

Experimental constraints on the high-temperature termination of the anhydrous 2 feldspar + L curve in the feldspar system at 11.3 kbar

HANNA NEKVASIL, WILLIAM J. CARROLL

Department of Earth and Space Sciences, State University of New York, Stony Brook, New York 11794, U.S.A.

ABSTRACT

The location of the eutectic and the limits of mutual crystalline solubility were determined by reversed experiments at 11.3 kbar in the anhydrous system anorthite-sanidine. These results differ greatly from those of earlier work by Ai and Green (1989) and indicate that the anhydrous eutectic lies at 19 ± 2 wt% An and 1280 ± 10 °C. This eutectic composition lies much closer to the H₂O-saturated eutectic than indicated by the previous data. Therefore, the amount of An depletion during crystallization of two feldspars from a hydrous melt along the 2 feldspar + L surface in the system An-Or-Ab-H₂O is significantly less than previously thought. Maximum mutual crystalline solubilities obtained are 9 wt% An in sanidine and 11 wt% Or in anorthite. Comparisons of these solubilities with various solution models for ternary feldspars permit assessment of these models and indicate that only the ternary feldspar models of Nekvasil and Burnham (1987) and Elkins and Grove (1990) yield calculated liquidus relations in good agreement with the data.

INTRODUCTION

The anhydrous system anorthite-sanidine [CaAl₂Si₂O₈-(An)]-[KAlSi₃O₈(Or)] is of major importance in evaluating the crystallization history of high-temperature silicic magmas such as trachytes and syenites. Within this system lies the high-temperature termination of the 2 feldspar + L curve (at the eutectic), which separates the plagioclase + L and the alkali feldspar + L fields in the ternary feldspar system and indicates the compositions of melts in equilibrium with two feldspars. Knowledge of the melt composition at the eutectic is required for development and evaluation of thermodynamic mixing models for Ca- and K-rich silicic melts. Additionally, the feldspar compositions at the anhydrous eutectic provide high-temperature limits of the solubility of Or in plagioclase and An in sanidine. These are needed to constrain mixing models of ternary feldspar solid solutions at high temperatures.

Phase relations in the system An-Or have been studied by several workers. Yoder et al. (1957) experimentally determined the liquidus relations and solidus temperature at 5 kbar under H₂O-saturated conditions. Their results showed the system to be characterized by a eutectic and limited solid solution in both crystalline phases. Schairer and Bowen (1947) studied this system at 1 atm. However, because of the incongruent melting of sanidine at low pressures, the eutectic between sanidine and anorthite is obscured by a field of leucite + L. Ai and Green (1989) experimentally investigated phase relations in the anhydrous system at 10 kbar. Their results indicated that the basic characteristics of the H₂O-saturated system are preserved at high temperatures. They located the eutectic at 30 wt% An and 1215 ± 15 °C and obtained maximum

crystalline solubilities of 18 ± 3 wt% (18 ± 3 mol%) Or in anorthite and 7 ± 3 wt% An in sanidine.

The results of Ai and Green (1989) can be compared in several ways with computational results. Several models for ternary feldspar solid solutions have been proposed (i.e., Ghiorso, 1984; Green and Usdansky, 1986; Nekvasil and Burnham, 1987; Fuhrman and Lindsley, 1988; Lindsley and Nekvasil, 1989; Elkins and Grove, 1990) that permit the calculation of coexisting feldspar compositions as functions of pressure and temperature. Table 1 indicates the calculated compositions of coexisting anorthite and sanidine at 10 kbar and 1215 °C using these models. (Calculated compositions based on the model of Green and Usdansky, 1986, have been omitted from Table 1, as this model unreasonably indicates no solubility of anorthite in sanidine at high temperatures and pressures.) As shown in Table 1, the calculated compositions are strongly dependent upon the model chosen. The wide variability among the solution models probably reflects the lack of experimental data in this compositional region and hence the lack of constraints on the mixing behavior of feldspar components at low Ab contents.

Calculation of liquidus relations in this system is possible using the method of Nekvasil (1986, 1988). The results of such calculations on the H₂O-saturated system An-Or at 5 kbar investigated by Yoder et al. (1957) indicate reasonable agreement with the composition of the eutectic, ~10 wt% An. However, the calculated eutectic temperature is approximately 20 °C above that reported by these workers. This disagreement is likely the result of using more recent experimental data (e.g., Erikson, 1979, which differ from those of Yoder et al., 1957) for the system An-H₂O in the model calibration. The eutectic

TABLE 1. Calculated coexisting anorthite and sanidine compositions at 10 kbar, 1215 °C, in the system An-Or

Source	$X_{\text{Or}}^{\text{An}^*}$	$X_{\text{An}}^{\text{San}}$
Experimental (Ai and Green, 1989)	0.17	0.07
Ghiorso (1984)	0.16	0.04
Nekvasil and Burnham (1987)	0.05	0.05
Fuhrman and Lindsley (1988)	0.18	0.14
Lindsley and Nekvasil (1989)	0.11	0.15
Elkins and Grove (1990)	0.05	0.06

Note: Mole fraction (Or) \cong weight fraction (Or) because the formula weights of Or and An are virtually identical.
* Mole fraction.

temperature and composition in the anhydrous system at 10 kbar can also be calculated using the method of Nekvasil (1988). These calculations yield a solidus temperature of 1286 °C and eutectic composition of 19 wt% An, thus differing markedly from the values of 1215 °C and 30 wt% An given by Ai and Green (1989).

Both the calculated ternary feldspar compositions and liquidus relations show major discrepancies when compared with the experimental data of Ai and Green (1989). Before serious doubt can be cast on the solid-solution models used in Table 1, as well as on the calculated liquidus relations, the available experimental data must be evaluated. The starting material for most of the experiments of Ai and Green (1989) was glass prepared from oxide mixes by melting on an Ir-strip heater. As indicated by Ai and Green (1989), this technique resulted in K loss and hence nonbinary compositions. It is possible that the first appearance of glass in their samples was at a temperature significantly below that of the binary eutectic temperature, either because of the loss of K or because of the presence of H₂O. Their samples were kept at 120 °C overnight before loading. However, from our own experience, this temperature is insufficient for drying, as weight loss can commonly be detected after further heating to higher temperatures. Their temperature uncertainty was probably higher than stated because of the use of Pt-PtRh thermocouples to control the high temperatures of their experiments (1000–1600 °C). Because of the significant experimental difficulties they encountered in this system, they were not able to reverse their critical experiments and were forced to use X-ray diffraction (XRD) and scanning electron microscopy for the identification of phases, as optical and microprobe analyses of the experimental products were very difficult. They concluded that the apparent slow reaction rates in their experiments were attributable to the high viscosities of the anhydrous melts.

In view of the importance of this system in constraining the position of the high-temperature 2 feldspar + L curve and in indicating mutual solid solubilities at high temperatures, experiments were undertaken in order to verify the results of Ai and Green (1989) for the temperature of the eutectic, as well as the compositions of all phases at this temperature. However, for these new ex-

periments, special efforts were made to overcome some of the difficulties that those workers encountered.

EXPERIMENTAL TECHNIQUE

Efforts were made to enhance the chances for obtaining reversed equilibrium data in this anhydrous system. The starting material for all experiments was crystalline. Preliminary experiments conducted on mechanical mixtures of synthetic crystalline anorthite (crystallized dry at 10 kbar) and sanidine (hydrothermally crystallized at 10 kbar) showed very little reaction in 4 d at 1300 °C. This might be a result of insufficient reduction in grain size of both phases, even after 12 h of mechanical grinding in alcohol, and hence insufficient surface free energy and anorthite-sanidine grain contacts to facilitate melting. Attempts were then made to obtain very fine-grained crystalline material by hydrothermally crystallizing a mechanical mixture of gels (ground for 1 h in alcohol) with 10 wt% H₂O at 5 kbar and 800 °C for 4 d. Optical examination of the products showed very fine-grained crystalline material and no evidence of glass. XRD revealed well-crystallized sanidine and anorthite with only minor mutual solid solubility. The resulting powder was reground for several hours in alcohol, dried at 500 °C for 1 h, and then stored at 120 °C.

For each experiment, the starting material was loaded into small Pt capsules (o.d.: 0.093 in.; i.d.: 0.088 in., length: 0.14 in.) that were welded at the bottom and then lightly crimped at the top. The capsules were then heated to 500 °C for ½ h, to dry the sample thoroughly, and welded shut immediately thereafter. All spacers in the furnace assembly, as well as the BN furnace sleeve, were dried at 1050 °C for 30 min in a N₂ atmosphere. The thermocouple was separated from the Pt capsule by a thin ceramic disk. An exterior talc or NaCl sleeve was used in the experiments, which were conducted in a solid-medium piston-cylinder apparatus with temperatures controlled using W₉₆Re₄-W₇₄Re₂₆ thermocouples. The friction correction for the two sleeve types (talc and NaCl) was calibrated for the high-temperature experiments using the reaction anhydrous magnesium cordierite = sapphirine + quartz (Newton et al., personal communication). The talc-BN sleeves require overpressurization of ~0.7 kbar (in contrast to the ~2-kbar correction required at the much lower temperatures of the ferrosilite breakdown reaction; Bohlen, 1984). Calibration of the NaCl-BN sleeves indicated no need for friction correction. Because the early experiments were conducted using the 2-kbar correction for talc-BN sleeves, the pressure of the experiments was actually close to 11.3 kbar. For this reason, later experiments with NaCl-BN were also conducted at this pressure. Several tests at 10 kbar indicated very little pressure effect on the liquidus temperatures. Triple-headed thermocouples were used to calibrate the temperature gradient within the capsules, which was found to be ~13 °C. The recorded temperature of each experiment is that at the centered hot spot. All experiments were held at the final temperature for 4–5 d.

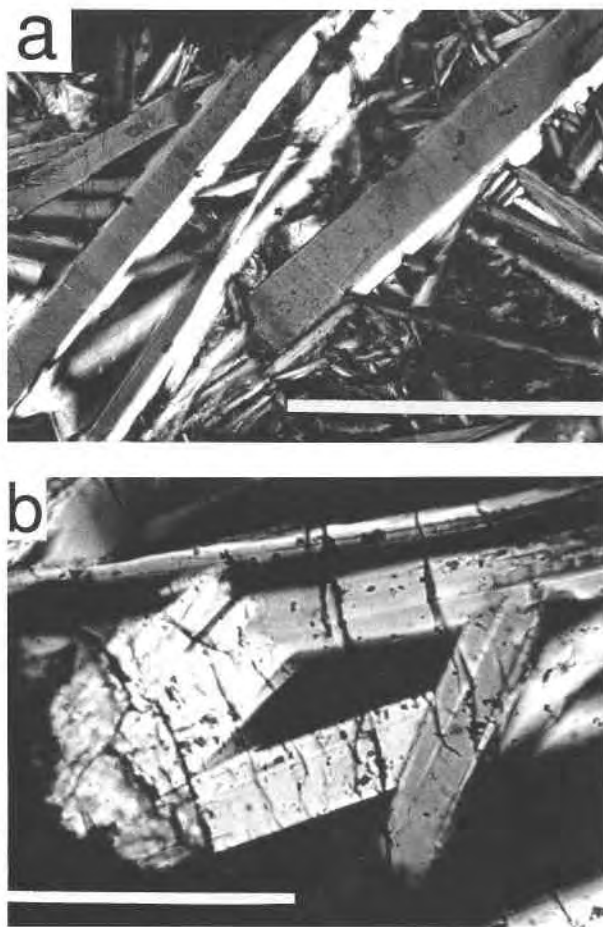


Fig. 1. Photomicrographs (crossed polarizers) showing textures of crystallization experiments. (a) Twinned sanidine phenocrysts with interstitial anorthite, crystallized from bulk composition $Or_{83}An_{15}$ at 1275 °C for 4 d after initial heating of crystalline starting material at 1425 °C for 1 d. The white bar indicates 0.25 mm. (b) Anorthite phenocrysts (and interstitial glass) crystallized from bulk composition $Or_{65}An_{35}$ at 1290 °C for 4 d after initial heating to 1425 °C. The white bar indicates 0.25 mm.

Melting experiments were conducted by taking the crystalline starting material directly to temperature. Crystallization experiments involved holding the charge above the liquidus temperature until completely molten (as determined by both XRD and optical examination of the quenched melt) and then rapidly dropping the temperature to the final value. For these crystallization experiments, the samples were superheated at the minimum temperature needed to render the sample completely molten within 24 h. This was done with the hope of preserving, as much as possible, nuclei within the melt in order to facilitate crystallization at the subliquidus temperatures. The Ir strip method used by Ai and Green (1989) for preparation of the starting glasses subjects the sample to very high temperatures. In addition to the volatilization of K, these temperatures may have resulted in

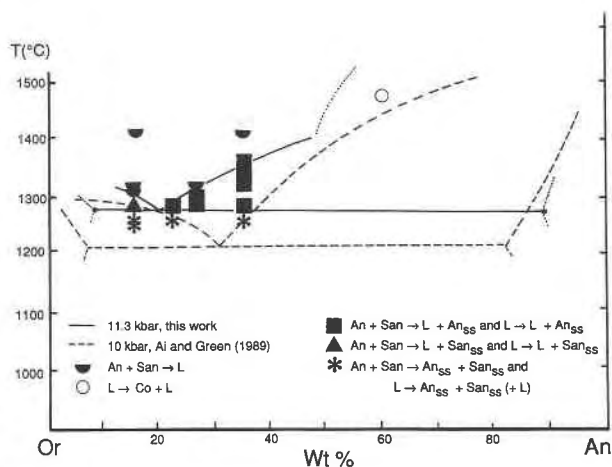


Fig. 2. Phase relations in the system An-Or at 11.3 kbar, based on the experimental results of this work (solid curves). Symbols represent experimental data and are as indicated within the figure. Dashed curves are based on the phase relations of Ai and Green (1989).

significant structural perturbation of the melt that prohibited attainment of equilibrium within the time frame and conditions of the experiments.

All experiments critical to the location of the eutectic and solidus temperature were reversed by conducting both melting and crystallization experiments. Experiment products were identified from optical properties and electron microprobe analysis.

EXPERIMENTAL RESULTS

After 4 d, all of the melting experiments above the eutectic temperature showed significant reaction and production of liquid. The crystalline material remained quite fine grained, however, and could only be identified by XRD. In contrast, the crystallization experiments yielded large (up to 1 mm long), homogeneous, euhedral crystals (Fig. 1a, 1b). These experiments gave no indication of the significant nucleation delay or sluggish crystal growth rates that have been considered characteristic of anhydrous silicic systems. The subsolidus crystallization experiments, however, did exhibit metastable persistence of a few vol% glass, which was not seen in the subsolidus melting experiments. Both the use of cryptocrystalline starting material and the elevated temperatures of the experiments may have contributed significantly to the success of the crystallization experiments. Additionally, the care taken to superheat only as much as necessary to obtain complete melting within 24 h may have been important. In trial experiments, when the same compositions were heated 200 °C above the liquidus before lowering to subliquidus temperatures, no crystallization was seen in 4 d, probably indicating destruction of the melt structure needed to initiate nucleation.

Figure 2 and Table 2 show the experimental results of this study, as well as the results of Ai and Green (1989; dashed curves in Fig. 2). The newly determined eutectic

TABLE 2. Anhydrous experimental data in the system An-Or at 11.3 kbar

Composition of starting material (wt%)	T (°C)	Products	
Or ₄₀ An ₆₀	1475	Co* + Gl	
Or ₆₅ An ₃₅	1275	An _{ss} + San _{ss}	
	1290	An _{ss} + Gl	
	1325	An _{ss} + Gl	
	1350	An _{ss} + Gl	
	1375	Gl	
	1425	Gl	
	1425; 1375	Gl	
	1425; 1350	An _{ss} + Gl	
	1425; 1325	An _{ss} + Gl	
	1425; 1290	An _{ss} + Gl	
	1425; 1275	An _{ss} + San _{ss} (+ Gl)	
	Or ₇₃ An ₂₇	1310	An _{ss} + Gl
		1325	Gl
		1425; 1325	Gl
1425; 1310		An _{ss} + Gl	
1425; 1290		An _{ss} + Gl	
Or ₇₈ An ₂₂	1275	An _{ss} + San _{ss}	
	1290	An _{ss} + Gl	
	1425; 1290	An _{ss} + Gl	
	1425; 1275	An _{ss} + San _{ss} + Gl	
Or ₈₅ An ₁₅	1250	An _{ss} + San _{ss}	
	1275	An _{ss} + San _{ss}	
	1290	San _{ss} + L	
	1325	Gl	
	1425; 1325	Gl	
	1425; 1310	Gl	
	1425; 1290	San _{ss} (+ Gl)	
1425; 1275	An _{ss} + San _{ss} (+ Gl)		

Note: Single temperature entries denote melting experiments. Double entries denote crystallization experiments (i.e., the sample was held at the first temperature for 24 h and then at the second temperature for 4 d).

* Corundum.

based on reversed data lies at ~19 wt% An and 1280 ± 10 °C. Because both sanidine (Boettcher et al., 1984) and anorthite (Goldsmith, 1980) exhibit incongruent melting at this pressure, the sanidine + L and anorthite + L fields do not extend to the sidelines. One preliminary data point was obtained for the bulk composition 65 wt% An, which yielded corundum + L, indicating that the field of incongruent melting behavior of anorthite extends well into the An-Or system. In contrast, no leucite was present at the bulk composition 85 wt% Or.

Electron microprobe analysis of glass in the products invariably yielded compositions within the binary and indicated no compositional heterogeneities. Compositional analysis of the synthetic feldspars from the crystallization experiments, however, was hampered by their morphology. Both An_{ss} and San_{ss} crystals were characteristically elongated and very thin platelike laths. For each of the subliquidus crystallization experiments, analysis of the crystalline products yielded a range of apparent crystal compositions extending toward the glass composition, despite a lack of optical evidence of zoning in the crystals. These compositional heterogeneities could be found among, as well as within, the crystals, although in the latter case, the changes in composition were generally progressive from one end of a crystal to another (rather

TABLE 3. Definitive electron microprobe analyses of crystalline experiment products at 1290 °C

	Bulk composition	
	Or ₆₅ An ₃₅ (wt%)	Or ₈₅ An ₁₅ (wt%)
SiO ₂	45.62	63.65
Al ₂ O ₃	34.24	20.22
CaO	17.89	1.72
K ₂ O	1.80	15.68
TOTAL	99.55	101.27
Cations normalized to 8 O atoms		
Si	2.121	2.911
Al	1.876	1.090
Ca	0.891	0.084
K	0.107	0.915
TOTAL	4.995	5.000
X _{An} (feldspar)	An ₆₉	An ₆₉

than symmetric relative to the center). It was possible to find several crystals from experiments at the lower subliquidus temperatures that showed no compositional changes along their length or width. Because of these characteristics, it is suspected that underlying glass was probably within the excitation volume during microprobe analysis. If so, the feldspar analyses represent composite crystal and glass compositions. Therefore, the most An-rich anorthite and Or-rich sanidine analyses from the crystallization experiments provide maximum mutual solubilities (9 wt% An in sanidine and 11 wt% Or in anorthite, as shown in Table 3). Because the analytical problems were compounded at temperatures with high ratios of melt to solid, the most Or-rich sanidine and An-rich anorthite were found in the experiment products close to the solidus temperature at 1290 °C. Analyses of the products at the subsolidus temperature of 1275 °C yielded compositions similar to these.

DISCUSSION

The new experimental data can be used to evaluate ternary feldspar solid-solution models in the Ab-poor region. Table 4 reports calculated anorthite and sanidine compositions at the newly determined eutectic temperature. Only the Nekvasil and Burnham (1987) and Elkins and Grove (1990) ternary feldspar solution models yield calculated solubilities within the limits indicated by the data (Table 3).

Liquidus relations can be calculated using the melt model of Nekvasil (1986) and Burnham and Nekvasil (1986) and any of the ternary feldspar models in Table 4. The solid curves in Figure 3 show the calculated liquidus relations using the melt model of Nekvasil (1986) and the ternary feldspar model of Lindsley and Nekvasil (1989). The high calculated solubility of An in sanidine in this model results in a very flat and narrow sanidine + L field. Although the calculated eutectic composition lies close to that indicated by the data, the solidus temperature is calculated to be ~30 °C higher. This results in poor agreement of the location of the calculated two-phase fields with the experimental data, in addition to

TABLE 4. Calculated coexisting anorthite and sanidine compositions at 11.3 kbar, 1280 °C, in the system An-Or

Source	X_{Or}^{An}	X_{an}^{San}
Experimental (this work)	<0.11	<0.09
Ghiorso (1984)	0.18	0.04
Nekvasil and Burnham (1987)	0.07	0.05
Fuhrman and Lindsley (1988)	0.22	0.17
Lindsley and Nekvasil (1989)	0.13	0.19
Elkins and Grove (1990)	0.06	0.08

the poor agreement of the calculated solid compositions with the data at the eutectic.

Calculated liquidus relations using the melt model of Nekvasil (1986) and Burnham and Nekvasil (1986) and the ternary feldspar solution model of Elkins and Grove (1990) are shown, for comparison, by the dashed curves in Figure 3. Use of this solid-solution model, with its lower calculated solubilities, results in very good agreement with the position of the eutectic, the two-phase fields, the solidus temperature, and feldspar compositions. The Elkins and Grove (1990) solid-solution model is very similar to that of Nekvasil and Burnham (1987), and use of the latter model also yields results in agreement with the eutectic data (i.e., 1286 °C; 19 wt% An, as mentioned earlier).

The new experimental data can be used to evaluate the effect of decreasing H_2O activity on melt compositions in equilibrium with two feldspars, thereby indicating the width of the 2 feldspar + L surface in the system An-Ab-Or- H_2O . Figure 3 shows the location of the 5-kbar eutectic in the H_2O -saturated system as determined by Yoder et al. (1957) (open star) and as calculated by Nekvasil and Burnham (1987) (solid star). If this degree of agreement between the calculated and experimental data is preserved at 10 kbar, where no experimental data are available for comparison with the calculated results (open square), the difference between the location of the H_2O -saturated eutectic (in anhydrous projection) and the dry eutectic is only on the order of 10 wt%, only half of the difference suggested by the data of Ai and Green (1989). This indicates a much smaller decrease than implied by the earlier data in the An content of a hydrous, but not H_2O -buffered, melt evolving across the 2 feldspar + L surface during the precipitation of two feldspars.

This study has provided constraints on the high-temperature termination of the 2 feldspar + L curve in the feldspar system, provided limits on the mutual solubility of anorthite and sanidine, permitted assessment of the effect of H_2O on this termination, and indicated that current solid- and melt-solution models can readily predict phase relations in this system. Additionally, this study has confirmed that anhydrous experiments on feldspars are sensitive to experimental techniques. However, it has also demonstrated that it is possible to obtain internally consistent, reversed data despite the notorious difficulties in dealing with anhydrous molten silicic systems.

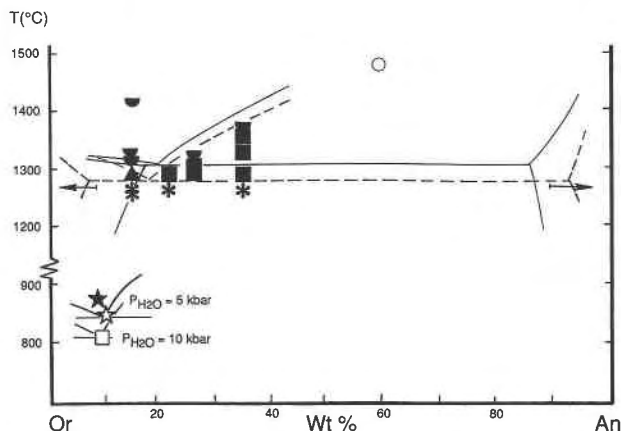


Fig. 3. Calculated phase relations in the system An-Or at 11.3 kbar. Experimental data are as in Fig. 2. The arrows indicate the possible range of anorthite and sanidine compositions at the eutectic temperature; the origins of the two arrows indicate the maximum amount of solid solution in coexisting anorthite and sanidine at the eutectic, as permitted by the new data. Liquidus phase relations calculated using the melt solution model of Nekvasil (1986) and Burnham and Nekvasil (1986) and the ternary feldspar solution model of Lindsley and Nekvasil (1989) are indicated by the solid curves. Dashed curves show the calculated results using the same melt-solution model as Nekvasil (1986) but using the solid-solution model of Elkins and Grove (1990). The 5-kbar, H_2O -saturated eutectic as determined by Yoder et al. (1957) is shown by the open star; the calculated eutectic, from Nekvasil and Burnham (1987), is given by the solid star. The calculated 10-kbar H_2O -saturated eutectic is shown by the open square.

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