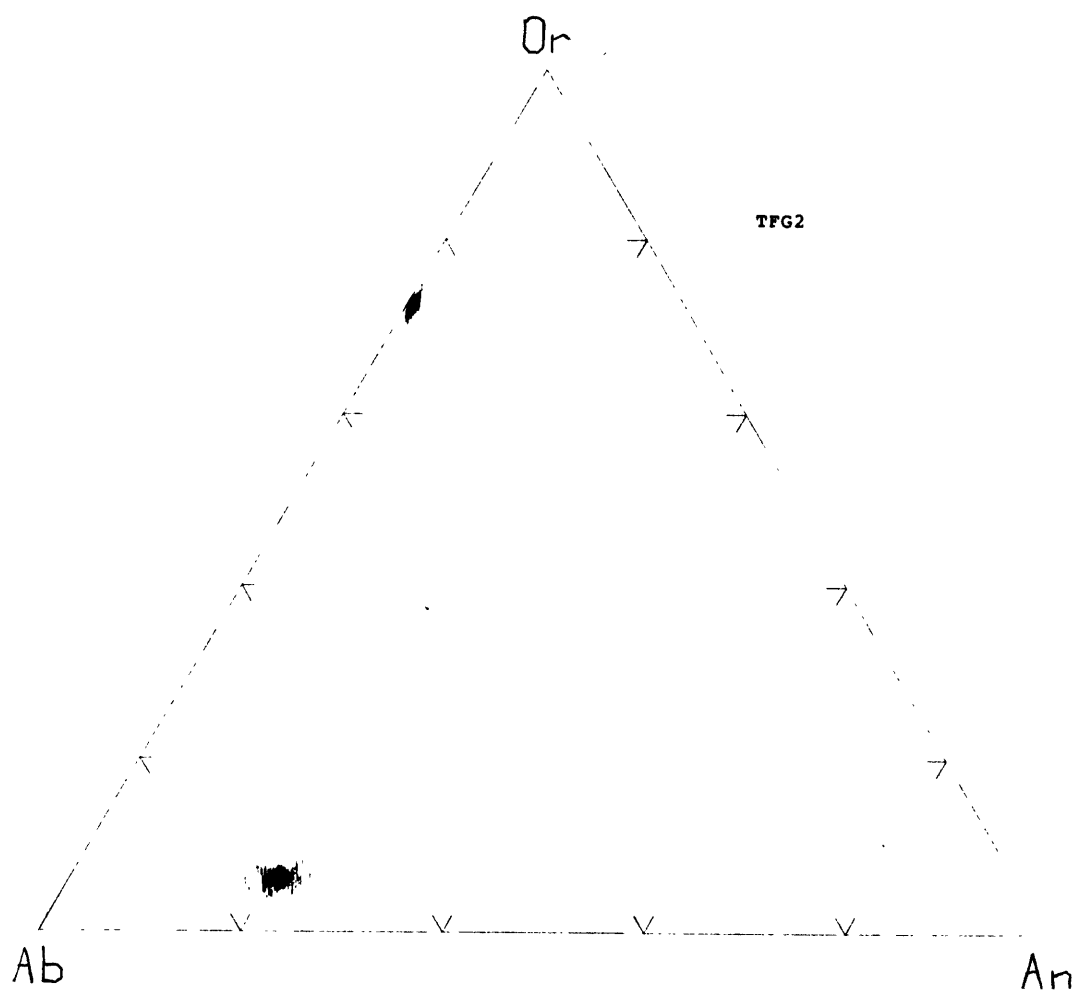


Figure 5-17: Run number TFG2: 1 σ error ellipses based on a Gaussian distribution of points around the alkali feldspar and plagioclase averages.

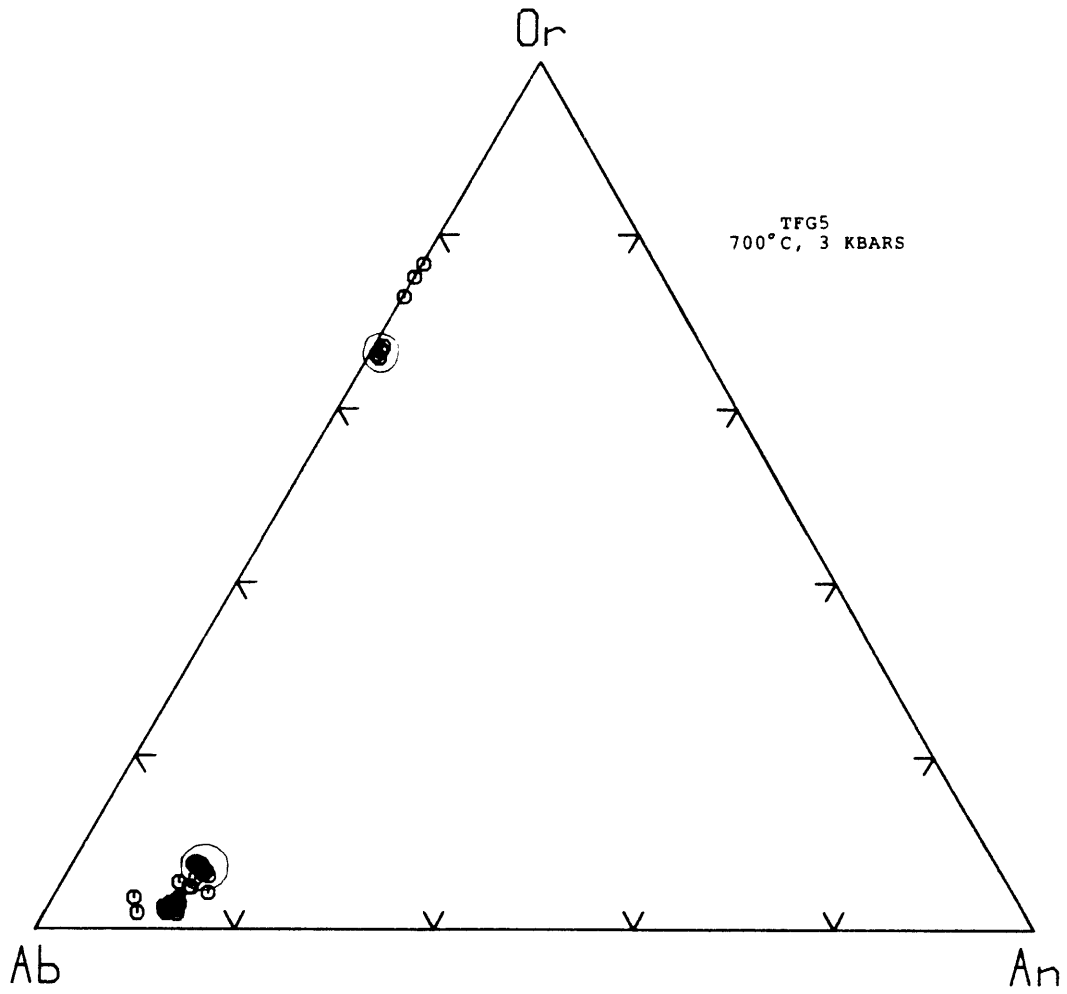


Figure 5-18: Ternary diagram for run number TFG5:
700° C, 3 kbars, 102 days. Each point
represents one electron microprobe rim analysis.
The analyses within the circles were averaged
to find the ternary pairs.

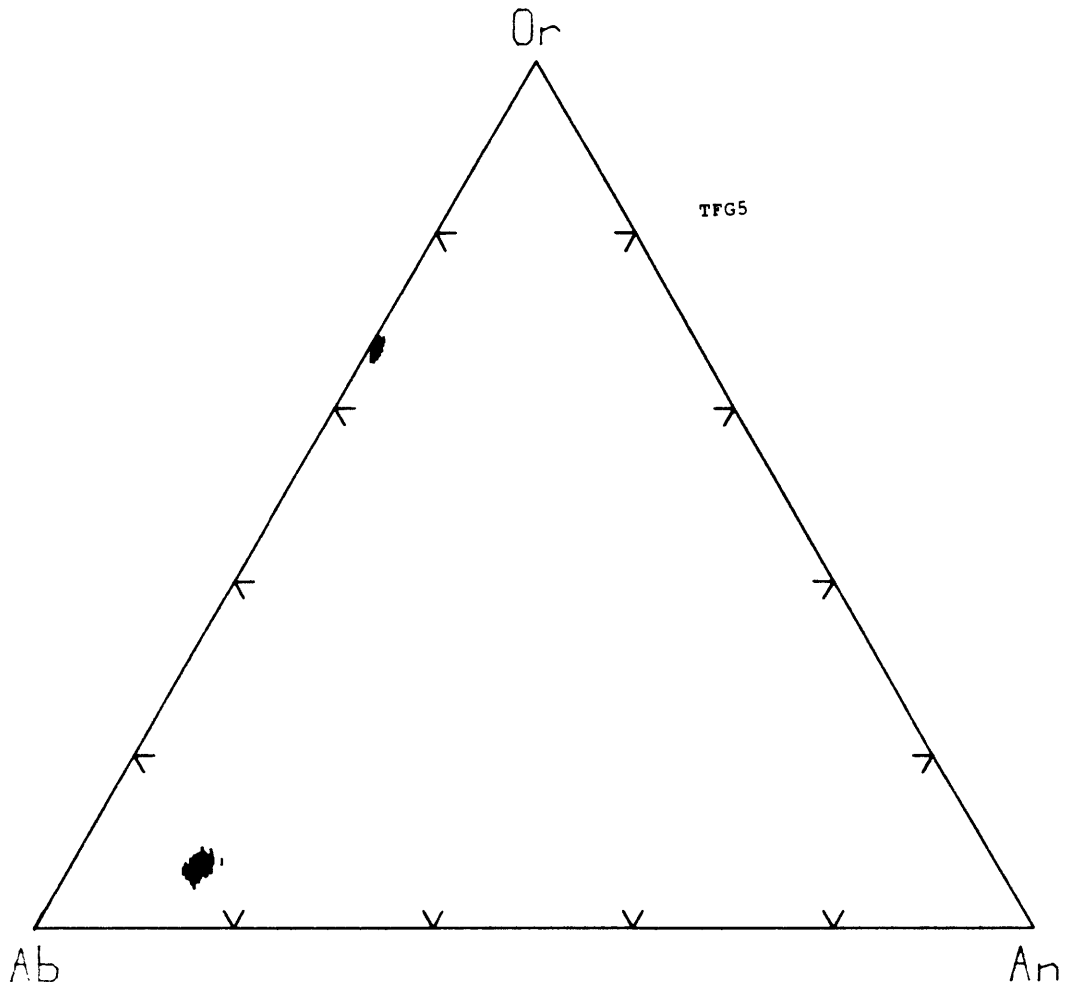


Figure 5-19: Run number TFG5: 1 σ error ellipses based on a Gaussian distribution of points around the alkali feldspar and plagioclase averages.

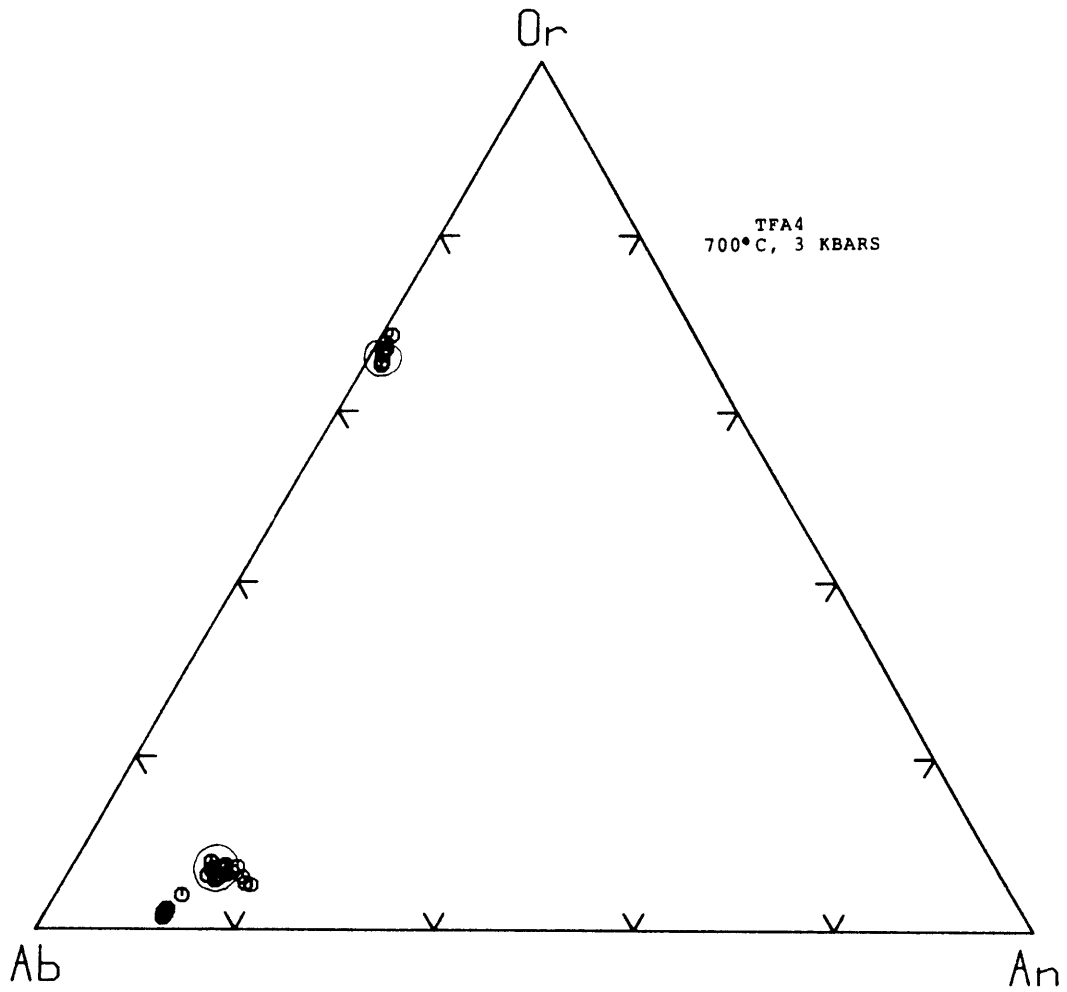


Figure 5-20: Ternary diagram for run number TFA4:
700° C, 3 kbars, 102 days. Each point
represents one electron microprobe rim analysis.
The analyses within the circles were averaged
to find the ternary pairs.

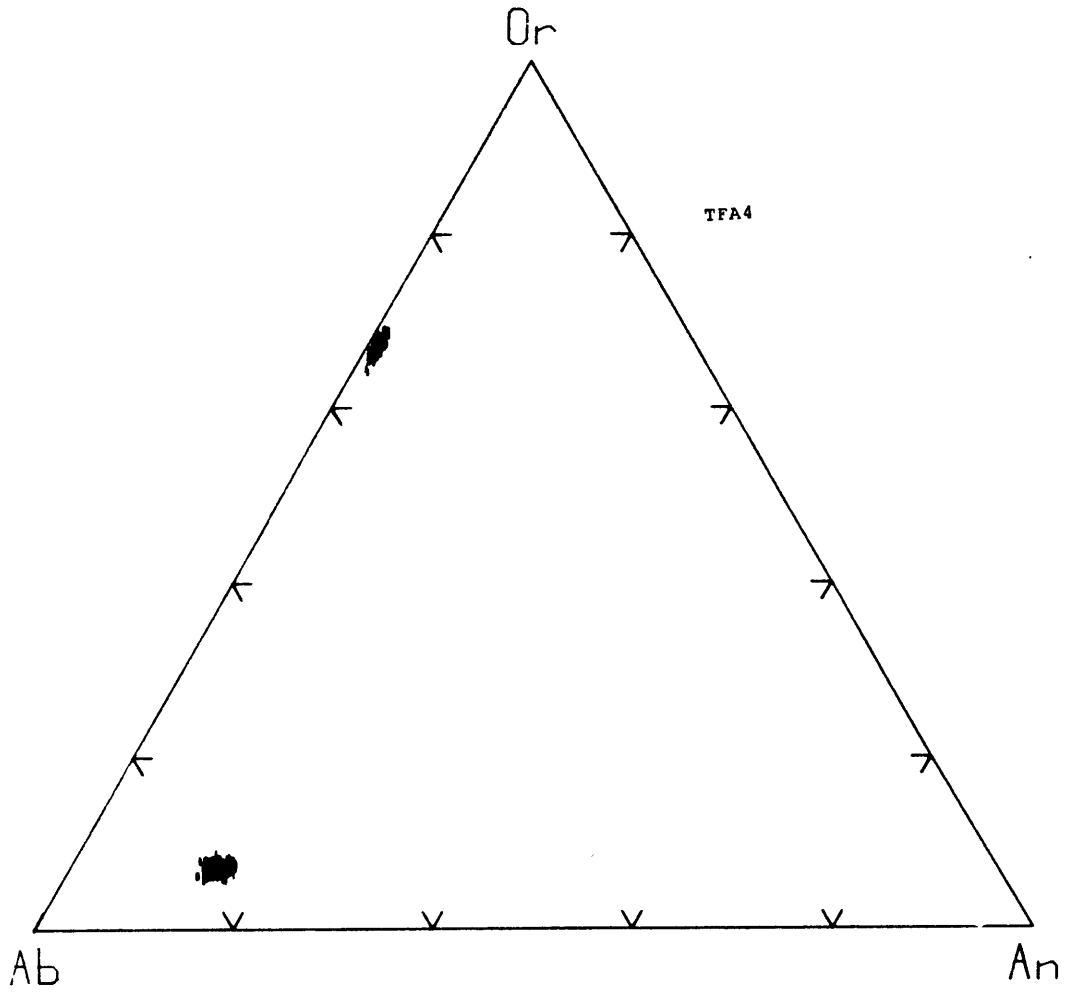
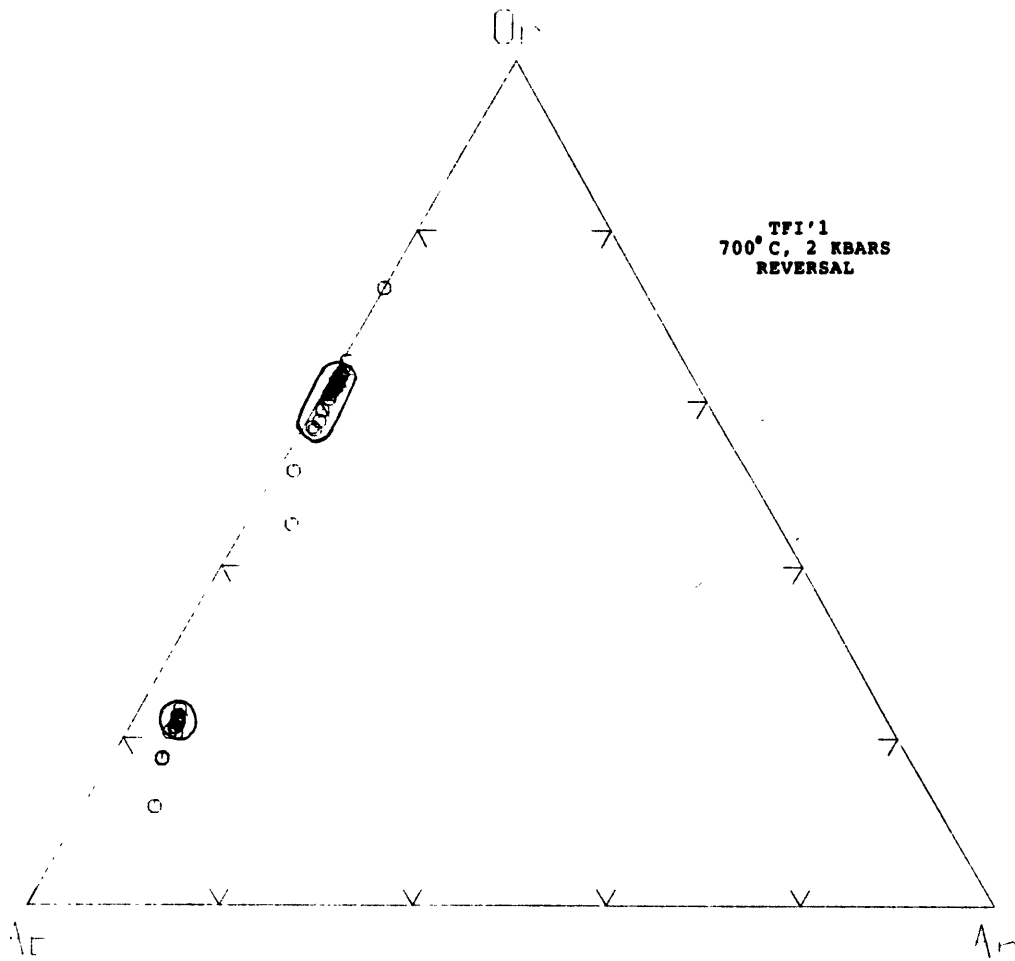


Figure 5-21: Run number TFA4: 1 σ error ellipses based on a Gaussian distribution of points around the alkali feldspar and plagioclase averages.



**Figure 5-22: Ternary diagram for run number TFI'1:
700° C reversal, 119 days. Each point represents
one electron microprobe rim analysis.**

**Some scatter toward the starting materials is seen.
The analyses within the circles were averaged
to find the ternary pair.**

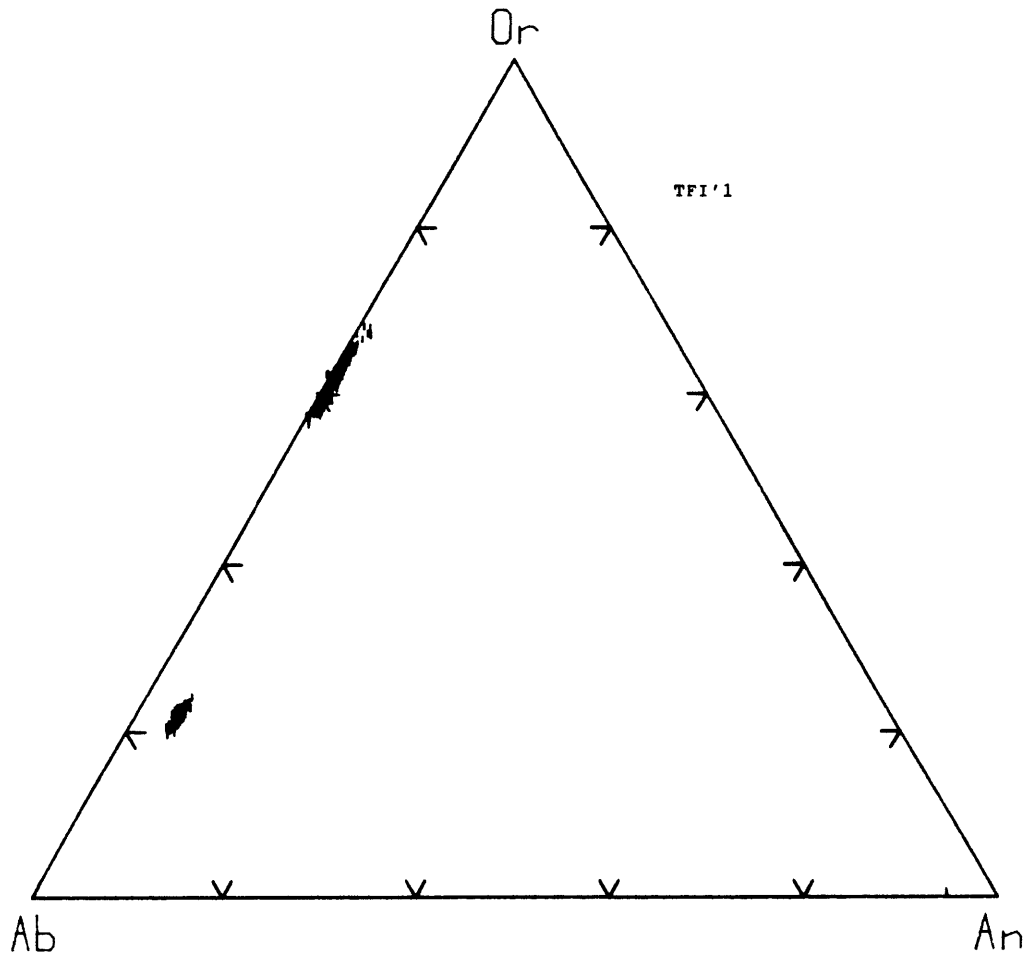


Figure 5-23: Run number TFI'1, reversal: 1 σ error ellipses based on a Gaussian distribution of points around the alkali feldspar and plagioclase averages.

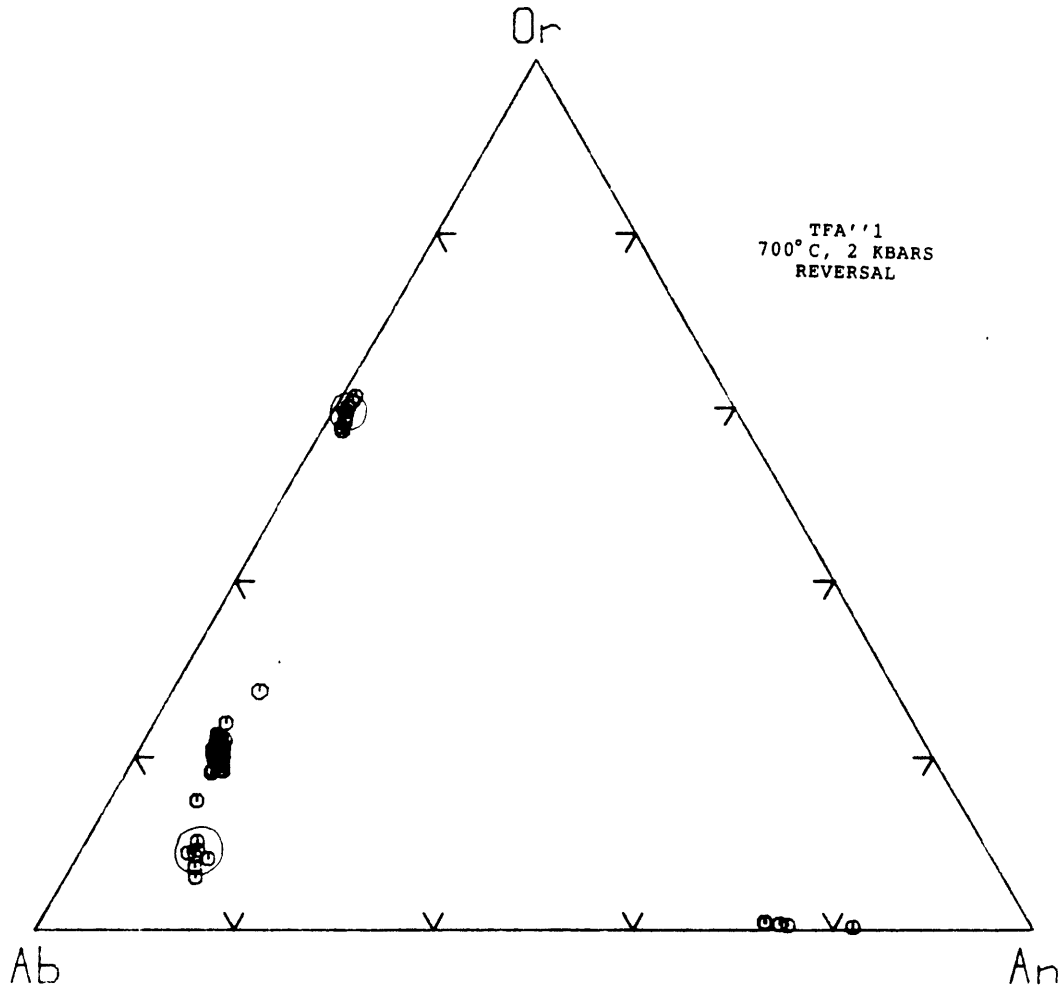


Figure 5-24: Ternary diagram for run number TFA''1: 700° C reversal, 119 days. Each point represents one electron microprobe rim analysis.

A large amount of rim material stayed at the composition of the Kilbourne Hole anorthoclase starting material, but a significant amount also reequilibrated to a ternary alkali feldspar and a ternary plagioclase composition. The analyses within the circles were averaged to find the ternary pair.

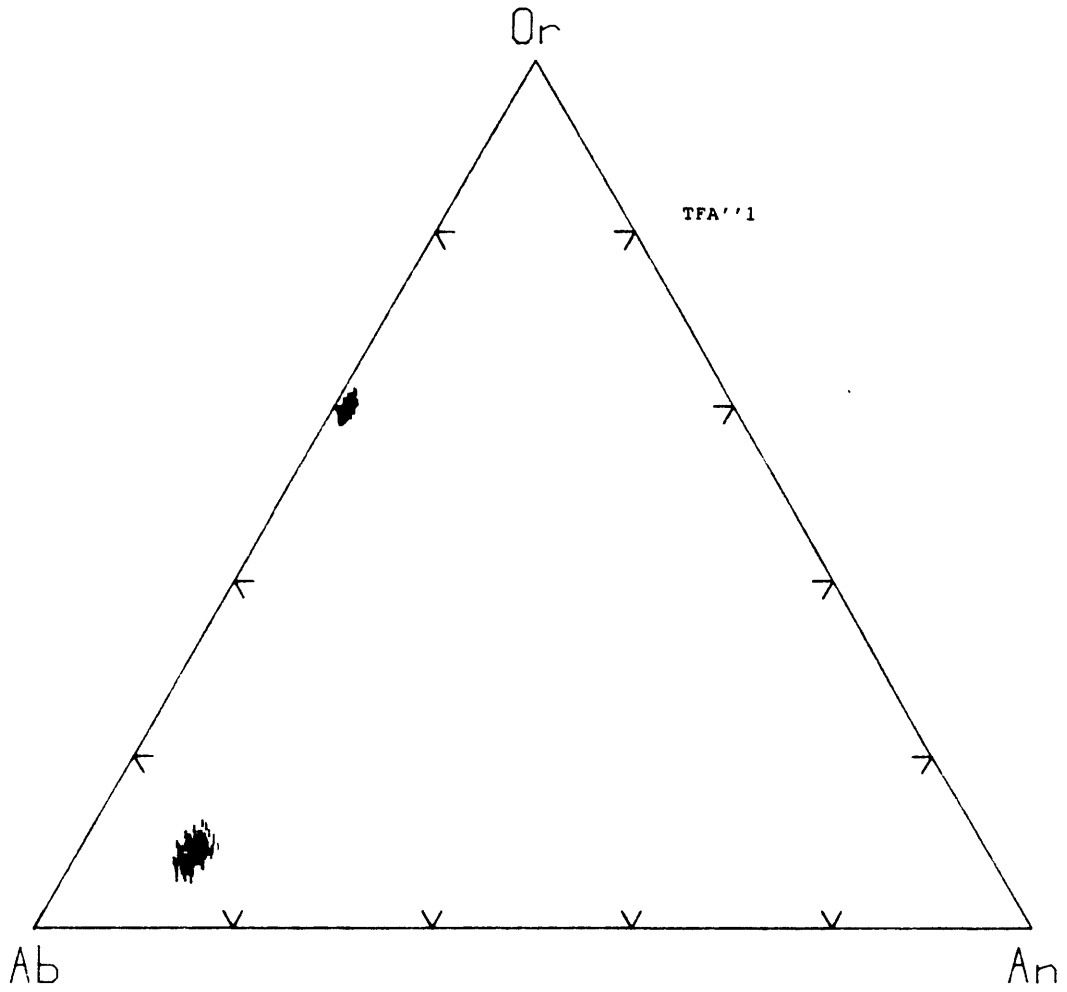


Figure 5-25: Run number TFA''1, reversal: 1 σ error ellipses based on a Gaussian distribution of points around the alkali feldspar and plagioclase averages.

**Table 5-II: Compositions of Averaged Run Products
from Microprobe Analyses**

T, P [°C, kb]	run number, ϕ	CaO	Na ₂ O	K ₂ O	Al ₂ O ₃	SiO ₂	An	Ab	Or
800, 2	TFK1 PL	5.486	7.323	1.516	24.690	60.637	.267	.645	.087
	TFK1 AF	0.359	2.867	12.553	19.192	65.082	.018	.253	.729
	TFL1 PL	6.940	6.775	1.134	25.856	59.102	.338	.596	.066
	TFL1 AF	0.354	2.512	12.849	19.237	65.037	.017	.225	.757
	TFG3 PL	6.905	6.973	1.436	25.669	60.412	.325	.594	.081
	TFG3 AF	0.447	2.626	12.680	19.489	65.923	.022	.234	.744
700, 2	TFG2 PL	4.384	8.436	1.007	23.100	63.380	.210	.732	.058
	TFG2 AF	0.174	3.019	12.090	18.640	64.902	.009	.273	.719
	TFE2 PL	3.254	9.176	1.150	22.131	64.852	.153	.782	.064
	TFE2 AF	0.183	3.728	11.294	18.852	66.007	.009	.331	.660
700, 2 REVERSALS	TFI'1 PL	0.967	8.440	3.782	20.793	66.109	.046	.736	.217
	TFI'1 AF	0.177	4.306	10.436	19.189	65.965	.009	.382	.609
	TFA''1 PL	2.554	9.456	1.506	21.499	65.571	.119	.797	.084
	TFA''1 AF	0.314	4.372	10.050	19.109	65.606	.016	.392	.593
	TFG5 PL	2.775	9.276	1.194	21.745	64.864	.131	.801	.068
	TFG5 AF	0.201	3.538	10.905	18.914	65.302	.010	.327	.663
700, 3	TFA4 PL	3.179	9.069	1.206	22.094	64.917	.152	.780	.068
	TFA4 AF	0.250	3.567	11.286	18.836	66.369	.013	.320	.667

**Table 5-III: Standard Analytical Error of the Mean σ/\sqrt{N}
for Averaged Run Product Oxides**

N is the number of analyses used in the average and
 σ is the standard deviation of the average.

run number	ϕ	N	CaO	Na ₂ O	K ₂ O	Al ₂ O ₃	SiO ₂
TFK1	PL	10	0.081	0.044	0.037	0.041	0.105
TFK1	AF	12	0.016	0.031	0.041	0.029	0.059
TFL1	PL	12	0.088	0.047	0.028	0.082	0.155
TFL1	AF	15	0.020	0.029	0.072	0.056	0.124
TFG3	PL	11	0.090	0.027	0.045	0.088	0.146
TFG3	AF	10	0.026	0.017	0.096	0.037	0.088
TFG2	PL	7	0.071	0.040	0.034	0.090	0.178
TFG2	AF	8	0.015	0.019	0.090	0.059	0.230
TFE2	PL	8	0.078	0.053	0.033	0.141	0.389
TFE2	AF	13	0.009	0.029	0.049	0.060	0.175
TFI'1	PL	11	0.016	0.063	0.040	0.054	0.156
TFI'1	AF	32	0.012	0.071	0.108	0.046	0.098
TFA''1	PL	8	0.069	0.041	0.080	0.072	0.257
TFA''1	AF	8	0.020	0.045	0.117	0.069	0.250
TFG5	PL	11	0.035	0.052	0.036	0.049	0.126
TFG5	AF	6	0.014	0.026	0.047	0.050	0.223
TFA4	PL	12	0.053	0.046	0.034	0.085	0.160
TFA4	AF	7	0.021	0.039	0.095	0.079	0.273

**Table 5-IV: 1 σ Standard Deviations in Weight% Oxide
of Electron Microprobe Analyses
Obtained from Counting Statistics**

Run number	ϕ	CaO	Na ₂ O	K ₂ O	Al ₂ O ₃	SiO ₂
TFK1	PL	0.057	0.090	0.042	0.124	0.115
TFK1	AF	0.017	0.059	0.124	0.096	0.190
TFL1	PL	0.060	0.088	0.039	0.102	0.111
TFL1	AF	0.016	0.054	0.131	0.097	0.190
TFG3	PL	0.089	0.087	0.040	0.102	0.174
TFG3	AF	0.025	0.056	0.127	0.097	0.191
TFG2	PL	0.071	0.093	0.034	0.116	0.118
TFG2	AF	0.018	0.059	0.124	0.095	0.190
TFE2	PL	0.060	0.101	0.037	0.109	0.123
TFE2	AF	0.018	0.064	0.115	0.093	0.125
TFI'1	PL	0.024	0.094	0.066	0.104	0.125
TFI'1	AF	0.012	0.068	0.110	0.096	0.126
TFA''1	PL	0.039	0.102	0.042	0.109	0.123
TFA''1	AF	0.014	0.070	0.113	0.097	0.193
TFG5	PL	0.039	0.127	0.038	0.108	0.121
TFG5	AF	0.012	0.082	0.109	0.094	0.123
TFA4	PL	0.041	0.129	0.038	0.108	0.123
TFA4	AF	0.013	0.081	0.116	0.093	0.015

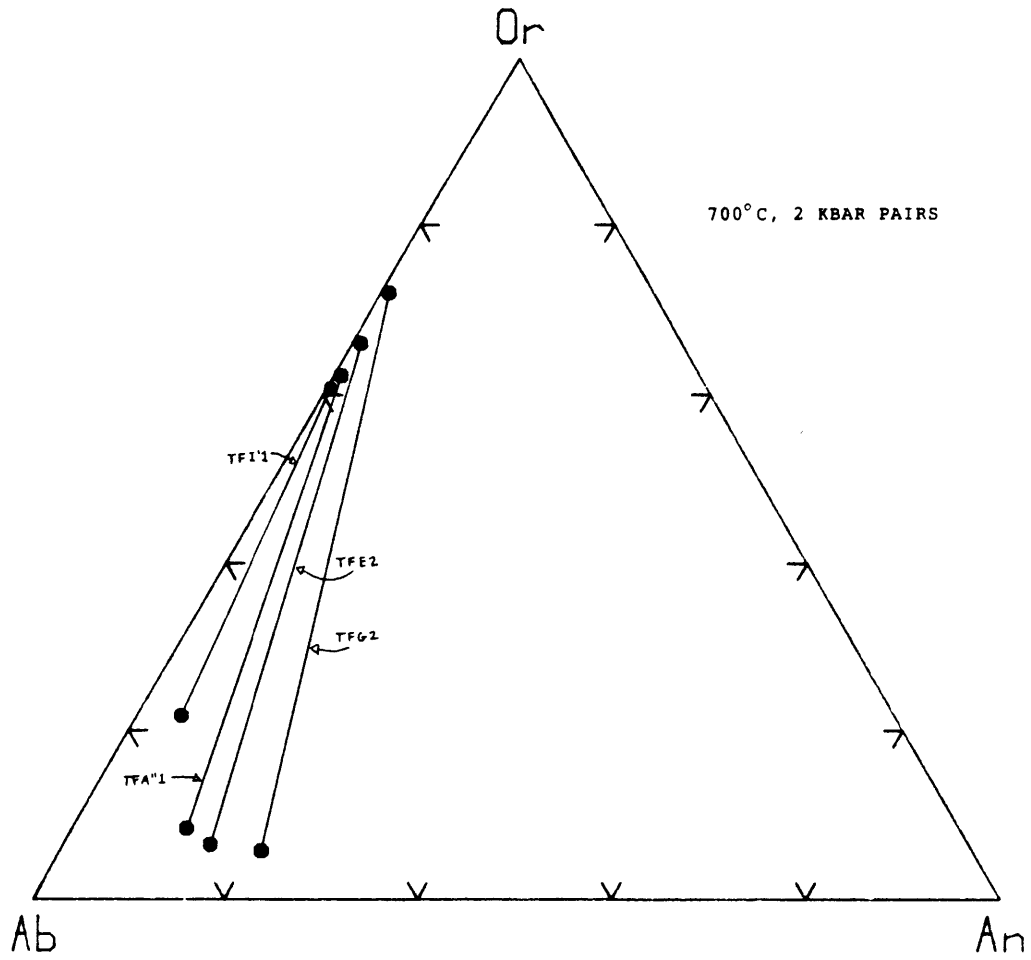


Figure 5-26: Plot of all 700° C, 2 kbar ternary pairs.

The points represent the averaged run products and the tie lines connect the alkali feldspar and plagioclase phases from one experiment.

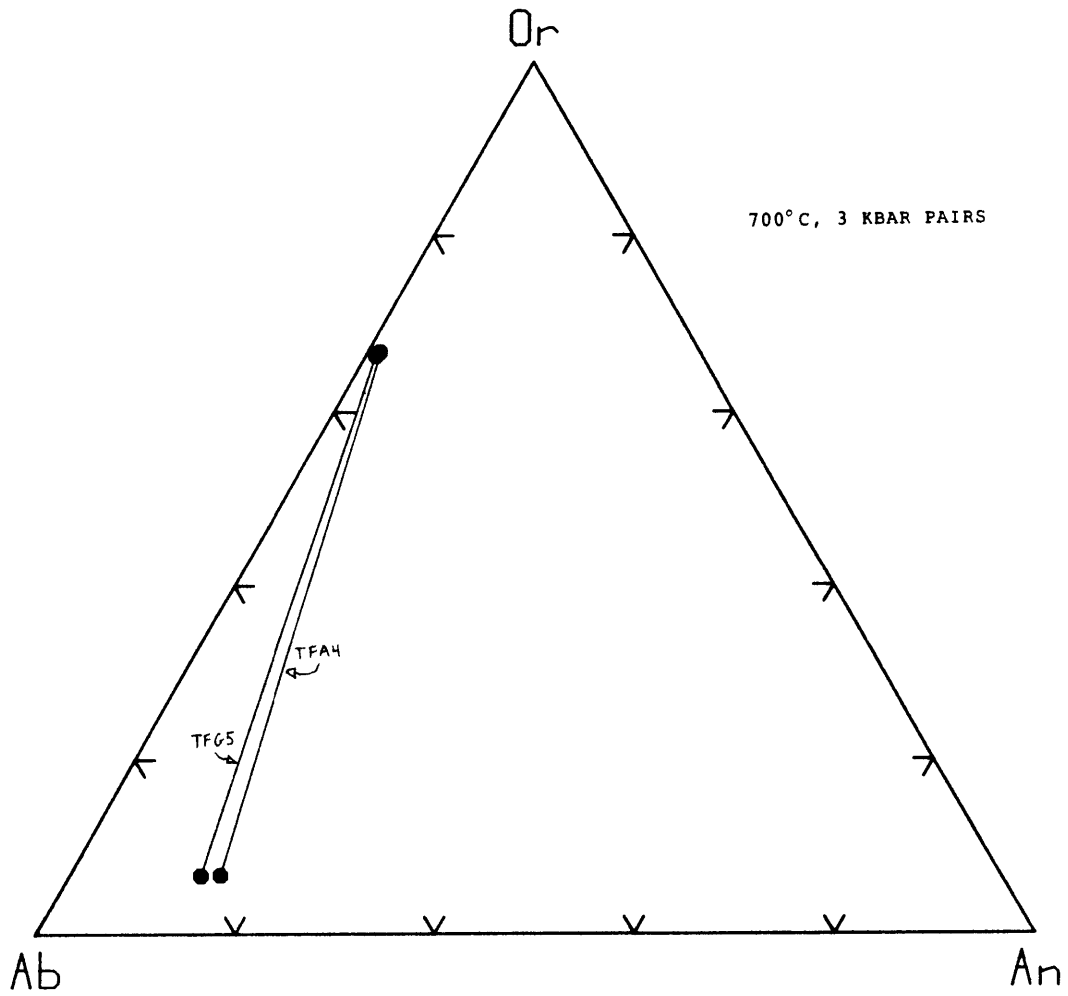


Figure 5-27: Plot of all 700° C, 3 kbar ternary pairs.

The points represent the averaged run products and the tie lines connect the alkali feldspar and plagioclase phases from one experiment.

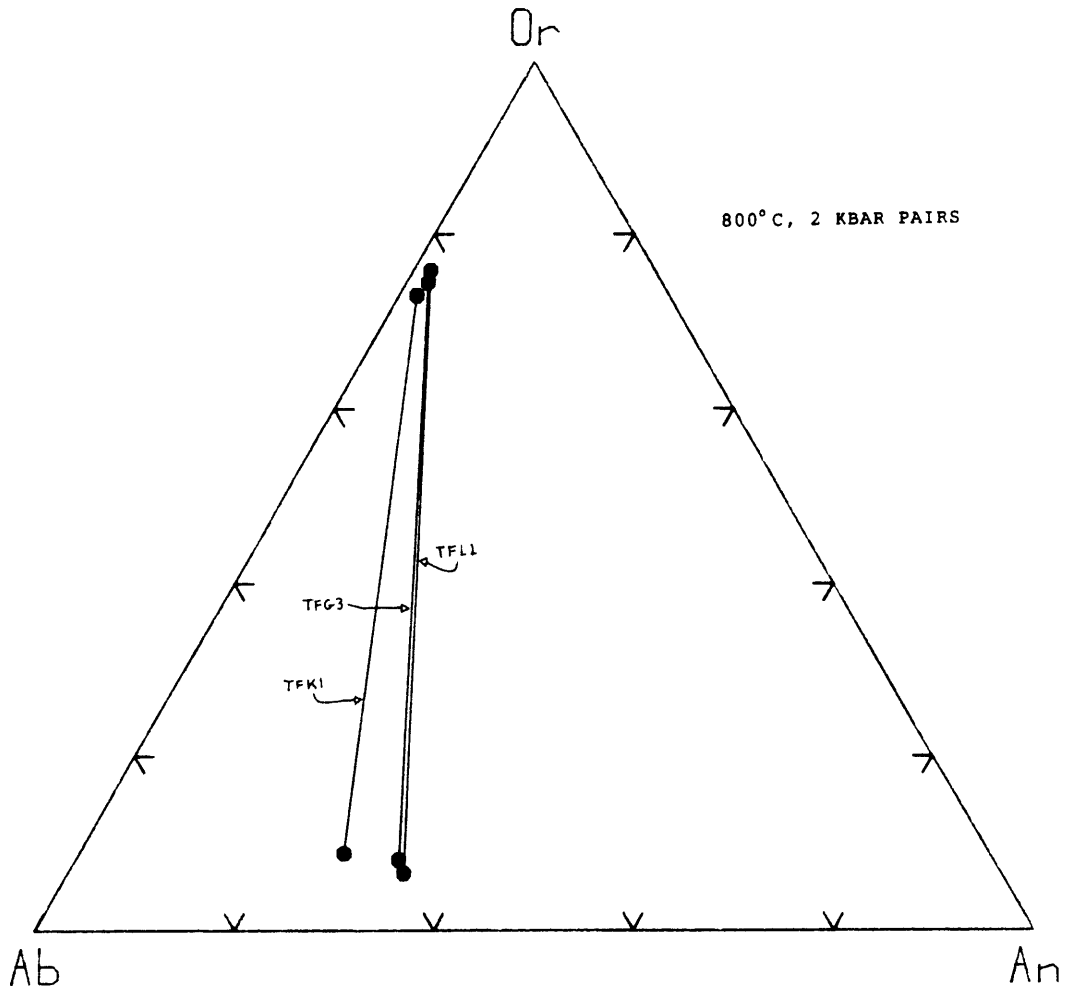


Figure 5-28: Plot of all 800° C, 2 kbar ternary pairs.

The points represent the averaged run products and the tie lines connect the alkali feldspar and plagioclase phases from one experiment.

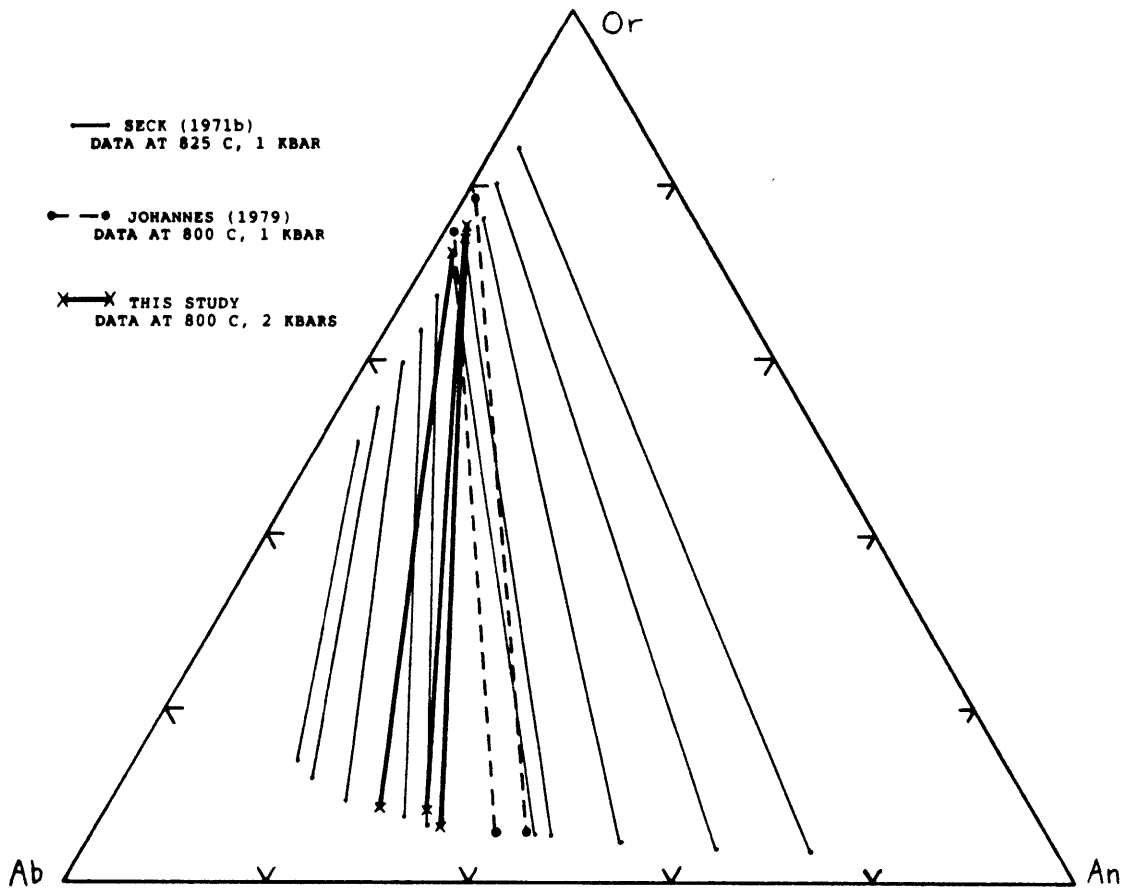


Figure 5-29: Ternary feldspar pairs from this study, from Seck (1971b) and from Johannes (1979), temperatures around 800° C.

Data from this study at 800° C and 2 kbars, data from Seck (1971b) at 825° C and 1 kbar, data from Johannes (1979) at 800° C and 1 kbar.

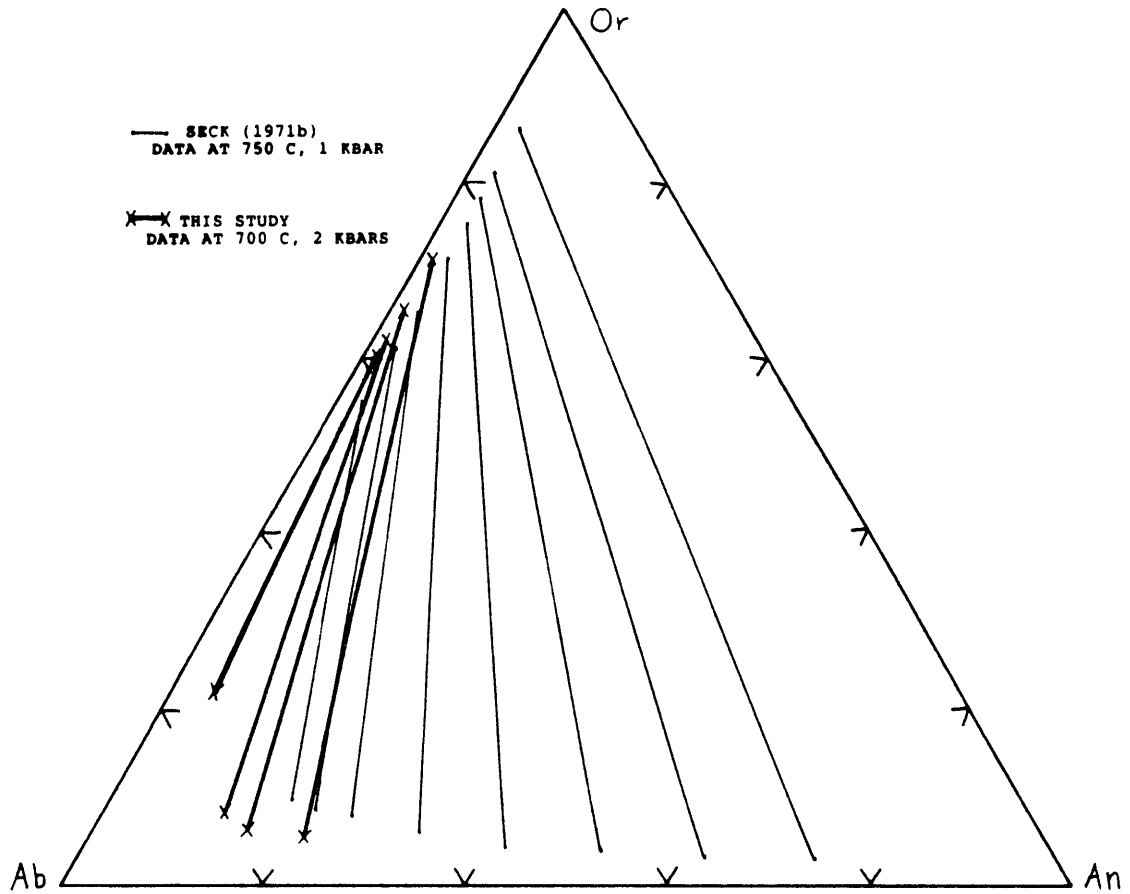


Figure 5-30: Ternary feldspar pairs from this study and from Seck (1971b), temperatures around 700° C.

Data from this study at 700° C and 2 kbars,
data from Seck (1971b) at 750° C and 1 kbar.

Chapter 6

PREVIOUS TERNARY FELDSPAR THERMOMETERS

Beginning with Barth (1951) many ternary feldspar thermometers have been proposed in the literature. Initially they considered only the albite contents of the coexisting alkali feldspar and plagioclase, but beginning with Powell and Powell (1977) attempts were made to take into consideration the anorthite in the alkali feldspar and the potassium feldspar in the plagioclase, the ternary nature of the problem. Many of these thermometers have been calibrated from Seck's (1971a, 1971b) data (Brown and Parsons, 1981; Ghiorso, 1984; Price, 1985; Green and Udansky, 1986a). The thermometers have become consistently more thermodynamically sophisticated and commensurately more complicated, and therefore more sensitive in their calibration to experimental error.

Barth (1951) examined the distribution of albite between alkali feldspars and plagioclases in natural rocks. Barth tabulated rocks containing two feldspars whose temperature of crystallization had been ascertained from other geologic indicators. Using this information, he suggests that albite distributes itself with a constant ratio between the two feldspar phases according to some temperature coefficient, and presents the following relation:

$$K_T = K_1 \exp(-\Delta E/RT)$$

where K is the ratio of distribution of albite between the alkali feldspar and the plagioclase and ΔE is the difference in energy between dissolving one mole of albite in anorthite and dissolving it in orthoclase. Barth chooses 2800 cal/mol for ΔE and constructs a graph of $1000/T$ vs. $\ln K$ using the linear solution to the first equation:

$$\ln K = -1400 (1/T) + .8$$

This was the first feldspar thermometer, and remained more or less unchanged until the 1970s.

Stormer (1975) added a firmer thermodynamic base to the Barth thermometer by using available Margules parameters and by incorporating pressure. The principle limiting assumption used by Stormer and his predecessors is that the potassium content has no effect on the plagioclase phase and the calcium component no effect on the alkali feldspar phase. Using this assumption Stormer derived the following equation, representing Barth's ratio of compositions by activities:

$$u_{ab, PL}^* - u_{ab, AF}^* = RT \ln (a_{ab, AF} / a_{ab, PL})$$

Recognizing that alkali feldspar solutions are non-ideal and therefore $a \neq X$ (where X =mole fraction), Stormer introduced the activity coefficient which relates activity to mole fraction. Stormer continued to treat the plagioclase binary as ideal. He used the Margules parameters of Thompson and Waldbaum (1969) and Waldbaum and Thompson (1969) in his original equation to create the following equation:

$$\ln K_{D, ab} = \ln \gamma_{ab, AF} = - (1/RT) (1 - X_{ab, AF})^2 \{ W_G^{ab} - 2X_{ab, AF} (W_G^{or} - W_G^{ab}) \}$$

After substituting the Margules functions of pressure and temperature, Stormer made a series of isobaric graphs of albite in plagioclase vs. albite in alkali feldspar showing temperature curves. In shape, these curves roughly agree with Seck's data.

In 1977 Whitney and Stormer modified the thermometer of Stormer (1975) to account for variation in the structural states of the feldspar. They did this by incorporating appropriate Margules parameters from previous experimental work. Since data for low albite was still lacking, Whitney and Stormer continued to treat low albite as ideal but otherwise treated feldspar solutions as non-ideal. The equations from Stormer (1975) are recast with new Margules parameters from Bachinski and Muller (1971).

Powell and Powell (1977) used a formulation thermodynamically identical to Stomer's (1975) model, but used the mole fractions $X_{ab,AF}$, $X_{ab,PL}$ and $X_{or,AF}$ in an attempt to take into consideration the anorthite content of alkali feldspar. Thus in their model anorthite and orthoclase play the same role in plagioclase, but anorthite is effectively treated as a vacancy in alkali feldspar. Brown and Parsons (1981) state that Powell and Powell's graphical results have no range of practical application because their high anorthite contents do not represent any naturally occurring feldspar pairs.

Feeling that the feldspar thermometers to date had neglected to accommodate the existing experimental data correctly, Brown and Parsons (1981) reviewed experimental determinations of relationships in the ternary system and presented a correct general graphical feldspar thermometer form. They started from the general form of Seck's thermometer. They inserted a polythermal curve representing the binary alkali feldspar solvus of Smith and Parsons (1974) to Seck's $X_{ab,PL}$ vs. $X_{ab,AF}$ plot. At or above the critical temperature on the binary solvus all isotherms must terminate on the solvus. Secondly, they note that isotherms on such a graph must become tangential to the $K_D=1$ line for compositions poor in albite, mirroring tie lines in the ternary system. Brown and Parsons point out the necessity of knowing both binary and ternary Margules parameters to a high level of accuracy before an acceptable thermodynamic thermometer can be formulated.

As described in the previous experimental studies chapter, Haselton et al (1983) performed their calorimetric investigation of excess entropy in the albite-sanidine binary and obtained a symmetrical entropy curve. They recast this data in the Margules parameters B_S and C_S of Thompson (1967). They combine their data with the high plagioclase excess terms of Newton et al (1980) and formulate a ternary thermometer in the style of Powell and Powell (1977). While their thermometer does not treat plagioclase as ideal, the model is still subject to the problems of treating the system as a double binary. No thermometer can be accurate without ternary interaction terms.

Ghiorso (1984) calibrated a feldspar thermometer using the ternary data of Seck (1971a, 1971b). He used regular asymmetric solution models for the excess free energy of mixing in the binaries and the Kerrick and Darken (1975) Al-avoidance model for the configurational entropy of mixing. As in other thermodynamic thermometers of the Brown and Parsons (1981) style, published Margules parameters for the albite-anorthite and albite-orthoclase binaries are incorporated as limiting cases. Ghiorso selected the data of Thompson and Hovis (1979) for the albite-orthoclase binary and Newton et al (1980) for the albite-anorthite binary. He satisfies heterogeneous equilibrium with the three equations of the form $a_{ab,AF} = a_{ab,PL}$ and substitutes Margules parameters and mole fraction expressions for the activities. The unknowns left are the Margules excess terms for the anorthite-orthoclase binary, $W_{or,an}$ and $W_{an,or}$, and the ternary Margules term $W_{an,ab,or}$. Ghiorso uses a least squares method to determine these unknowns at the four specific temperatures at which Seck ran experiments. The solutions to the unknowns can then be recast into functions of temperature. Ghiorso notes that his model fits Seck's data more closely at higher temperatures and attributes this to the run products' closer approach to equilibrium at those temperatures.

Price (1985) used a statistical thermodynamics approach to treat mixing on structural sites. His formulation differs from those of Kerrick and Darken (1975) in that mole fractions of "components" (generally ions or atoms on sites) rather than mole fractions of end members (such as $CaAl_2Si_2O_8$) are used in the expression of the ideal contribution to activity. Price claims that his expression is correct for ternary contributions, while Kerrick and Darken's (1975) is only correct in the binaries. Price uses his data plus that of a number of other binary and ternary experiments, including Seck (1971a, 1971b), Smith and Parsons (1974) and Hovis and Waldbaum (1977) to derive activity vs. composition relations for albite in alkali feldspar in a manner similar to Haselton et al (1983). Price substitutes his own rather than Kerrick and Darken's (1975) expression for the ideal

contribution to activity. He then equates formulas for $a_{ab,AF}$ and $a_{ab,PL}$ and recasts the result into an expression for temperature. This thermometer achieves a better fit with Seck's data than did Haselton et al (1983).

Green and Usdansky (1986a) estimate the excess Gibbs free energy of mixing functions for the anorthite-orthoclase binary using the published Margules parameters for the anorthite-albite binary (Newton et al, 1980), the albite-orthoclase binary (Haselton et al, 1983) and Seck's (1971a, 1971b) ternary data. The three binary excess terms are combined with Price's (1985) ternary ideal activity terms and cast into a ternary thermometer. This approximates the ideal thermodynamic thermometer suggested by Brown and Parsons (1981) except that the ternary excess terms are set equal to zero. Like Ghiorso (1984), this feldspar thermometer considers all three components and not just albite. To calculate conditions of equilibrium, the authors calculate the pressure-temperature variation of the anorthite, albite and orthoclase exchange reactions, determine the intersection(s) of the univariant curves, and compute the centroid of the intersection in terms of temperature and pressure. They found this method preferable to the iterative least-squares method of minimizing residuals in activity equations used by Ghiorso (1984). While they recognize that its accuracy is limited by the accuracy of Seck's data, the authors feel that this represents the correct formulation of a thermobarometer.

Chapter 7

DATA ANALYSIS

With ideal mixing, the Gibbs free energy of solution can be modelled as

$$G_{sol} = G_{mmix} - T\Delta S_{cmix} \quad (1)$$

where G_{mmix} is the ideal Gibbs free energy of mechanical mixing and $-T\Delta S_{cmix}$ is the change in energy due to ideal chemical site mixing. To obtain the ΔS_{cmix} term the Al-avoidance entropy model of Kerrick and Darken (1975) will be used. Their method results in the equation:

$$\begin{aligned} \Delta S_{cmix} = & -R(X_{ab} \ln [X_{ab} (1 - X_{an}^2)] \\ & + X_{or} \ln [X_{or} (1 - X_{an}^2)] \\ & + X_{an} \ln [X_{an} (1 - X_{an})^2 / 4] \end{aligned} \quad (2)$$

In the feldspar system none of the solutions can be accurately modelled as ideal, so excess terms free energy terms which account for deviation from ideality must be calibrated from experimental data. Equation 1 then takes on this form:

$$G_{sol} = G_{mmix} - T\Delta S_{cmix} + G^{ex} \quad (3)$$

where G^{ex} is the excess free energy.

A commonly used approximation of the excess free energy is the Margules equation. The Margules equation assumes that the excess free energy can be approximated by a power series expansion in terms of composition. The Margules equation describes an asymmetric regular binary solution as follows:

$$G_{A,B}^{ex} = W_{A,B} X_A X_B^2 + W_{B,A} X_A^2 X_B \quad (4)$$

where X_A and X_B refer to mole fractions of end members A and B and W is the Margules interaction term.

To form an accurate thermodynamic feldspar thermometer excess free energy data is needed for each of the three binaries and the ternary system. Presently there is good experimental data available for the anorthite-albite and the albite-orthoclase binaries but not for the anorthite-orthoclase binary. Equations can be formed which allow the anorthite-orthoclase Margules terms and the ternary Margules terms to be solved for as unknowns.

Margules excess terms for the three binaries can be combined to generate an expression for the excess free energy of the solid solution in the ternary system. Anderson and Lindsley (1981) discussed a method which allows the incorporation of ternary excess terms and results in the following equation for G^{ex} :

$$\begin{aligned}
 G^{ex} = & W_{ab,an} X_{ab} X_{an} (X_{an} + .5X_{or}) + W_{an,ab} X_{ab} X_{an} (X_{ab} + .5X_{or}) \\
 & + W_{ab,or} X_{ab} X_{or} (X_{or} + .5X_{an}) + W_{or,ab} X_{ab} X_{or} (X_{ab} + .5X_{an}) \\
 & + W_{or,an} X_{or} X_{an} (X_{an} + .5X_{ab}) + W_{an,or} X_{or} X_{an} (X_{or} + .5X_{ab}) \\
 & + W_{ab,or,an} X_{ab} X_{an} X_{or} + W_v P X_{ab} X_{or} \quad (5)
 \end{aligned}$$

$W_{ab,an}$, $W_{an,ab}$, $W_{ab,or}$ and $W_{or,ab}$ are known, and $W_{an,or}$, $W_{or,an}$ and $W_{ab,or,an}$ are not well known. Ghiorso (1984) found the ternary Margules term, $W_{ab,or,an}$, to be relatively insignificant compared to the Margules terms for the anorthite-orthoclase binary. The ternary feldspar pair data from this study will be used to solve for the remaining unknowns: $W_{an,or}$ and $W_{or,an}$, the Margules terms in the anorthite-orthoclase binary, following the method of Ghiorso (1984).

For any two coexisting feldspars the conditions for equilibrium are that the chemical potentials of the ternary components are equal in coexisting plagioclase and alkali feldspar pairs, as follows:

$$\mu_{ab, AF} = \mu_{ab, PL} \quad (6a)$$

$$\mu_{an, AF} = \mu_{an, PL} \quad (6b)$$

$$\mu_{or, AF} = \mu_{or, PL} \quad (6c)$$

or, equivalently,

$$\mu_{ab, PL} = \mu_{ab, PL}^{\circ} - RT \ln a_{ab, PL} \quad (7a)$$

$$\mu_{ab, AF} = \mu_{ab, AF}^{\circ} - RT \ln a_{ab, AF} \quad (7b)$$

$$\mu_{an, PL} = \mu_{an, PL}^{\circ} - RT \ln a_{an, PL} \quad (7c)$$

$$\mu_{an, AF} = \mu_{an, AF}^{\circ} - RT \ln a_{an, AF} \quad (7d)$$

$$\mu_{or, PL} = \mu_{or, PL}^{\circ} - RT \ln a_{or, PL} \quad (7e)$$

$$\mu_{or, AF} = \mu_{or, AF}^{\circ} - RT \ln a_{or, AF} \quad (7f)$$

Substituting equations 7a, b, c, d, e and f into 6a, b and c the following equations are obtained:

$$\Delta \mu = \mu_{ab, AF}^{\circ} - \mu_{ab, PL}^{\circ} = RT \ln (a_{ab, PL} / a_{ab, AF}) \quad (8a)$$

$$\Delta \mu = \mu_{an, AF}^{\circ} - \mu_{an, PL}^{\circ} = RT \ln (a_{an, PL} / a_{an, AF}) \quad (8b)$$

$$\Delta \mu = \mu_{or, AF}^{\circ} - \mu_{or, PL}^{\circ} = RT \ln (a_{or, PL} / a_{or, AF}) \quad (8c)$$

We will assume the standard states of plagioclase and alkali feldspar are the same, hence $\Delta \mu = 0$. This assumption is probably acceptable over the temperature range of the experiments, limited to plagioclases more albite rich than Ab₆₀. Solving the Darken equation:

$$RT \ln a_i = -T \Delta S_{cmix} + G^{ex} + (1 - X_i) \left((-T \Delta S_{cmix} + G^{ex}) / X_i \right) \quad (9)$$

T, P, X_k/X_j

in turn for albite, anorthite and orthoclase generates analytical expressions for their activities. After substituting the equations for G^{ex} and ΔS_{cmix} the following three equations are obtained:

$$\begin{aligned}
 a_{ab} &= x_{ab} (1 - x_{an}^2) \\
 &\exp\{ [W_{ab,or} [x_{or}^2 (1 - 2x_{ab}) + x_{or} x_{an} (.5 - x_{ab})] \\
 &\quad + W_{or,an} [2x_{ab} x_{or}^2 + x_{or} x_{an} (.5 + x_{ab})] \\
 &\quad + W_{ab,an} [x_{an}^2 (1 - 2x_{ab}) + x_{or} x_{an} (.5 - x_{ab})] \\
 &\quad + W_{an,ab} [2x_{ab} x_{an}^2 + x_{or} x_{an} (.5 + x_{ab})] \\
 &\quad + W_{or,an} [x_{or} x_{an} (-.5 - x_{an} + x_{or})] \\
 &\quad + W_{an,or} [x_{or} x_{an} (-.5 - x_{or} + x_{an})] \\
 &\quad + W_v P x_{or}^2 (1 + x_{an})] / RT \} \tag{10a}
 \end{aligned}$$

$$\begin{aligned}
 a_{or} &= x_{or} (1 - x_{an}^2) \\
 &\exp\{ [W_{ab,or} [2x_{ab}^2 x_{or} + x_{ab} x_{an} (.5 + x_{or})] \\
 &\quad + W_{or,ab} [x_{ab}^2 (1 - 2x_{or}) + x_{ab} x_{an} (.5 - x_{or})] \\
 &\quad + W_{ab,an} [x_{ab} x_{an} (-.5 - x_{an} + x_{ab})] \\
 &\quad + W_{an,ab} [x_{ab} x_{an} (-.5 - x_{ab} + x_{an})] \\
 &\quad + W_{or,an} [x_{an}^2 (1 - 2x_{or}) + x_{ab} x_{an} (.5 - x_{or})] \\
 &\quad + W_{an,or} [2x_{or} x_{an}^2 + x_{ab} x_{an} (.5 + x_{or})] \\
 &\quad + W_v P x_{ab} (x_{ab} + x_{an})] / RT \} \tag{10b}
 \end{aligned}$$

$$\begin{aligned}
 a_{an} &= .25x_{an} (1 + x_{an})^2 \\
 &\exp\{ [W_{ab,or} [x_{ab} x_{or} (-.5 - x_{or} + x_{ab})] \\
 &\quad + W_{or,ab} [x_{ab} x_{or} (-.5 - x_{ab} + x_{or})] \\
 &\quad + W_{ab,an} [2x_{ab}^2 x_{an} + x_{ab} x_{or} (.5 + x_{an})] \\
 &\quad + W_{an,ab} [x_{ab}^2 (1 - 2x_{an}) + x_{ab} x_{or} (.5 - x_{an})] \\
 &\quad + W_{or,an} [2x_{or}^2 x_{an} + x_{ab} x_{or} (.5 + x_{an})] \\
 &\quad + W_{an,or} [x_{or}^2 (1 - 2x_{an}) + x_{ab} x_{or} (.5 - x_{an})] \\
 &\quad + W_v P x_{an} (1 + x_{an})^2] / RT \}
 \end{aligned}$$

$$-W_v \text{ P X}_{ab} \text{ X}_{or} / \text{RT} \quad (10c)$$

These are substituted into equations 6a through 6c, the conditions for heterogeneous equilibrium. After substitution the equations may be simplified to the form:

$$k_i = a_i W_{or, an} + b_i W_{an, or} \quad (11)$$

where $i=3$ (there is a separate equation for the conditions of equilibrium for anorthite, albite and orthoclase) and k_i , a_i , b_i and are known functions of the temperature, pressure and compositions of the coexisting feldspars. A least squares technique is then used to solve for the two unknowns $W_{an, or}$ and $W_{or, an}$ at each ternary experimental temperature. There are more than one pair of equilibrium feldspars at any given temperature and there are three final equations in the form of equation 11, so the number of equations to be solved by least squares at each temperature is equal to the number of experiments multiplied by three.

See table 7-I for the published Margules parameters for the anorthite-albite and albite-orthoclase binaries used in the regression of the data from this study. The parameters for the anorthite-orthoclase binary were left as unknowns.

The data sets from Seck (1971a), Johannes (1979) and this study have been used together to solve for $W_{or, an}$ and $W_{an, or}$. These experiments represent temperatures from 650° C to 900° C and pressures from .5 to 3 kbars. Using the method of Ghiorso (1984) outlined above, $W_{an, or}$ and $W_{or, an}$ were determined at each experimental temperature. Different pressures were determined separately from one another (they appear as separate values in table 7-II). All the data is generally consistent so it was all used together to solve for the temperature dependence. The temperature dependence was determined by a linear regression of each excess parameter vs. temperature.

Table 7-I: Thermodynamic Parameters used in Regression

Thompson and Hovis (1979)		
$W_{ab,or}$	$7.404-5.12T$	(cals)
$W_{or,ab}$	4.0780	(cals)
W_v	0.0862	(cals/bar)
Newton et al (1980)		
$W_{ab,an}$	6746.1	(cals)
$W_{an,ab}$	2024.7	(cals)

Table 7-II contains the excess parameters determined at each temperature and the equations obtained by regressing them. The data and the lines are shown on an energy vs. temperature graph in figure 7-1. Note that Seck's (1971b) 650° C data for the $W_{an,or}$ parameter is consistent with the trends defined by the 700 and 800° C data from this study. The errors are large on some of the data from Seck (1971b) and from this study because the $W_{ab,or,an}$ parameter is neglected and only the binary excess terms $W_{an,or}$ and $W_{or,an}$ are used. Some of the large errors on data from this study can be attributed to the relatively small number of experiments used. These large errors may also reflect the problems of achieving equilibrium at lower temperatures. Recall that the experiments in this study using natural starting materials at 600° C showed no reaction after run times of half a year (189 days). Seck's gel starting compositions at 650° C appear to have been approaching equilibrium values.

The Margules parameters for the three binaries can be substituted into the three equations 10a-c and those in turn into equations 8a-c. These equations can then be used as a geothermometer.

Table 7-II: Results of the Regression of the Feldspar Data of Seck (1971b), Johannes (1979) and This Study

At each temperature the excess parameter and a 1 error are given in calories. Experiments used were run at pressures from .5 to 3 kbars.

T[° C]	650	700	750	800	825	900
----- <i>W_{or,an}</i> -----						
Seck:	12925.17 433.33		14739.02 1052.83		13485.81 144.89	13353.13 105.58
Johannes:				11878.65 474.09		
This Study:		16211.14 2577.01 18478.94 976.30		13435.07 531.29		
----- <i>W_{an,or}</i> -----						
Seck:	10631.99 173.67		10787.56 452.85		12053.50 79.38	12506.49 63.21
Johannes:				14735.94 181.07		
This Study:		11269.71 545.60 10226.61 202.92		12250.47 155.53		
Data Points:	39	18	51	15	39	33

FITTED EQUATIONS: (T[° K])

$$W_{or,an} = 26374.56 - 11.611T$$

$$W_{an,or} = 214.15 + 11.161T$$

Traditionally, feldspar geothermometers have used only the albite component of the alkali feldspar and the plagioclase because the anorthite content of alkali feldspar and the orthoclase content of plagioclase are small and difficult to measure. The equation used in this case would be $\mu_{ab,PL} = \mu_{ab,AF}$. Ideally, temperature can be solved for in the equations given using any feldspar component and a numerical method for finding the root of a non-linear equation. However, the temperatures obtained from the three components are likely to be different. If the feldspars were at complete equilibrium, the compositional analyses

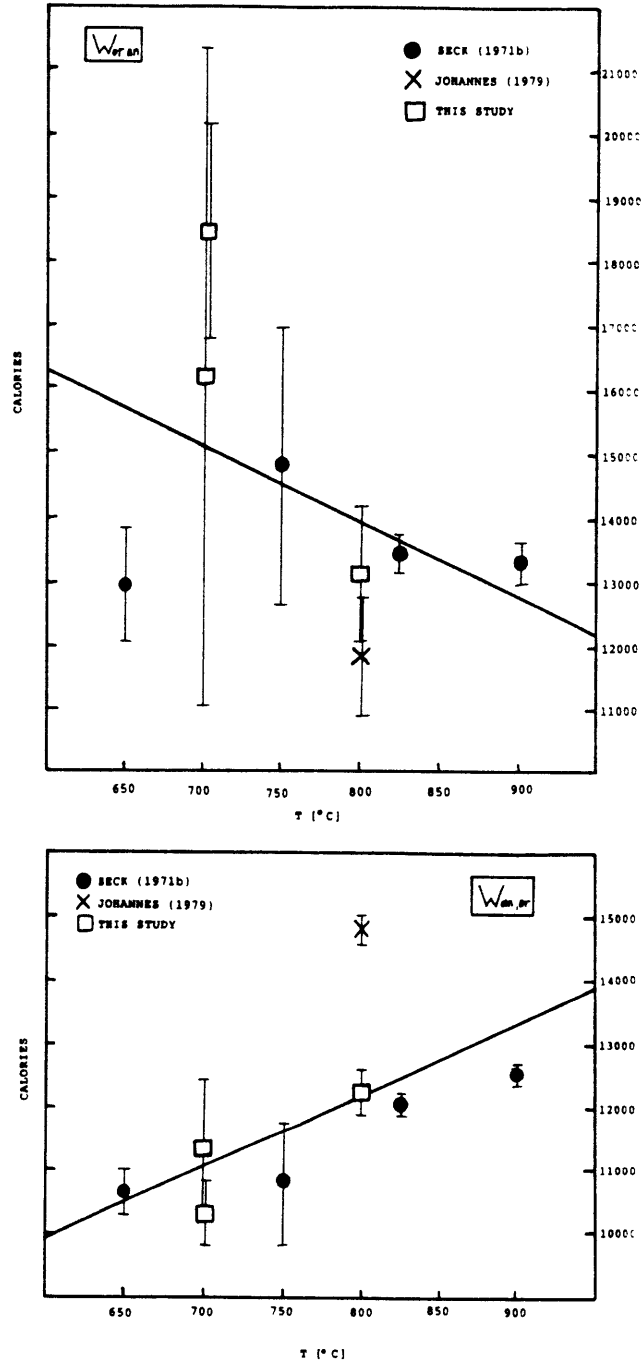


Figure 7-1: Excess parameters plotted as a function of temperature.

Error brackets delineate 2 standard deviations. Solid lines are the fitted equations given in table 7-II.

error-free, the experimental data used for the model perfect and the model a perfect fit for the data the temperature solutions to the three activity equations 6a-c might be expected to be the same. Practically, the temperature solutions must be assumed to be different, so the equation:

$$f_i(T) = \mu_{i, PL} - \mu_{i, AF} \quad (12)$$

will be non-zero for at least two of the three components. The goal is to simultaneously satisfy the following equations as closely as possible:

$$\mu_{ab, PL} - \mu_{ab, AF} = 0 \quad (13a)$$

$$\mu_{an, PL} - \mu_{an, AF} = 0 \quad (13b)$$

$$\mu_{or, PL} - \mu_{or, AF} = 0 \quad (13c)$$

Ghiorso (1984) conveniently writes this minimization in the following manner:

$$\min [f_{ab}^2(T) + f_{an}^2(T) + f_{or}^2(T)] \quad (14)$$

This problem can be solved for temperature using a minimization algorithm. By bringing equations 13a-c as close to zero as possible the conditions of equilibrium are satisfied as closely as possible for each of the three components and the most mutually realistic temperature results.

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