

## The alkali-feldspar solvus at 1 kilobar water-vapour pressure

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**SUMMARY.** The compositions of feldspar pairs crystallized from stoichiometric alkali feldspar gels with water at  $P_{H_2O} \approx 1$  kbar in runs of up to 3000 hours' duration vary with Na:K in the starting material. This is because, for most bulk compositions, rapid nucleation in the gel leads to growth of one feldspar phase outside the solvus. The composition of this initial feldspar phase can be thought of as reflecting the configuration of the liquidus-solidus curves in the system Ab-Or. In general, the attainment of the stable equilibrium solvus (binodal) requires that one phase approach the binodal from outside; for compositions with  $< 30$  mole % Or this phase becomes more potassic with time, with  $> 30$  mole % Or, more sodic. Homogeneous gels of bulk composition  $Ab_{70}Or_{30}$  initially crystallize feldspar pairs inside the binodal, which rapidly ( $< 17$  hours) unmix to define a solvus-like curve (probably the spinodal, with an apparent critical point at  $602^\circ\text{C}$  and 31 mole % Or) and then unmix slowly, giving a solvus after 3000 hours with a critical point at  $657^\circ\text{C}$  and 36 mole % Or.

Because this curve has been approached from two directions it is the best approximation to the binodal (metastable only with respect to Al-Si order) obtained. It is similar to the 2 kbar 'peralkaline' solvus of Orville, 1963, provided an adjustment for pressure of  $16^\circ\text{C}/\text{kbar}$  is made. Differences between solvi determined by Luth and Tuttle (1966) for 'non-stoichiometric' bulk compositions may reflect differences in initial crystallization behaviour, as may the breaks in the solvus limbs suggested by Luth *et al.* (1974).

SINCE the earliest determination of the alkali-feldspar solvus in the system  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  by Bowen and Tuttle (1950) at  $P_{H_2O} = 0.982$  kbar, numerous workers have obtained solvus curves at higher pressures and for compositions off the stoichiometric feldspar join. Luth (1974), Luth, Martin, and Fenn (1974), and Goldsmith and Newton (1974) have summarized much of this data and utilized methods of thermodynamic analysis devised by Thompson and Waldbaum (1969). We will refer to much of this recent data in some detail in the present paper, which is concerned with the location of the solvus for compositions on the alkali feldspar join at about 1 kbar water-vapour pressure.

We began the present study to establish the limits of unmixing in alkali feldspars as part of a study of Al-Si ordering in anorthoclases (begun by Parsons, 1968*b*) and as a preliminary to determination of solvi for compositions containing Ca (Smith, in preparation). We noted, however, that our feldspar pairs were not conforming to a simple test for equilibrium—that different bulk compositions (in terms of Na:K) within the solvus should yield the same pair of coexisting feldspars when crystallized at the same temperature. These compositional differences persisted for the products of runs of at least 1500 hours duration and showed no tendency to disappear with time. Subsequently Morse (1970) and Seck (1972) have reported this 'bulk composition

effect' although their sets of observations concerned starting materials with excess  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , whereas our starting materials were 'stoichiometric'. We have investigated it in some detail and looked at the direction from which equilibrium is approached, with time, during crystallization from gels.

By making use of differences in the crystallization behaviour of different gel starting materials we have obtained a solvus curve bracketed by approach from two directions along the composition axis, avoiding the difficulty (Luth and Tuttle, 1966) of obtaining reversals of equilibrium about the solvus by approaching from higher and lower temperatures. Goldsmith and Newton (1974), alone among previous workers, give great attention to the reversibility of equilibrium in experiments to locate the solvus. They used different types of starting material to approach equilibrium from different directions, and located the solvus at  $P_{\text{H}_2\text{O}} \geq 9$  kbar, at which pressures reaction rates are greatly enhanced. We discuss aspects of the data of previous workers in the light of our findings and comment on the application of Thompson and Waldbaum's (1969) thermodynamic model to the alkali feldspars, in particular the usefulness of the tests for equilibrium that they suggest. We explain our different solvus curves and the crystallization behaviour that leads to them on the basis of their thermodynamic data.

#### *Experimental methods*

*Starting materials.* For most syntheses these were stoichiometric gels with various Ab:Or ratios made by the technique of Roy (1956) as modified by Hamilton and MacKenzie (1960) using the following reagents: 'Analar' sodium and potassium carbonates, British Aluminium Co. 'super-purity' aluminium, and either Monsanto or B.D.H. Tetraethylorthosilicate. Some gels were members of a series used by Parsons (1968, 1969) in previously described experiments; duplicates were later made by Smith using different reagent batches. No systematic differences in products were observed. The only phase other than feldspar obtained in our study was analcime, an expected product at low temperatures (MacKenzie, 1957). We do not, therefore, have any reason to believe that our materials were accidentally off-composition. During the course of the runs some dissolution into the vapour phase will occur and in this sense the solid phases will depart *slightly* from the ideal feldspar composition if the solution is incongruent. For the same reason  $P_{\text{H}_2\text{O}}$  will be *slightly* less than 1.034 kbar.

Two types of gel material were used. Some were 'homogeneous' gels in which Na and K were mixed in solution, others were 'mixed' gels, made by grinding together in an agate mortar for 20 minutes weighed quantities of end-member gels of albite and orthoclase composition. The comparability of data obtained from homogeneous and mixed gels also supports our belief that our starting materials are essentially stoichiometric.

*Synthesis.* Gels were crystallized in welded gold capsules containing 10 to 20 mg of gel (dried at 110 °C before weighing) with about 10 wt % deionized water. Runs were done in Tuttle bombs with temperatures measured by internal thermocouples calibrated against the melting points of zinc (419.4 °C) and NaCl (800.4 °C) recorded on a Honeywell recording potentiometer and maintained to  $\pm 10$  °C throughout runs.

The pressure medium was water and pressures were measured on Budenberg Bourdon gauges and maintained to  $\pm 1000$  lb/in<sup>2</sup> of 15000 lb/in<sup>2</sup> (0.069 kbar of 1.034 kbar) at which all runs were carried out. Temperature overshoot during warm-up was avoided but the rate of reaching the desired temperature varied appreciably from run to run. Other results of this study suggest that this, and factors such as the occasional appearance of pressure leaks during warm-up, necessitating quenching, may account for some of the apparently random variations in solvus data points that characterize both our own and earlier work.

*X-ray technique.* After optical inspection the composition of feldspar phases was obtained by measuring the separation of the feldspar  $\bar{2}01$  reflections from the  $101$  reflection of B.D.H. 'Analar' KBrO<sub>3</sub> run as an internal standard in smear mounts on a Phillips diffractometer using the following instrument conditions: Cu-K $\alpha$  radiation at 36 kV, 24 mA; scanning speed  $\frac{1}{2}^\circ/\text{min}$ ; slits  $1.0^\circ\text{-}0.1^\circ\text{-}1.0^\circ$ ; chart speed 800 mm/hr; ratemeter 4; time constant 4. Each set of reflections was scanned through three complete oscillations, and the resulting six sets of separations averaged. Resolved peaks were measured at  $\frac{2}{3}$  peak height (from background) to 0.001 inch using a vernier rule and converted to  $2\theta$ . Feldspar compositions were obtained using a curve relating  $2\theta$  to Ab:Or in the present series of starting materials crystallized at 850 °C, a curve used previously (Parsons, 1968, 1969), and which differs by a maximum of  $N_{\text{Or}}$  0.02 from the curves of Orville (1963) and Tuttle and Bowen (1958) but by up to 0.06 from the curve of Goldsmith and Newton (1974), which gives values consistently lower in Or for median compositions. Because of these uncertainties our  $\bar{2}01$  calibration data are given in Appendix 1.

Two-phase assemblages away from the top of the solvus (critical region) gave sharp  $\bar{2}01$  reflections even in short (*c.* 2 hours) runs. Separations of such reflections can be measured to the equivalent of  $N_{\text{Or}} = \pm 0.004$ . Near the top of the solvus there are observational problems because of poor resolution; this is particularly serious for bulk compositions away from the central part of the system because of the relative weakness of reflections from the subordinate phase. In some instances therefore peak positions were estimated near peak tops for poorly resolved reflections, and these are noted 'p' in Table I.

Many runs outside the measurable two-phase region gave diffuse reflections. We have attempted to crudely quantify this effect by measuring the peak width at  $\frac{1}{4}$  peak height (from background), and recording this in  $2\theta$  ('W' in Table I). The included KBrO<sub>3</sub> standard gave W values between 0.21 and 0.27 °  $2\theta$ , with an average of 0.23° (6 mounts).

Estimates of structural state were made using the 060- $\bar{2}04$  reflection method of Wright (1968), with KBrO<sub>3</sub> as internal standard. Analcime was detected by inspection of diffraction patterns.

### Terminology

To clearly distinguish starting materials from crystalline products the following terminology will be used:

*Starting materials.* e.g. Ab<sub>70</sub>Or<sub>30</sub>(H) = homogeneous gel composition in weight %,

or  $\text{Ab}_{70}\text{Or}_{30}(\text{M})$  = 'mixed' gel made by grinding weighed quantities of end-member gels, in weight %.

*Crystalline products.*  $N_{\text{Or-K}}$  and  $N_{\text{Or-Na}}$  = mole fraction Or in K-rich and Na-rich phase respectively of two phase assemblage ( $N_{2\beta}$  and  $N_{2\alpha}$  of Thompson and Waldbaum, 1969).  $N_{\text{Or-Fsp}}$  = mole fraction Or in assemblage in which only one feldspar phase could be distinguished by X-ray means.  $N_{\text{crit}}$ ,  $T_{\text{crit}}$  = critical composition and critical temperature.  $\mu_{\text{Or-Na}}$ , etc. = chemical potential of  $\text{KAlSi}_3\text{O}_8$  in the Na-rich phase, etc.

*Solvus.* The present study (and the work of others) has generated a large number of solvus-like curves, many of which appear to be equilibrium curves, the nature of which we shall discuss later. In the present paper we shall use the term *solvus* for all these curves, which depict observed systematic compositional variation in two-phase assemblages with respect to temperature.

*Binodal.* Our data allow us to derive a solvus that is approached by compositional changes from the two directions (a type of reversal of equilibrium), which we think is a good approach to the *binodal*. This is the 'true' stable equilibrium solvus, defined by the binodal points on the curves of Gibbs free energy for the system (fig. 4). Strictly the binodal would be defined by feldspar phases with equilibrium degrees of Al-Si ordering; this is probably not achieved by us or others, and the 'binodal' curve is metastable with respect to Al-Si ordering.

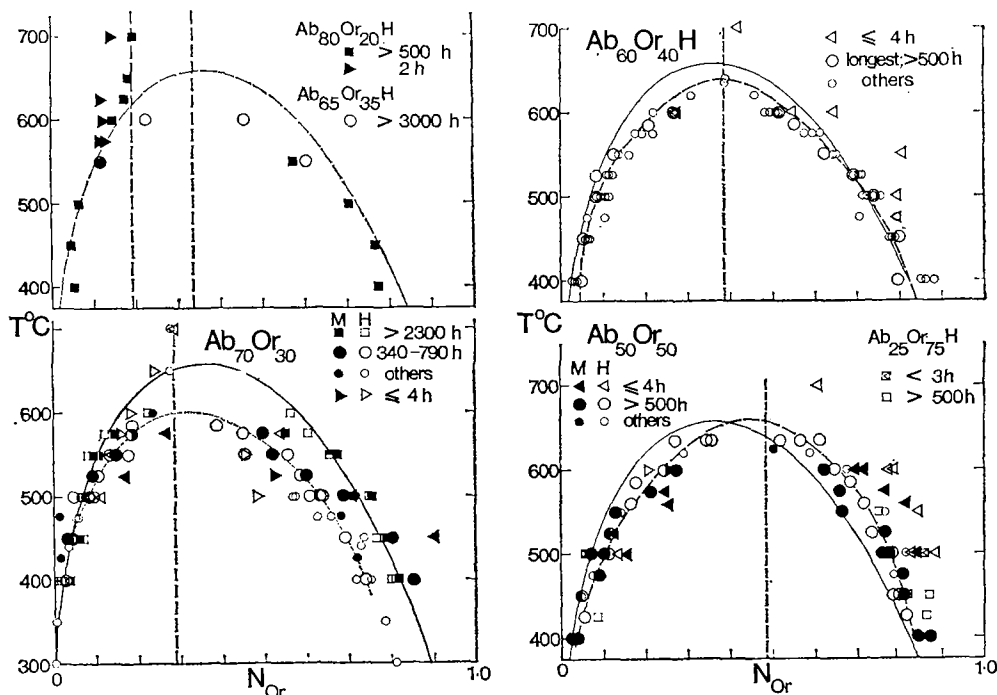
*Spinodal.* A homogeneous alkali feldspar grown above the solvus may break down by *spinodal decomposition* (Owen and McConnell, 1971). This occurs when the feldspar is cooled inside the coherent spinodal curve, which lies everywhere within the binodal. Our experiments are not analogous to this situation, because we are nucleating phases inside the binodal from amorphous gel. We find, however, that although gels of certain bulk compositions may evolve feldspar phases with compositions central within the binodal these are transient and only observed in the shortest runs (*c.* 2 hours). They rapidly ( $< 17$  hours, and probably while remaining gel crystallizes) change to phases lying on a curve approximating to the *chemical spinodal*, which is defined by the points of inflexion on the Gibbs energy curves (fig. 4) where  $d^2G/dN^2 = 0$ .

It seems unlikely that textures due to spinodal decomposition would be observed (by electron microscopy) in our products and the observed *spinodal* is probably rapidly attained by complete structural reorganization during crystal growth. A helpful explanation of exsolution mechanisms is given by Yund and McAllister (1970).

### Results

*Variation in solvus curves with bulk composition.* Compositions of feldspar phases occurring together after crystallization for various periods of time from different bulk compositions and from both homogeneous and mixed gels are given in Table I. Figs. 1 and 2 show the very systematic and pronounced differences that exist in feldspar pairs produced by the different starting compositions and persist in runs of at least 3000 hours' duration. The data shown are ranked in respect of the lengths of the run. Runs of between 340 and 790 hours for  $\text{Ab}_{70}\text{Or}_{30}$  (which will be referred to as '500 hour' runs) were selected as being broadly comparable (in run length) with the solvi

given by Luth and Tuttle (1966). Similarly the  $> 500$  hour runs on  $\text{Ab}_{60}\text{Or}_{40}$  and  $\text{Ab}_{50}$  are mainly close to 500 hours in length, and the few longer runs on these compositions (which are up to 1500 hours' duration) differ only slightly from runs of around 500 hours' duration. The broken solvus curves on figs. 1 and 2 are therefore all



FIGS. 1 and 2: FIG. 1 (left): A (top). Compositions of feldspar phases crystallized from bulk compositions of  $\text{Ab}_{80}\text{Or}_{20}$  and  $\text{Ab}_{65}\text{Or}_{35}$  compared to the  $\text{Ab}_{70}\text{Or}_{30}$  presumed binodal. B (bottom). Compositions of feldspar phases defining the binodal solvus (solid curve) obtained by combining  $\text{Ab}_{70}\text{Or}_{30}(\text{H})$  and (M) '> 2300 hour data' (squares) and using the 'r-s' extrapolation and smoothing method of Thompson and Waldbaum, 1969. Large circles indicate data from runs of broadly similar length to runs of Luth and Tuttle (1966). Apices of triangles point in direction of subsequent change in composition with time. Broken curve shows 'solvus' for '340-690 hour' data. FIG. 2 (right): A (top). Feldspar compositions and solvus (broken curve) obtained from bulk composition  $\text{Ab}_{60}\text{Or}_{40}$  compared to the  $\text{Ab}_{70}\text{Or}_{30}$  binodal (solid curve). B (bottom). Feldspar compositions obtained from bulk compositions  $\text{Ab}_{50}\text{Or}_{50}$  and  $\text{Ab}_{25}\text{Or}_{75}$ , compared to the  $\text{Ab}_{70}\text{Or}_{30}$  binodal (solid curve). The broken curve is the exchange solvus obtained from the  $\text{Ab}_{50}\text{Or}_{50}$  data.

equally valid as complete equilibrium curves on the criteria used by Bowen and Tuttle (1950) and Luth and Tuttle (1966). Data points used to generate these curves can be identified in Table I. The curves have been drawn by eye except for  $T_{\text{crit}}$  and  $N_{\text{crit}}$  which were obtained using the 'r-s' method of Thompson and Waldbaum (1969; see our Table III), and for convenience they will be referred to as '500 hour' solvi even though some longer runs are included.

There is close agreement on the position of the Na-rich limbs of all the '500 hour' solvi, except for the values from  $\text{Ab}_{80}\text{Or}_{20}$  at temperatures above 550 °C. The K-rich

TABLE I. Composition of feldspar phases (mole fraction Or)

Temp. (°C)	N <sub>Or-Na</sub>	N <sub>Or-K</sub>	Length of run (hours)	Regression	Run no.
<b>Bulk composition Ab<sub>90</sub>Or<sub>10</sub> (wt %, homogeneous gel).</b>					
400	0.052	0.774	1482		474-3
450	0.043	0.768	1300		471-3
500	0.066	0.704	576		504-3
550	0.119	0.571	3043		735-1
575	0.119	—	2		785-1
	0.122	—	2		785-2
600	0.119	—	2		786-1
	0.119	—	2		786-2
<b>Bulk composition Ab<sub>90</sub>Or<sub>10</sub> (wt %, homogeneous gel).</b>					
300	0.000	0.810	502		461-1
350	0.002	0.784	502		462-1
400	0.024	0.739	504	D	443-1
	0.038	0.719	1482		474-2
	0.027	0.742	1482		473-2
	0.009	0.813	2538		794-2
	0.017	0.803	2538	A, C	794-3
440	0.034	0.728	1482	A, C	472-2
450	0.046	0.690	719	D	392-1
	0.041	0.735	1300		471-2
	0.070	0.784	2472	A, C	795-2
	0.042	0.767	2472	A, C	795-3
475	0.052	0.625	116		398-2
	0.053	0.659	218		406-1
500	Broad, unresolved				486-1
	0.111	0.481	4		485-1
	0.088	0.572	17		484-1
	0.063	0.567	140		447-1
	0.097	0.637	340	D	515-1
	0.081	0.608	549	D	428-1
	0.046	0.633	576	D	504-1
	0.073	0.705	960		793-3
<b>Bulk composition Ab<sub>70</sub>Or<sub>30</sub> (wt %, mixed gel).</b>					
400	0.024	0.856	503	E	571-2
	0.034	0.816	2538	B, C	794-1
425	0.014	0.718	1755		642-1
450	Analtime	0.903			576-2
	0.036	0.803	525	E	500-2
	0.062	0.790	2472	B, C	795-1
475	0.013	0.677	1552		657-3
500	Analtime	0.707			577-2
	0.084	0.687	580	E	556-2
	0.071	0.708	960		793-1
	0.066	0.687	960		793-2
Temp. (°C)	N <sub>Or-Na</sub>	N <sub>Or-K</sub>	Length of run (hours)	Regression	Run no.
600	0.147	W = 0.510	2323		302-3
	0.143	W = 0.47	3239		734-1
625	0.114	W = 0.53	2		787-1
	0.114	W = 0.57	2		787-2
650	0.171	W = 0.45	2315		301-2
	—	W = 0.41	540		204-3
	0.186	W = 0.34	1476		305-1
700	0.191	W = 0.30	1822		300-3
500	0.069	0.746	2930	A, C	792-3
525	0.106	0.586	790	D	391-1
550	0.140	0.455P	3		550-2
	0.147	p	67		203-3
	0.157	p	174		201-3
	0.178	0.455P	474	D	200-3
	0.133	0.554	600	D	199-3
	0.082	0.654	2949	A, C	790-1
575	0.162	0.543P	2		785-3
	0.186	0.450P	454	D	412-1
	0.123	0.606	2304	A, C	789-1
585	0.188	0.390P	505	D	463-1
600	0.184	0.274	2		786-3
	0.274	W = 0.68°	173		394-1
	0.288	W = 0.57°	3233		302-2
	0.224	0.503P	3239	A, C	734-2
620	—	W = 0.52°	2423		703-1
625	0.242	W = 0.72°	2		787-3
	0.280	W = 0.57°	2315		301-1
650	—	W = 0.46°	1476		305-2
700	—	W = 0.48°	168		106
	0.280	W = 0.27°	1488		118-2
500	0.058	0.751	2930	B, C	792-1
525	0.172	0.528	1		575-2
	0.093	0.600	523	E	573-2
550	0.149	0.520	576	E	555-2
	0.096	0.671	2949	B, C	790-1
	0.109	0.653	2949	B, C	790-2
575	0.269 broad	0.493P	1		578-2
	0.188	0.550	500	E	588-1
600	0.148	0.550	2304	B, C	789-1
	0.235 asym.		530		554-2

Bulk composition Ab <sub>88</sub> Or <sub>12</sub> (wt. %, homogeneous gel).									
550	0.119	0.606	3043	735-3					
Bulk composition Ab <sub>90</sub> Or <sub>10</sub> (wt. %, homogeneous gel).									
400	0.038	0.881	168	356-1					
	0.028	0.861	285	424-2					
	0.031	0.854	503	571-3	F				
450	0.047	0.795	1482	474-1	F, G				
	0.062	0.790	168	356-1	F, G				
	0.059	0.787	576	546-1	F				
	0.064	0.778	719	392-2	F, G				
475	—	0.931	1300	471-1	F, G				
	—	0.799	6	350-1					
	0.104	0.798	168	346-1					
	0.062	0.706	218	406-2					
500	—	0.794	2	486-2					
	0.112	0.714	4	485-2					
	0.106	0.756	17	484-2					
	0.094	0.723	89	349-1					
	0.086	0.740	549	428-2	F				
	0.085	0.740	586	530-1	F, G				
525	0.122	0.705	24	340-1					
	0.116	0.711	168	342-1					
	0.113	0.692	336	343-1					
	0.122	0.692	790	391-2	F				
Bulk composition Ab <sub>90</sub> Or <sub>10</sub> (wt. %, homogeneous gel).									
400	0.036	0.854	285	424-3					
425	0.052	0.817	580	466-2	H				
450	0.047	0.783	719	392-3	H				
	0.047	0.709	1370	465-2	H				
475	0.075	0.788	218	406-3					
500	—	0.883	2	486-3					
	0.133P	0.829	4	485-3					
	0.106	0.816	17	484-3					
	0.109	0.783	549	428-3	H				
525	0.116	0.733	790	391-3	H				
550	—	0.845	2	487-2					
Bulk composition Ab <sub>90</sub> Or <sub>10</sub> (wt. %, mixed gel).									
400	0.037	0.869	503	751-1	J				
	0.025	0.842	1512	614-1	I				
450	0.047	0.808	525	560-1	J				
475	0.084	0.809	525	586-1	J				
500	0.152	0.834	1	577-1	K				
	0.104	0.774	580	586-1	J				
	0.068	0.758	1512	613-1	J				
525	0.118	0.773	1	575-1	K				
	0.111	0.762	523	573-1	J				
Bulk composition Ab <sub>90</sub> Or <sub>10</sub> (wt. %, homogeneous gel).									
425	0.085P	0.863	580	466-3					
450	p	0.816	525	560-3					
	p	0.870	1370	465-3					

p = 2 $\theta$  reflection poorly resolved, b = broad, W = 2 $\theta$  reflection width at  $\frac{1}{2}$  peak height, (2 $\theta^\circ$ , Cu-K $\alpha$ ).

limbs show large systematic differences of at least 10 mole % Or; using the '500 hour' curves for  $\text{Ab}_{70}\text{Or}_{30}$  and  $\text{Ab}_{50}\text{Or}_{50}$  to estimate the temperature of beginning of unmixing for a feldspar of bulk  $\text{Ab}_{30}\text{Or}_{70}$  would give values differing by 120 °C. There is relatively low scatter of data points from all but the shortest runs about each of the curves, which are clearly distinguished, and duplicate runs always gave values agreeing to within 4 mole % Or. The more Ab-rich the bulk composition of the gel, up to  $\text{Ab}_{70}\text{Or}_{30}$  (figs. 1B, 2), the greater the Na content of the feldspar on the K-rich limb of the solvus. The bulk composition  $\text{Ab}_{30}\text{Or}_{70}$  (fig. 1A) shows a reversal of this trend, and, at high temperatures, the Na-rich limb is more sodic than the  $\text{Ab}_{70}\text{Or}_{30}$  '500 hour' solvus.

A similar relationship between bulk composition (in terms of Na:K) and apparent solvus position has been noted by Morse (1970) and Seck (1972) but their starting materials were peraluminous-persilicic. Luth and Tuttle produced differences in solvi of similar magnitude but at constant Na:K with added alkali silicate, alumina, or silica. Their solvus for a 'stoichiometric'  $\text{Ab}_{60}\text{Or}_{40}$  gel is essentially identical to our curve for this composition. Our data shows that 'non-stoichiometry' is not a prerequisite for obtaining a multiplicity of solvus curves; on the criteria for equilibrium adopted by these earlier workers varying the Na:K ratio alone will produce variation of similar magnitude.

We have investigated this bulk composition effect in some detail by doing very short runs ( $\leq 4$  hours, indicated by triangles with apices pointing towards the result of longer runs) and exploring subsequent changes with time up to 3200 hours, in particular for the composition  $\text{Ab}_{70}\text{Or}_{30}$ . The changes in feldspar pairs with time and subsequent development of an apparent multiplicity of solvi can be understood in terms of a thermodynamic model, for which we rely on the data and methods of Thompson and Waldbaum (1969), who in turn based their equations of state on analysis of the peralkaline phase equilibrium data of Orville (1963) and Luth and Tuttle (1966). We shall show that these solvi are closely similar to our binodal, discussed below.

*Changes with time in feldspar pairs from  $\text{Ab}_{70}\text{Or}_{30}$  gel.* Long runs ( $> 2300$  hours) on both (H) and (M) starting materials of this composition gave the square symbols shown on fig. 1, which were used to generate the solid solvus curve shown on figs. 1 and 2. This curve has been smoothed and extrapolated above 600 °C by the 'r-s' method of Thompson and Waldbaum. It is very similar in form to the 2 kbar solvus of Orville (1963), obtained by ion-exchange in alkali chloride solution (see fig. 7). The '> 2300 hour' solvus lies everywhere outside the '500 hour'  $\text{Ab}_{70}\text{Or}_{30}$  solvus. When crystallized for 2 hours below 550 °C the  $\text{Ab}_{70}\text{Or}_{30}$ (H) material gave feldspars giving a very broad, diffuse  $\bar{2}01$  reflection, indicating that a range of compositions was present (fig. 3). After 4 hours two phases were resolved, both well inside the '> 2300 hour' solvus, which after longer runs moved further apart, the Or-rich phase becoming considerably enriched in Or with time, the opposite of what occurred with more Or-rich bulk compositions. This starting material alone among our starting materials exhibited conventional unmixing behaviour with time. There is a sudden change in rate of unmixing (after *c.* 17 hours), best shown by the 500 °C data, and the '340-790



hour' runs (fig. 1) merely represent a stage in the slow part of this unmixing process. Above 550 °C the first Na-rich feldspar to crystallize was more sodic than the final value; the K-phase  $\bar{2}01$  reflections were weak and therefore poorly resolved in these runs.

The  $\text{Ab}_{70}\text{Or}_{30}(\text{M})$  gel behaved quite differently to its homogeneous equivalent, although after > 2300 hours the (H) and (M) data are indistinguishable. At < 500 °C short runs gave analcime and a feldspar lying outside the K-rich limb of the '> 2300 hour' solvus (fig. 1). Analcime rapidly disappears and after 500 hours the feldspar pairs have both become more sodic and lie close to the '> 2300 hour solvus'. Two runs of *c.* 1500 hours duration (642-1, 657-3) gave more sodic K-feldspars lying on the '500 hour' solvus for the (H) material, but the Na-feldspars are abnormally sodic (these pairs are the small solid circles at 425° and 475 °C, fig. 1). The longest runs (> 2300 hours) gave feldspar pairs both phases of which were more potassic than the 1500-hour runs. The (M) gel thus appeared to be following a path involving initial inward movement (of the K-phase) followed by subsequent separation. The two 1500-hour points are anomalous in a sense, but are thermodynamically explicable (see below), if the '500 hour' solvus is, in fact, close to the spinodal. At higher temperatures (> 500 °C) the (M) gel generates feldspar pairs inside the solvus, which subsequently unmix.

*Changes with time in feldspar pairs from  $\text{Ab}_{60}\text{Or}_{40}$  and  $\text{Ab}_{50}\text{Or}_{50}$  gels.* Runs of > 500 hours on these compositions produced changes of lesser magnitude and, for  $\text{Ab}_{50}\text{Or}_{50}$ , opposite sense to the  $\text{Ab}_{70}\text{Or}_{30}(\text{H})$  data. From Table I it can be seen that the  $\text{Ab}_{60}\text{Or}_{40}$  data changed little with time, except for the shortest runs when a relatively potassic feldspar grew initially. After 24 hours the data for the K-phase become static or irregular in direction of change with time. The Na-phase becomes slightly, but consistently, more sodic with time. The data points (fig. 2) are essentially coincident with '> 2300 hour' solvus points, although they lie inside the extrapolated  $\text{Ab}_{70}\text{Or}_{30}$  solvus in the critical region.

The  $\text{Ab}_{50}\text{Or}_{50}(\text{H})$  and (M) solvi show more marked changes with time. Both crystallize very potassic K-feldspar initially, which (below 600 °C) is rapidly (within 1 hour in the case of the (M) gel) joined by a Na-phase more potassic than the 'final' values found. With time both phases become more sodic so that, observed at intervals, we see the entire solvus becoming more asymmetrical and skewed towards Ab. However, the data do not overlap the  $\text{Ab}_{70}\text{Or}_{30}$  '> 2300 hour' solvus, although some data points approach it closely (the one  $\text{Ab}_{50}\text{Or}_{50}(\text{M})$  point slightly inside the  $\text{Ab}_{70}\text{Or}_{30}$  solvus (fig. 2B) is a single phase giving a skewed reflection very close to the bulk composition).

*Reversal of equilibrium.* It can be seen from the foregoing that the data as a whole constitute a type of equilibrium reversal, at least in so far as the K-rich solvus limb is concerned. The feldspar compositions crystallizing from  $\text{Ab}_{70}\text{Or}_{30}$  move outward with time, reaching the position of the essentially unchanging feldspar pairs from  $\text{Ab}_{60}\text{Or}_{40}$  after *c.* 2000 hours, while the  $\text{Ab}_{50}\text{Or}_{50}$  K-rich solvus limb moves towards these curves from the direction of Or. The  $\text{Ab}_{70}\text{Or}_{30}$  solvus is therefore bracketed by approach from two directions from the materials of the different bulk compositions;

it is bracketed by the  $\text{Ab}_{70}\text{Or}_{30}(\text{H})$  and (M) data (below  $500^\circ\text{C}$ ) apart from the two anomalous pairs noted above, and it is very similar to the bracketed peralkaline solvus of Orville (1963). For these reasons we believe that the  $\text{Ab}_{70}\text{Or}_{30}$  '> 2300 hour' data are the best approach to the true binodal obtained by us, and we shall therefore refer to this data set as 'the binodal' in subsequent discussion. If a difference exists between our curve and the true binodal the latter is likely to lie *slightly* outside our '> 2300 hour' data points. This curve represents an equilibrium curve metastable only with respect to Al-Si order-disorder (see later section).

TABLE II. *Composition of feldspar phases (mole fraction Or) in auxiliary experiments*

Symbols as Table I

Run. no. Starting material	First crystallization			Final crystallization			Comments		
	$T(^{\circ}\text{C})$	Hours	Products	$T(^{\circ}\text{C})$	Hours	Products			
			$\text{N}_{\text{Or-Na}}$ $\text{N}_{\text{Or-K}}$			$\text{N}_{\text{Or-Na}}$ $\text{N}_{\text{Or-K}}$			
591-3 $\text{Ab}_{70}\text{Or}_{30}(\text{H})$	750°	191	Single phase	500°	857	0.052 0.739	Completely unmixed to two phases		
591-1 $\text{Ab}_{60}\text{Or}_{40}(\text{H})$						(1 N NaOH + KOH in fluid)		0.059 0.729	Partially unmixed
591-2 $\text{Ab}_{50}\text{Or}_{50}(\text{H})$								0.133 0.672	
505-1 $\text{Ab}_{70}\text{Or}_{30}(\text{H})$	400°	150	Two phases presumed	550°	430	0.056 0.636	Charges raised to final temp. without removal from bomb		
788-2 $\text{Ab}_{80}\text{Or}_{20}(\text{H})$	525°	168	0.116 0.711	525°	210	0.096 0.698	Small change in same direction as direct runs		
797-1 $\text{Ab}_{30}\text{Or}_{70}(\text{H})$	635°	1000	0.356p 0.519	635°	168	$\text{N}_{\text{Or-Fsp}} 0.523$	Originally poorly resolved two-phase assemblage; now single asymmetric reflection		
797-3 $\text{Ab}_{50}\text{O}_{40}(\text{H})$						0.270 0.613		W = 0.64	
								0.346 0.567	Originally well resolved two-phase assemblage, now poorly resolved Na-phase

*Auxiliary experiments.* We carried out a number of additional experiments, using crystalline starting materials or an alkaline fluid phase or both, which support the preceding analysis; some representative examples are noted here. Clearly much more could be done along these lines to elucidate the processes involved in equilibration. Some of the starting materials used in this study were crystallized in the presence of excess alkali as NaOH or KOH, as was done by Trembath (1973).

For run 591 (Table II) single-phase assemblages were crystallized at  $750^\circ\text{C}$ , removed from the bomb, crushed, and further crystallized for 857 hours in the presence of a 1:1 mixture of 1 N NaOH and KOH at  $500^\circ\text{C}$  (using water alone as the fluid produced virtually no change in this time). The bulk  $\text{Ab}_{70}\text{Or}_{30}$  starting material had completely reacted to two phases,  $\text{Ab}_{60}\text{Or}_{40}$  showed three phases, while  $\text{Ab}_{50}\text{Or}_{50}$  showed only slight reaction to compositions inside the presumed binodal plus a strong reflection near the original starting composition. The products of the two better-reacted experiments plot on the binodal (fig. 7), further evidence for its identification. Ease of exsolution under the conditions of this experiment should be a function of supersaturation (Yund and McAllister, 1970) and if this applies here the

ease of reaction implies a critical composition near  $\text{Ab}_{70}\text{Or}_{30}$  (our binodal), not the apparent critical compositions of our other solvi.

Run 505-1 (Table II) was carried out in order to establish whether equilibrium would be approached in a reasonable time when a feldspar pair synthesized at low temperatures was taken to higher temperatures. The K-phase lies close to the presumed binodal although the Na-phase plots outside it.

The remaining runs in Table II involved the crushing and re-running of material at the same temperature as the first synthesis. It was thought that the persistence of the different solvi might be due to difficult diffusion through outer layers of crystals, either because of some form of zonation, or non-stoichiometry in the outer layers because of removal of alkalis in the vapour phase. Regrinding produced little effect on bulk  $\text{Ab}_{60}\text{Or}_{40}$  below the critical region (788-2) although the small change observed for this run is in the same direction as that observed in continuous runs, with time. More marked effects are seen for the runs on  $\text{Ab}_{50}\text{Or}_{50}$  in which one phase is outside the equilibrium solvus. Strikingly, the runs numbered 797 (Table II) both show progressive sideways movement of the initial two-phase assemblage, to an assemblage in which two phases are only poorly resolved or shown only by a broad  $\bar{2}01$  peak. These runs support the view that the  $\text{Ab}_{70}\text{Or}_{30}$  curve is the best approximation to the binodal and that the other solvi are curves of a different type.

Near the top of the solvus (above *c.* 575 °C) the  $\text{Ab}_{60}\text{Or}_{40}$  data and the  $\text{Ab}_{70}\text{Or}_{30}$  data fall somewhat inside the extrapolated binodal. Perhaps this means that the extrapolated binodal curve is not the true binodal. However, in this region, where the degree of supersaturation is least, unmixing of assemblages crystallizing initially inside the binodal would be expected to be difficult (Yund and McAllister, 1970). Some evidence suggesting that the extrapolated value of  $T_{\text{crit}}$  is correct is given by the  $\bar{2}01$  peak-width values ('W'-values) listed in Table I. Clearly the reflections are significantly and persistently diffuse up to at least 650 °C. However, this evidence should be viewed with care because Parsons (1969) reported a diffuse but measurable two-phase assemblage produced from gel  $\text{Ab}_{55}\text{Or}_{45}$  after 5 hours at 700 °C at  $P_{\text{H}_2\text{O}}$ , 30 000 lb. in<sup>-2</sup>, well outside the two-phase region.  $\text{Ab}_{70}\text{Or}_{30}(\text{H})$  gave a diffuse reflection after 168 hours at 700 °C (above the binodal), which sharpened with time. Clearly, outside and above the binodal, two-phase assemblages or assemblages showing a range of compositions may evolve and persist for long periods. Orville (1963) shows diffractometer peaks illustrating similar effects. Perhaps differences between  $\bar{2}01$  determinative curves, such as those of Goldsmith and Newton (1974) and the present authors, can be accounted for in this way. The former curve was for ostensibly homogeneous crystals synthesized at 700 °C, 1 kbar  $P_{\text{H}_2\text{O}}$  for 24 hours, the latter was for synthesis at 850 °C, 0.3 kbar for 48 hours. The discrepancies are in the direction and over the compositional range predicted from the model of metastable behaviour we develop below.

*Structural state of feldspar phases.* We have considered the possibility that the '500 hour' solvi are all equilibrium solvi, each representing a different metastable equilibrium for crystals with different degrees of Al-Si order. Parsons's (1968) experiments suggest that at 500 °C Al-Si ordering would be essentially complete after about

500 hours for feldspars on the sodic limbs of our solvi, while equilibration with respect to Al-Si order is widely believed to be much slower for K-rich feldspars. It seems likely (Smith and MacKenzie, 1961; Parsons, 1968) that compositions close to the alkali feldspar end-members have a higher equilibrium degree of order than median compositions at the same temperature. Tuttle and Bowen (1958) and Bachinski and Müller (1971) show that the solvus for highly ordered frameworks lies outside that for disordered frameworks; the distribution of our '500 hour' solvi is not out of keeping with any of these considerations. As a preliminary to more detailed work using lattice-parameters we have estimated structural state by the method of Wright (1968). We were not able to obtain values for the Na-rich feldspar phases because of diffuseness of the 060 and  $\bar{2}04$  reflections. The K-rich phases all plot close to the high-albite-high-sanidine line (Wright, 1968), although there is a slight tendency for the K-rich phases from the  $\text{Ab}_{25}\text{Or}_{75}$  gel to be more highly ordered. It seems unlikely that structural state differences could be the cause of the solvus differences, although the 060- $\bar{2}04$  values for  $\text{Ab}_{25}\text{Or}_{75}$  could result from the more extreme compositions of K-feldspars crystallized from this gel. Further, the overstep, with time, of the solvus limbs for  $\text{Ab}_{70}\text{Or}_{30}(\text{M})$  and  $\text{Ab}_{60}\text{Or}_{40}(\text{H})$  over the '500 hour' solvus of  $\text{Ab}_{50}\text{Or}_{50}$  would suggest that variations in degree of order are not controlling the solvus curves.

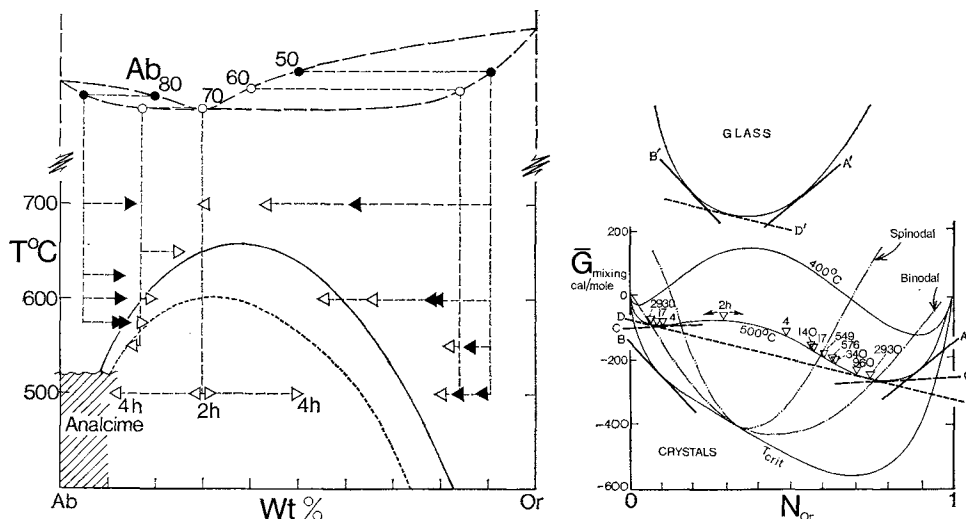
#### Discussion

*Qualitative model of initial crystallization behaviour.* We noted during our short experiments that only our  $\text{Ab}_{70}\text{Or}_{30}(\text{H})$  material initially crystallized feldspars inside the binodal. Other starting materials produced one phase outside the binodal. Rather similar behaviour has been noted by Piwinski and Martin (1970) when recrystallizing a partially melted granitic rock at subsolvus temperatures. Goldsmith and Newton (1974) recorded the same behaviour for a gel ( $\text{Ab}_{50}\text{Or}_{50}$ ) crystallized at  $P_{\text{H}_2\text{O}} = 9$  kbar, and, like us, used this behaviour to bracket the binodal.

Fig. 3 illustrates schematically the metastable crystallization behaviour of these feldspar gels, noted by Parsons (1969). In that paper it was shown that when gels are crystallized below the solidus the crystals present after short periods (1 to 3 hours) have compositions that would be appropriate for a gel crystallizing near the liquidus even though, in the present study, crystallization may be 400 °C below the solidus. Because of the flat and asymmetric nature of the liquidus-solidus curves for the system Ab-Or (Tuttle and Bowen, 1958; Morse, 1970) compositions more potassic than the binary minimum (in the vicinity of  $\text{Ab}_{70}\text{Or}_{30}$ ) will initially precipitate a very potassic feldspar (fig. 3), which must subsequently accept inward diffusion of sodium if it is to generate an unzoned single-phase feldspar. The reverse is true for bulk compositions more sodic than the binary minimum (actually its equivalent in the  $T$ - $P$  region where melt is metastable), which initially precipitate more sodic feldspars. Fig. 3 shows that this model satisfactorily describes the development of feldspars outside the solvus from compositions located within it.

With falling temperature the compositions of early metastable crystals may intersect the binodal. This occurs for the  $\text{Ab}_{70}\text{Or}_{30}(\text{H})$  gel, which at 500 °C crystallizes a range of feldspar compositions within the binodal, which subsequently unmix. The

$\text{Ab}_{70}\text{Or}_{30}(\text{H})$  gel shows the most variable early crystallization behaviour of all our compositions; we have already noted that in earlier experiments (Parsons, 1969) a two-phase assemblage was obtained, transiently, at  $700^\circ\text{C}$ . It seems that this uncertainty in behaviour is related to the close proximity of the binary minimum ( $\text{Ab}_{70}\text{Or}_{30}$ , at



FIGS. 3 and 4: FIG. 3 (left). Generalized representation of metastable crystallization behaviour exhibited by homogeneous alkali-feldspar gels (and glasses). Triangles are compositions of feldspars present after short periods (1 to 3 hours), with apices pointing in the direction of subsequent equilibration. Broken tie lines join these points to the appropriate bulk composition, which is depicted as lying on the liquidus, even though, in reality, the melting interval is not intersected at the temperature of crystal growth. This model describes how bulk compositions inside the binodal can initially crystallize feldspars well outside the solvus, and explains the reversal of direction of equilibration exhibited on either side of the metastable equivalent of the binary minimum. The bulk composition  $\text{Ab}_{70}\text{Or}_{30}$ , close to the binary minimum, shows two types of behaviour; equilibrating from inside the solvus at low temperatures. The approximate limit of metastable crystallization of analcime is shown. The solid curve is our binodal, the broken curve approximates to the spinodal, estimated from fig. 1. Liquidus and solidus are constructed from Morse, 1970, except that a minimum, not a eutectic, is depicted. FIG. 4 (right). Gibbs energy of mixing ( $\bar{G}$ ) curves (solid curves) for sanidine crystalline solutions at 1 bar taken from Waldbaum and Thompson, 1969, fig. 2. A hypothetical  $\bar{G}$  curve for a metastable glass is also shown. Triangles are observed compositions of phases obtained from  $\text{Ab}_{70}\text{Or}_{30}(\text{H})$  gel after the run times shown (in hours) at  $500^\circ\text{C}$ ,  $P_{\text{H}_2\text{O}} \approx 1$  kbar. The significance of the tangents A–D is discussed in the text. The binodal (shown as a broken curve) is defined by all common tangents such as D–D; the chemical spinodal by the points of inflexion on the  $\bar{G}$  curves, also shown as a broken curve.

1 kbar (Bowen and Tuttle, 1950)  $\text{Ab}_{71.5}\text{Or}_{28.5}$ , at 5 kbar (Morse, 1970)); this proximity leads to the development of feldspar pairs lying inside the binodal throughout much of the subsolvus range, although not in the region above  $550^\circ\text{C}$  (fig. 3).

The earliest crystalline sodic phase observed from  $\text{Ab}_{70}\text{Or}_{30}(\text{M})$  below  $525^\circ$  was analcime. It is accompanied by a K-rich feldspar more Or-rich than the final K-feldspar, and subsequently reacts with fluid to give an albitic feldspar phase. This rapid analcime growth seems to deplete the gel locally in Na, causing subsequent nucleation

of a rather K-rich feldspar phase. This behaviour reflects the failure of alkali homogenization in the mixed gel as crystallization begins, while the reverse behaviour of  $\text{Ab}_{70}\text{Or}_{30}(\text{H})$  reflects the failure of alkali diffusion to give compositions on the solvus limbs during crystal growth. In both cases the rate of feldspar-framework growth appreciably exceeds (as it *must* exceed to some extent) the rate of alkali redistribution, and the (H) and (M) starting materials thus generate the feldspar assemblages that have been used to bracket our binodal.

*Thermodynamic explanation.* In a preceding section we pointed out the similarity between our presumed binodal and the solvus obtained by Orville, 1963. We will therefore now apply qualitatively the thermo-dynamic data of Waldbaum and Thompson (1969), which are based on Orville's data, and use their methods to derive an internally consistent model for both the short- and long-term phenomena we have described. We shall support the assertions made in the present section with analysis using the 'r-s' method of Thompson and Waldbaum (1968), in the following section.

Fig. 4 shows Gibbs energy of mixing curves ( $\bar{G}$ ) for sanidine crystalline solutions at 1 bar from Waldbaum and Thompson's (1969) fig. 2. These curves will differ insignificantly at 1 kbar. We shall discuss the data with respect to the 500 °C  $\bar{G}$  curve; behaviour at  $T_{\text{crit}}$  and 400 °C can be deduced by the reader for the other  $\bar{G}$  curves given. Also shown is a generalized  $\bar{G}$  curve for metastable glass or gel, which is the starting material at all the temperatures depicted. Of course the shape of this curve is not known experimentally and the curve is merely drawn to satisfy our present observations geometrically. However, it is similar to the curve given by Waldbaum and Thompson (their fig. 6) for liquids of alkali feldspar composition in equilibrium with crystals at the liquidus (obtained from Schairer's (1950) liquidus), and the reader unfamiliar with the geometry of these relationships should consult their paper.

Thompson and Waldbaum (1968) discuss the conditions for *complete equilibrium*, where, in our case,  $\mu_{\text{Or-Na}} = \mu_{\text{Or-K}}$ , and for *partial* or *exchange equilibrium* where  $\mu_{\text{Ab-Na}} - \mu_{\text{Or-Na}} = \mu_{\text{Ab-K}} - \mu_{\text{Or-K}}$ , and equilibrium is attained through the vapour phase.

The former condition applies only for phases at the binodal (the common tangent D, fig. 4), while the second condition is a type of metastable equilibrium represented graphically by parallel tangents such as CC'. Exchange equilibrium may also exist between gel and crystals, shown by the tangents A and A'; in fact the composition of crystals that can nucleate and subsequently grow in gel, well below the melting interval, is specified by the exchange equilibrium condition. Superimposing the  $\bar{G}$  curve for the glass (fig. 4) on the 500 °C  $\bar{G}$  curve for the crystals so that AA' becomes a common tangent represents the situation when glass and crystals are in complete equilibrium in the melting interval. Unless the  $\bar{G}$  curve for the glass changes shape significantly with falling temperature, this model explains the observed crystallization behaviour of these gels shown on fig. 3, and justifies the simple way of imagining the process (as if it were controlled by liquidus–solidus relationships) used in fig. 3.

The parallel tangents A' and A thus represent starting composition ( $\text{Ab}_{50}\text{Or}_{50}$ ) and composition of the potassic initial crystals (after 1 hour,  $N_{\text{Or}} = 0.88$ ) observed in run 486-3 (Table I). As crystallization proceeds the composition of residual gel and

crystals becomes more sodic, and an initial single feldspar phase is joined by an Ab-rich second phase, in exchange equilibrium with any remaining gel and the earlier crystals through the vapour phase. Feldspar pairs defined by such tangents as  $CC'$  may therefore evolve and, our experiments suggest, persist for long periods. The whole family of isothermal subcritical  $\bar{G}$  curves can generate, from appropriate starting materials ( $Ab_{50}Or_{50}$ ,  $Ab_{25}Or_{25}$  in our experiments), a multiplicity of solvus-like curves whose position depends on starting composition (which controls the magnitude of the compositional changes needed to establish complete equilibrium) and time. These curves are equilibrium curves of a type; they involve ion-exchange equilibrium through the vapour phase and we shall call them *exchange solvi*. They represent metastable equilibrium, in respect of both Al-Si order-disorder and alkali distribution.

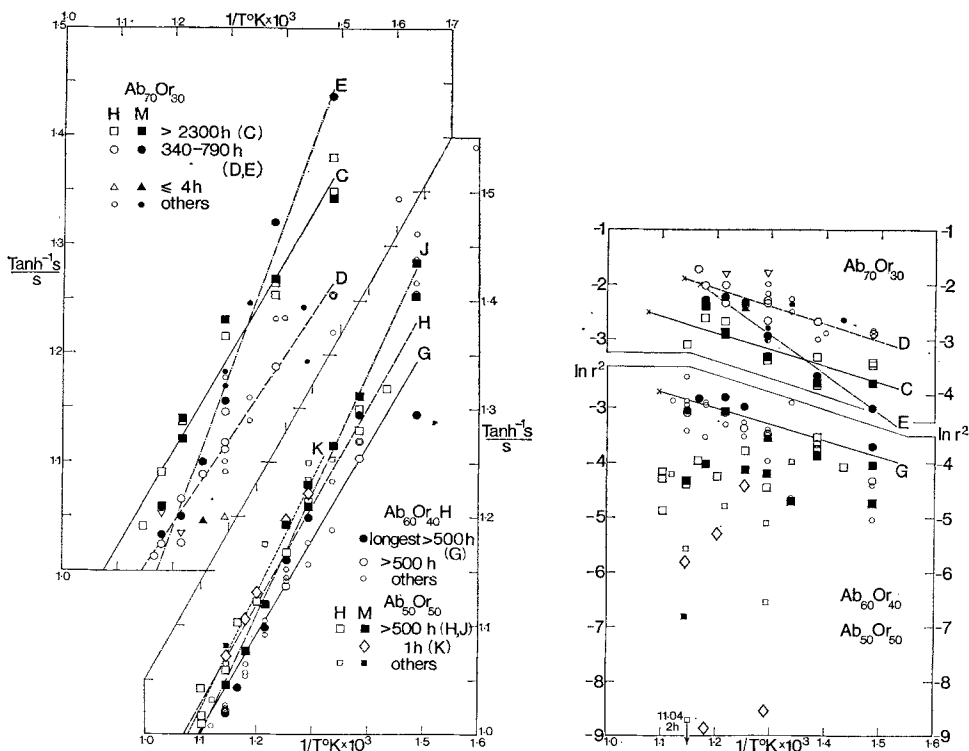
The tangents  $BB'$  indicate how sodic bulk composition (such as  $Ab_{80}Or_{20}$ ) may produce an initial crystalline phase more sodic than the binodal. The tangent B is shown on the  $\bar{G}$  curve for  $T_{crit}$  because this behaviour is only observed at temperatures  $> 575^\circ\text{C}$  (fig. 4).

Composition  $Ab_{60}Or_{40}$  initially evolves potassic feldspars outside the binodal, in exchange relationship with residual gel, but, by the time a second phase has appeared both phases are close to the binodal, so that subsequent changes with time are slight. At temperatures above about  $525^\circ\text{C}$  both phases (with one anomalous exception) lie inside the extrapolated binodal, and if this is the true binodal, presumably would unmix with time.

The composition  $Ab_{70}Or_{30}(H)$  initially crystallizes within the spinodal throughout the whole range of temperatures. The time-numbered points on the  $500^\circ\text{C}$   $\bar{G}$  (fig. 4) show compositions obtained from this material at  $500^\circ\text{C}$ . The sudden change in rate of phase separation after *c.* 17 hours is close to the spinodal, as are the '500 hour' values. We also noted previously two 1500-hour runs (642-1, 657-3) from  $Ab_{70}Or_{30}(M)$  that gave one phase near the K-rich spinodal, with an abnormally sodic Na-rich phase. It seems that for some reason (perhaps related to temperature fluctuations during warm-up, or undetected leaks in capsules) the two phases adopted a condition of exchange equilibrium. It is a requirement for exchange equilibrium of this type that one phase must lie between binodal and spinodal, because phases inside the chemical spinodal will break down rapidly to compositions at the spinodal. For the same reason runs crystallizing initially some compositions inside the spinodal ( $Ab_{70}Or_{30}(H)$ , 2 hours) break down very quickly ( $< 4$  hours) to phases at the chemical spinodal, and runs on compositions giving one phase outside the binodal should give a second phase between binodal and spinodal. Fig. 2B therefore shows an *approximation* to the spinodal for the shortest runs on the sodic limb, while the  $Ab_{70}Or_{30}(H)$  data gives an *approximation*, after  $< 17$  hours, to the spinodal on the potassic limb. The over-all scatter of points (figs. 1 and 2) is in good qualitative agreement with the shape of the  $\bar{G}$  curves derived by Thompson and Waldbaum (1969), which show a narrower  $\bar{G}$  trough for the Na-rich side, implying a narrower region between spinodal and binodal, as well as a narrower field in which phases in exchange equilibrium outside the binodal may evolve.

*Analysis by 'r-s' method.* Thompson and Waldbaum (1969) have suggested that it is

possible to distinguish between feldspar pairs in 'complete equilibrium' and those in 'exchange equilibrium' (not in contact and therefore able to equilibrate only through the fluid phase). They define two quantities  $s$  and  $r$  which in our terminology are  $s = N_{Or-K} - N_{Or-Na}$  and  $r = N_{Or-K} + N_{Or-Na} - 1$ ;  $s$  would be expected to behave



FIGS. 5 and 6: FIG. 5 (left). Thompson and Waldbaum (1969) parameter  $s$  plotted as  $(\tanh^{-1}s)/s$  against  $1/T$  ( $^{\circ}K$ ) for data sets indicated in Table I. Lines are least squares regressions. Critical temperatures calculated by this method (Table III) were used for figs. 1 and 2. Standard deviations of regressions are given in Table III. 'Others' refers to data points not included in the regressions. FIG. 6 (right). Thompson and Waldbaum (1969) parameter  $r$  plotted as  $\ln r^2$  against  $1/T$  ( $^{\circ}K$ ). Symbols are as used on fig. 5 and the diagram is divided into an upper section for the  $Ab_{70}Or_{30}$  data and a lower section for  $Ab_{80}Or_{40}$  and  $Ab_{50}Or_{50}$ . Lines are least squares regressions. These are not shown for the  $Ab_{50}Or_{50}$  data; standard deviations are given in Table III. Crosses are at  $T_{crit}$  obtained from Table III.

smoothly with temperature even for phases in exchange equilibrium, while  $r$  should behave smoothly only for phases in complete equilibrium.

Functions of  $s$  and  $r$  that give linear or near-linear plots against  $1/T$  ( $^{\circ}K$ ) are  $(\tanh^{-1}s)/s$  and  $\ln r^2$ . These functions are plotted on figs. 5 and 6, together with least squares regression lines through certain sets of data identified in Tables I and III.  $(\tanh^{-1}s)/s$  becomes 1 at  $T_{crit}$ , which can therefore be calculated from the regression equations and  $N_{crit}$  can be calculated from  $\ln r^2$  by regression  $T_{crit}$ . Critical constants obtained in this way are given in Table III, and were used to draw all the solvi on figs. 1 and 2.



For data approaching complete equilibrium it is reasonable to use the regression equations to generate a smoothed solvus, which may be extrapolated outside the range of the data; this has been done for the  $\text{Ab}_{70}\text{Or}_{30}$  '> 2300 hour' data (fig. 1).

$(\tanh^{-1}s)/s$  increases as  $s$  increases and therefore phases that are unmixing in a conventional way should show increase in  $(\tanh^{-1}s)/s$  with time. This is clearly shown by regressions D and C (fig. 5) for the  $\text{Ab}_{70}\text{Or}_{30}(\text{H})$  data. In fact these data are not for phases in exchange equilibrium but for phases approaching complete equilibrium from the spinodal. The regression line E shows an equally smooth plot through  $\text{Ab}_{70}\text{Or}_{30}(\text{M})$  products, which is clearly a fortuitous result because low- and high-temperature points were for phases equilibrating from different directions.

From the configuration of the  $\bar{G}$  curves (fig. 4) one can deduce that phases approaching complete equilibrium from the exchange equilibrium condition should show a decrease in  $s$  with time. This should be smaller than changes in  $s$  during unmixing. Also, the over-all variation in  $s$  between different starting compositions should be less than variations in  $s$  during unmixing. This is strikingly shown by the lower section of fig. 5. Decrease in  $s$  is shown by the small difference between regressions K and J. All the data are linear and smoother than the  $\text{Ab}_{70}\text{Or}_{30}$  data.

Regression K is for pairs of feldspars crystallized after 1 hour from  $\text{Ab}_{50}\text{Or}_{50}(\text{M})$  gel. Regression K gives a value of  $T_{\text{crit}}$  essentially identical (Table III) to  $T_{\text{crit}}$  from regression C (our presumed binodal). Since it is impossible to have two crystalline phases even in only exchange equilibrium above the true value of  $T_{\text{crit}}$  (the  $\bar{G}$  curve must have a binodal flexure, even for exchange equilibrium), this seems to confirm that the true value of  $T_{\text{crit}}$  is indeed near to, or slightly above, 657 °C.

Regression H, for runs in exchange equilibrium after > 500 hours confirms this, giving  $T_{\text{crit}} = 660$  °C. The data for  $\text{Ab}_{60}\text{Or}_{40}(\text{H})$  shows little change with time, although the apparent value of  $T_{\text{crit}}$  increases slightly with time (regressions F and G, Table III), in keeping with the data points from this composition with respect to the  $\text{Ab}_{70}\text{Or}_{30}$  binodal.

The function  $\ln r^2$  is sensitive to the mean of the phase compositions, and reflects the asymmetry of the solvus. Solvi skewed towards Ab (as all our solvi are) will give negative values of  $\ln r^2$  which will become closer to 0 as the solvus becomes more asymmetric. Spinodal and binodal are further apart on the K-rich solvus limb (fig. 4) and when unmixing is occurring  $\ln r^2$  should become more negative with time. This is shown by regressions D and C, fig. 6, for  $\text{Ab}_{70}\text{Or}_{30}$ . Bulk compositions tending towards complete equilibrium from exchange equilibrium should show increasing asymmetry with time, and  $\ln r^2$  should become less negative. This is shown, to the small degree expected, by the  $\text{Ab}_{60}\text{Or}_{40}$  data (note the similarity to regression C), and also, to a larger extent, by the  $\text{Ab}_{50}\text{Or}_{50}$  data.

It is clear from fig. 6 that the smoothness of  $\ln r^2$  is not significantly different between C, D, E, and G (least-squares standard deviations are given in Table III), although we believe on other grounds that the data points for C represent the nearest approach to complete equilibrium. However, the exchange equilibrium  $\text{Ab}_{50}\text{Or}_{50}$  data are very irregular, in particular the shortest runs, and regressions have not been attempted. With time they show a general tendency to approach the  $\text{Ab}_{60}\text{Or}_{40}$  data. The  $\ln r^2$

method has therefore successfully distinguished the exchange equilibrium data from data representing phases unmixing from within the binodal, but has not distinguished between the latter. It is clear to us that as a method of distinguishing data offering the best approach to the binodal, the 'r-s' method is a blunt tool, and no substitute for 'time and motion' (Goldsmith and Newton, 1974) synthesis studies.

*Comparison with other work.* It seems likely that the importance of early crystallization effects has been underrated by many previous workers. Eugster *et al.* (1972) have noted analogous effects for the system paragonite–muscovite. Goldsmith and Newton

TABLE III. Critical data calculated from least-squares regressions of  $(\tanh^{-1}s)/s$  and  $\ln r^2$  on  $1/T$  °K

Starting material	Regression:* selection criterion	Standard deviations		$n$ †	$T_{crit}$ (°C)	$N_{crit}$
		$(\tanh^{-1}s)/s$	$\ln r^2$			
Ab <sub>70</sub> Or <sub>30</sub> (H)	A: all > 2300 h	0.0183	0.3136	8	654.7	0.369
Ab <sub>70</sub> Or <sub>30</sub> (M)	B: all > 2300 h	0.0281	0.2480	6	660.8	0.333
Ab <sub>70</sub> Or <sub>30</sub> (H)+(M)	C: combined > 2300 h	0.0207	0.2924	14	657.0	0.357
Ab <sub>70</sub> Or <sub>30</sub> (H)	D: 340–790 h, 400 °C	0.0159	0.1668	10	601.2	0.307
Ab <sub>70</sub> Or <sub>30</sub> (M)	E: 500–580 h	0.0163	0.1876	6	581.0	0.318
Ab <sub>60</sub> Or <sub>40</sub> (H)	F: all > 500 h	0.0305‡	0.2114	13	625.7	0.376
Ab <sub>60</sub> Or <sub>40</sub> (H)	G: longest at $t$ , > 500 h	0.0348‡	0.2272	7	638.7	0.371
Ab <sub>50</sub> Or <sub>50</sub> (H)	H: all > 500 h	0.0131	0.3158	11	659.8	regression
Ab <sub>50</sub> Or <sub>50</sub> (M)	J: all > 500 h	0.0157	0.5055	10	636.8	
Ab <sub>50</sub> Or <sub>50</sub> (M)	K: 1 h	0.0078	2.2770	5	656.2	applied

\* Listed in Table I.

†  $n$  = number of data points in regression.

‡ Large value of S.D. greatly influenced by data points for 400° and 450° C.

(1974) report precisely the same crystallization behaviour as we observed in a feldspar gel (Ab<sub>50</sub>Or<sub>50</sub>), but at high pressures, and use this as one side of a synthesis bracket. Orville (1963, p. 223) noted that some feldspar glasses crystallize inhomogeneously outside the solvus and he shows  $\bar{2}01$  diffractometer peaks illustrating precisely the type of diffuse reflections we obtain from our materials. He suggested that the differences between his ion-exchange solvus and the solvus of Bowen and Tuttle (1950) could result from this effect.

Other workers (Luth and Tuttle, 1966; Morse, 1970) have stated that bulk compositions within the binodal would not yield compositions outside the binodal and handled their data points accordingly. Data points inside the outermost points observed were presumed to lie between the spinodal and binodal curves. This philosophy led Morse (1970) to the rapidly widening solvus curve shown on fig. 7 (we show it redrawn to share the same  $T_{crit}$  as our binodal, which requires  $dT_{crit}/dP$  of 18 °C/kbar) and is tantamount to drawing a solvus curve around both 'solvi' on fig. 2B.

The only data obtained at the same  $P_{H_2O}$  as our experiments are those of Bowen and Tuttle (1950). Their data points are shown on fig. 7. A glass with a bulk composition of Ab<sub>60</sub>Or<sub>40</sub> was used, and, as our exchange equilibrium model predicts, the K-phase data points are displaced towards Or.

All other data points shown on fig. 7 for experiments at  $P_{\text{H}_2\text{O}} > 1$  kbar have been adjusted downwards by  $16^\circ\text{C}/\text{kbar}$ . This is the value of  $dT_{\text{crit}}/dP$  obtained by applying the 'r-s' method to Orville's (1963) 2 kbar data ( $T_{\text{crit}} = 673^\circ\text{C}$ , Thompson and Waldbaum, 1969) and our 'presumed binodal' ( $657^\circ\text{C}$ ). We have already pointed out the similarity between our 'presumed binodal' and Orville's (1963) curve. Our data points lie slightly inside his points at high temperatures (those shown are points 'selected' by Thompson and Waldbaum, 1969), but departures, if any, from the true binodal would be most likely in the critical region, at low supersaturations. Our smoothed binodal is essentially identical to Orville's curve except for the K-rich limb below  $500^\circ\text{C}$ . However, it is interesting that Orville's point at  $500^\circ\text{C}$  is for a crystalline material changing composition inwards from pure Or, and could conceivably be too potassic. Our peralkaline data points lie on our binodal; these were from crystalline starting materials inside the spinodal. It is possible (see earlier section) that the K-rich limb of the true binodal lies outside our curve but it should lie inside Orville's  $500^\circ\text{C}$  point.

We obtained our binodal from 'stoichiometric' starting materials, whereas Orville's curve was obtained in the presence of excess alkali. Clearly peralkaline conditions enhance the rate but do not change the compositions of phases in complete equilibrium. Goldsmith and Newton (1974) also found that at  $P_{\text{H}_2\text{O}} \geq 9$  kbar 'stoichiometric' and peralkaline equilibria were essentially the same.

Luth and Tuttle (1966) used a gel ( $\text{Ab}_{60}\text{Or}_{40}$ ) at  $P_{\text{H}_2\text{O}} = 2$  kbar. Their data points are shown on fig. 7, recalculated for a pressure correction of  $16^\circ/\text{kbar}$  (we have used our  $2\theta 1$  calibration curve and their  $2\theta$  values because Luth (1974) has stated that the determinative curve used by him and Tuttle was not correct; differences caused by this replotting are small,  $N_{\text{Or}}$ , *c.* 0.02). Our  $\text{Ab}_{60}\text{Or}_{40}$  curve and the Luth-Tuttle (1966)

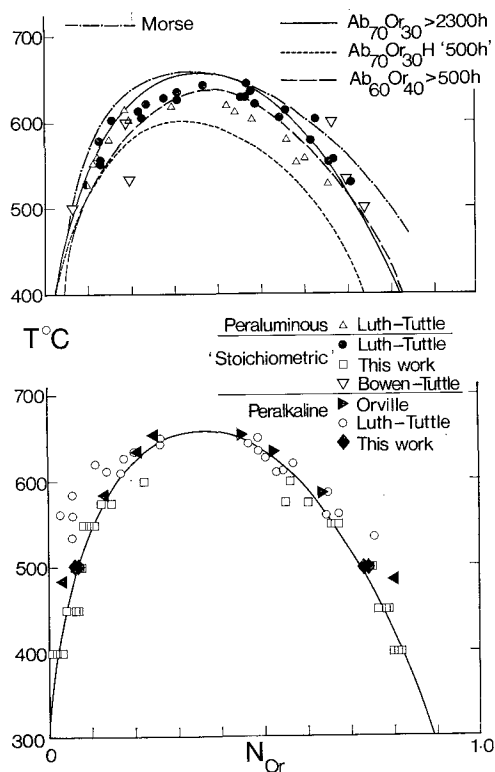


FIG. 7. Comparison of the compositions of feldspars obtained by other workers from both 'stoichiometric' and 'non-stoichiometric' starting materials, with various solvus curves obtained in this study. All 2 kbar data (Luth and Tuttle, 1966, and Orville, 1963) has been adjusted down by  $16^\circ\text{C}/\text{kbar}$ ; Morse's (1970) curve has been drawn to share  $T_{\text{crit}}$  with our binodal (solid curve). Orville's data points are drawn so that the apices of the triangles indicate change in crystalline phase compositions with time in his runs, and are points 'selected' by Thompson and Waldbaum, 1969.

curve are indistinguishable if this pressure correction is made, further support for the stoichiometry of our starting materials. There seems every reason to think that Luth and Tuttle's gel was crystallizing in the same way as ours, and that their  $\text{Ab}_{60}\text{Or}_{40}$  solvus is, like ours, not a complete equilibrium solvus.

The status of peraluminous and persilicic-peralkaline (i.e. added  $(\text{Na,K})_2\text{O}\cdot 2\text{SiO}_2$ ) data needs review in the light of our findings. The Luth-Tuttle, 1966, data of this type are shown on fig. 7. Clearly the peraluminous runs on  $(\text{Ab}_{60}\text{Or}_{40})_{97}(\text{Al}_2\text{O}_3)_3$  lie inside the binodal, while the runs on  $(\text{Ab}_{60}\text{Or}_{40})_{97}(\text{NS}_{60}\text{KS}_{40})_3$  gave points lying outside the data of Orville and ourselves, at least on the Ab-rich limb. The more recent data of Luth, Martin, and Fenn (1974) and Seck (1972) agree broadly with the earlier data at low pressures. We believe that the idea should be entertained that these solvus differences arise because of changes in the shape of the free-energy surface of the amorphous starting materials as compositions move away from the Ab-Or join in the system  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ , and that the apparent differences in solvi arise because of differences in the composition of early-crystallized phases. These differences, as our study shows, fundamentally influence the solvus curves obtained in experimentally practicable times, by controlling both the direction from which complete equilibrium is achieved and the magnitude of the changes required to achieve complete equilibrium. Peralkaline conditions (as alkali chloride or hydroxide) appear to influence the rate of equilibration but not the equilibrium itself. Our data also show that some materials reach equilibrium from different directions at different temperatures; clearly behaviour like this could very well generate breaks in solvus limbs like those postulated by Luth, Martin, and Fenn (1974). We note that the break occurs at 495 to 524 °C, 1.25 kbar, which is the temperature range over which we observe changes in direction of equilibration with time in our  $\text{Ab}_{70}\text{Or}_{30}(\text{M})$  data, and where our  $\text{Ab}_{70}\text{Or}_{30}(\text{H})$  and  $\text{Ab}_{60}\text{Or}_{40}(\text{H})$  data begin to lie inside our presumed binodal. These departures have been explained in terms of direction and rate of equilibration and we think that the similarity between our binodal and Orville's (1963) binodal (fig. 7) is not due to chance. Transient growth of analcime is another possible control on the composition of early feldspar compositions, and 500 °C is the highest temperature at which we observed analcime in our runs. Breaks in solvi and the sensitivity of solvus curves to 'non-stoichiometry' must be proved by reversals or at least 'time and motion' studies before being accepted as indicating real differences in Na:K ratio between feldspars in complete equilibrium.

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## APPENDIX I

Data for  $2\theta_{201}$ /composition curve used to obtain composition of feldspar phases in this study. Feldspars crystallized at 850 °C,  $P_{H_2O}$  5000 lb/in<sup>2</sup>, for 48 hours; Cu-K $\alpha$  radiation.

Wt % Or	mole % Or	$2\theta_{101}KBrO_3 -$ $2\theta_{201}Fsp$	$2\theta_{201}$	Wt % Or	mole % Or	$2\theta_{101}KBrO_3 -$ $2\theta_{201}Fsp$	$2\theta_{201}$
0	0	1·805	22·010	45	43·53	1·328	21·533
5	4·74	1·753	21·958	50*	48·51	1·252	21·457
10	9·48	1·700	21·905	55	53·52	1·175	21·380
15	14·26	1·651	21·856	65	63·63	1·073	21·278
20*	19·06	1·605	21·810	75*	73·86	0·975	21·180
25	23·89	1·543	21·748	85	84·23	0·883	21·088
30*	28·76	1·498	21·703	90	89·45	0·833	21·038
35*	33·66	1·435	21·640	95	94·72	0·785	20·990
40*	38·58	1·372	21·577	100	100·00	0·760	20·965

\* Starting materials, this study.