An experimental study of ordering in sodium-rich alkali feldspars

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Summary. Variations in the value of $2\theta_{131}-2\theta_{1\bar{3}1}$ of two anorthoclase feldspars of compositions $Ab_{95}Or_5$ and $Ab_{90}Or_{10}$ were investigated by hydrothermal crystallization of gels for long periods in the temperature range 500–950 °C, at water-vapour pressures up to 15 000 lb/in.^{2}. The results are compared to those obtained by MacKenzie (1957) for pure albite. It is shown that the variation in $2\theta_{131}-2\theta_{1\bar{3}1}$ is largely the result of Al–Si order–disorder and that at 700 °C and above the magnitude of the variation in the anorthoclases suggests that the degree of order is like that in albite, but at lower temperatures, particularly below 600 °C, the variation is less, and the anorthoclases are less ordered than albite at the same temperatures. At 600 °C and above the rate of attainment of equilibrium is the same for all three compositions. Below 600 °C $Ab_{95}Or_5$ behaves differently to albite. At low temperatures the equilibrium degree of Al–Si order in mixed Na–K feldspars is a function of composition as well as of temperature of crystallization.

SYSTEMATIC experimental investigation of the process of Al–Si ordering in alkali feldspars has been restricted to experiments on pure albite by MacKenzie (1957), who used the separation of the 131 and $1\bar{3}1$ reflections in X-ray diffraction patterns as a measure of the degree of order in albites synthesized hydrothermally at various temperatures. The present paper is concerned with the investigation of ordering in two potassium bearing alkali feldspars close to albite in composition, $Ab_{95}Or_5$ and $Ab_{90}Or_{10}$ (wt. %).

MacKenzie (1957) stressed that two albites with identical values of $2\theta_{131}-2\theta_{1\bar{3}1}$ may differ in their response to subsequent heat treatments so that the parameter does not define uniquely any particular arrangement of Al and Si, an observation recently extended by Grundy, Brown, and MacKenzie (1967). Whilst it must be appreciated that any methods of tracing changes in ordering that rely only on lattice parameters, or, most simply, on variations in 2θ of particular X-ray reflections, may obscure subtleties of structural configuration, they nonetheless represent the only convenient methods of tracing the ordering process in hydrothermally crystallized material. The value of $2\theta_{131}-2\theta_{1\bar{3}1}$ has been used more recently by Eberhard (1967) in repeating some of MacKenzie's (1957) experiments on albite, and extending them to calcium-bearing plagioclases, and the method has been adopted in the present study.

Some evidence that ordering could occur in homogeneous anorthoclase feldspars (using the term 'anorthoclase' in the manner defined by Smith and MacKenzie, 1958) was provided by MacKenzie's (1952) investigation of the relationship between composition and the temperature of the monoclinic–triclinic displacive transformation in sodium-rich feldspars. Anorthoclases crystallized hydrothermally at lower temperatures were found to attain monoclinic symmetry at higher temperatures than material of the same composition crystallized 'dry'.

Lattice parameters for high-temperature alkali feldspars, originally determined by Donnay and Donnay (1952), have recently been redetermined by Orville (1967) for alkali feldspars crystallized at 800 °C and 1000 bars H_2O pressure for from 5 to 7 days, but none of these workers attempted to establish whether their material was the equilibrium form at the temperature of synthesis. Orville (1967) also made a series of metastable supposedly highly ordered alkali feldspars intermediate between microcline and low albite, by using an ion-exchange technique with natural ordered starting materials, and Wright and Stewart (1968) have performed similar exchange experiments on forms with intermediate degrees of order. These products do not give information on the stable existence or otherwise of ordered forms in the region above the solvus.

Two conflicting hypotheses exist as to the effect on Al–Si ordering of the presence of both Na and K in the feldspar framework. Smith and MacKenzie (1961) suggest that relative to pure $NaAlSi_3O_8$ and $KAlSi_3O_8$ simultaneous presence of both cations would promote disorder at any particular temperature and they therefore suggest an alkali feldspar phase diagram in which lines representing a constant degree of ordering slope downwards from both end-members towards intermediate compositions. These ideas were criticized by Laves (discussion to same paper), who maintained that ordering of Al and Si would be mainly a function of temperature alone and that any effect of the presence of different cations would be limited to a slight increase in disorder in more sodium-rich feldspars in equilibrium at any particular temperature.

Choice of experimental points

In the case of albite MacKenzie (1957) was able to investigate the ordering process over a wide range of temperature from 1000 °C to 450 °C.

Homogeneous anorthoclases are stable over a narrower range of temperature, a lower limit being imposed by the alkali feldspar solvus, and, to a lesser extent, an upper limit being imposed by the downward slope of the solidus.

Numerous authors (e.g. Smith and MacKenzie, 1958; Tuttle and Bowen, 1958), have suggested that the degree of Al–Si order may influence the form of the solvus, and the existence of some perthites from plutonic rocks that do not homogenize even when held at temperatures well above the solvi obtained for synthetic crystals (Tuttle and Bowen, 1958; Czamanske, 1965) suggests that unmixing may occur in ordered crystals at higher temperatures than for disordered crystals. Solvi obtained using synthetic materials (Tuttle and Bowen, 1958; Orville, 1963; Luth and Tuttle, 1966), whilst representing equilibrium curves for those particular synthetic materials, are not necessarily the curves that would be obtained for feldspars with Al–Si configurations stable in the temperature range in which the solvus was determined.

The temperatures and pressures at which the runs in the present study were carried out were chosen with respect to the existing data on the solvus and solidus shown on fig. 1. The X-ray diffraction patterns of anorthoclases crystallized at the temperatures and pressures shown were investigated. It will be shown that much of the variation found in them is due to Al–Si ordering, but it will be recognized that the exact location of the solvus in feldspars in which an equilibrium degree of Al–Si ordering has been achieved is uncertain, so that at temperatures in the region close to the solvus shown, effects possibly due to unmixing as well as ordering must be discussed.

The compositions $Ab_{95}Or_5$ and $Ab_{90}Or_{10}$ were chosen because they can exist over a wider range of temperatures than more potassic compositions, and there seemed greater likelihood of detecting variations due to ordering. It was initially uncertain whether addition of even small amounts of potassium would greatly slow down or even prevent the ordering process and the closeness to albite permitted direct comparison with MacKenzie's (1957) data.

Experimental technique

Gel starting materials were crystallized in the presence of water at constant temperature and pressure for different periods of time, at the temperatures shown on fig. 1. At and below 850 °C a water-vapour pressure of 15 000 lb/in.^{2} was used. Runs were also carried out at lower pressures, 5000 lb/in.^{2} at 850 and 900 °C, and 3000 lb/in.^{2} at 950 °C.

A few runs were carried out on the crystalline products of earlier runs, which had been X-rayed and were then replaced in gold capsules and run for a further period. These are marked with an asterisk in tables I and II, and the time quoted is the total time in such cases. This procedure does not appear to have led to any systematic differences from the products of runs carried out continuously (see for example, run 205–2).

Starting materials. The feldspars studied were produced by the crystallization of dehydrated gels made up at 5 wt. % Or intervals over the compositional range of the alkali feldspars. The gel making technique is essentially that of Roy (1956), as modified by Hamilton and MacKenzie (1960), using 'Analar' sodium and potassium carbonates, 'Super purity' aluminium, supplied by the British Aluminium Co., and tetra-ethylorthosilicate (T.E.O.S.), supplied by Monsanto Ltd.

The maximum dimension of the gel particles after final grinding was about 0·05 mm, in the form of very thin flakes, but most particles were much finer. The gels were dried at 110 °C before making up a batch of charges.

About 20 mg of gel together with about 5 mg of deionized water were enclosed in electrically welded gold capsules about $\frac{5}{8}$ in. long × $\frac{3}{32}$ in. diameter. The charges were weighed before and after the runs, and those showing change in weight were presumed to have leaked, and were discarded.

Hydrothermal apparatus. 'Cold Seal' type pressure vessels are used, made of Nimonic 105 alloy. These are 9 in. long × 1 in. outside diameter, with an internal diameter of $\frac{1}{4}$ in. Most of the internal volume of the bomb is occupied by a length of pressure tubing through which passes a 0·062-in. diameter Inconel sheathed chromel-alumel thermocouple. The thermocouple junction emerges into a cylindrical cavity drilled into one end of this supporting tube. Three capsules can be accommodated in this cavity, each lying in contact with the thermocouple. The sheathed thermocouple and the pressure connection to the bomb are separated at a 'T'-shaped connection outside the seal of the bomb. Pressure is transmitted to the bombs by water and generated in a stainless-steel ram compressed by an hydraulic jack. The pressures are measured on Budenburg gauges and maintained to within about ±1000 lb/in.^{2} in the longer runs at 15 000 lb/in.^{2}. Thermocouple outputs are monitored on an Ether recording potentiometer and the thermocouples and this instrument were calibrated against the melting points of zinc (419·5 °C) and sodium chloride (801 °C). A few early runs were carried out in bombs in which thermocouples were placed in a well on the outside of the bomb, the temperature difference between this point and the point where the capsules were held being established by inserting another thermocouple into the bomb. This calibration was later checked against the sheathed thermocouples at the pressures of the runs concerned. (In Tables I and II runs numbered lower than 115 were carried out in this way.) The bombs are heated in horizontal tube furnaces regulated by Ether 'Transitrol' controllers, and the quoted temperatures maintained to within ±10 °C. After the runs the bombs were cooled rapidly in a compressed air stream.

X-ray technique. The run products were inspected optically to establish whether the charge was wholly crystalline. X-ray measurements were made on smear mounts on a Phillips X-ray diffractometer. Cu radiation was used throughout. All 2θ values quoted in the text are for Cu-$K\alpha$ radiation. The measurements quoted are for the separation of the 131 and $1\bar{3}1$ reflections. Each pair of reflections was scanned six times, three times in each direction, and the peaks measured at $\frac{2}{3}$ the peak heights. The measurements were made with a vernier ruler reading to

0·001 in., and then converted to 2θ. The quoted values are averages of the six measurements. Instrument settings used were: scale factor 4; time constant 8; multiplier 1; chart speed 400 mm/hr; scanning speed ¼°/min.; slits: divergence 1°, receiving 0·1, scatter 1°. Chayes and MacKenzie (1957) discuss the errors inherent in measuring the separation of two diffractometer peaks in this way, calculating a standard error of $\pm 0{\cdot}004°$ 2θ. Duplicate smears of the run products in the present study always agreed to within this limit. Some of the runs at low temperatures gave slightly diffuse diffractometer traces, and errors may be a little larger in these cases.

Results

The data given in Tables I and II and plotted on figs. 3 and 4 show that changes in $2\theta_{131}-2\theta_{1\bar{3}1}$ occurred with increasing time in the course of these experiments, with a gradual approach to a series of final limiting values each characteristic of the different temperatures of synthesis. There are thus strong similarities to the data of MacKenzie (1957) on pure albite. MacKenzie was able *to interpret the variation in* $2\theta_{131}-2\theta_{131}$ solely as a result of Al–Si order–disorder, but in the case of the sodium–potassium feldspars investigated in the present study, variations in the composition of the crystals may also influence the value of $2\theta_{131}-2\theta_{1\bar{3}1}$. Fig. 2 demonstrates the sensitivity of $2\theta_{131}-2\theta_{1\bar{3}1}$ to composition and also, as will be reasoned later, to structural state. For crystals formed between 600 and 850 °C a change in composition of 1 % Ab towards albite would be roughly the same as, and indistinguishable from, crystals of the initial bulk composition crystallized at a temperature 30 °C higher. Possible causes of variations in composition are lack of complete crystallinity, unmixing, or direct crystallization of more than one feldspar phase.

In the former case crystals of different composition to that of the starting material will coexist with residual glass of a different composition, the first formed crystals produced during the crystallization of any particular composition bearing a similar relationship to the starting composition as do crystals and liquid coexisting at the liquidus. Compositions in the range under study will initially crystallize feldspar closer to albite in composition. This effect has been investigated more fully and will be described in a subsequent paper.

For the majority of the runs carried out crystallization was a rapid process. Optical examination of the products often revealed small quantities of glass, which could be detected even in many of the longer runs. However, in many of the shortest runs ($<$ 10 hr) at all temperatures and in all the runs at 850 °C and $P_{\mathrm{H_2O}} = 15\,000$ lb/in.^{2}, except the longest under these conditions, appreciable quantities of glass were

TABLE I. Values of $2\theta_{131}-2\theta_{1\bar{3}1}$ (Cu-$K\alpha$ radiation) for $Ab_{95}Or_{5}$ (wt. %) crystallized for different lengths of time (in hours) at various temperatures and water vapour pressures.

Run no.	*Time*	$2\theta_{131}-2\theta_{1\bar{3}1}$
500 °C 15 000 lb/in.^{2}		
235–1	48	1·808°
231–1	168	1·780
231–2	168	1·768
208–2	402	1·765
227–1	1006	1·768
227–2	1006	1·751
242–1	2777	1·716
242–2*	2777	1·704
600 °C 15 000 lb/in.^{2}		
188–2	10	1·847
188–3	10	1·848
183–2	23	1·828
183–3	23	1·812
182–2	47	1·826
182–3	47	1·825
214–3	47	1·810
148–2	92	1·814
181–2	159	1·801
181–3	159	1·792
169–3	235	1·786
166–2	331	1·787
166–3	331	1·775
167–3	331	1·767
157–1	333	1·776
142–1	456	1·745
142–3	456	1·757
171–2	1002	1·734
171–3	1002	1·731
139–3	2273	1·686
800 °C 15 000 lb/in.^{2}		
234–2	10	1·848
218–1	24	1·845
234–1	67	1·825
218–2	120	1·821
220–1	165	1·819
220–2	165	1·819
232–1*	331	1·829
232–2*	331	1·822
850 °C 5000 lb/in.^{2}		
96	2	1·904
225–1	10	1·858
79	24	1·862
115–1	96	1·845
162–3	120	1·864
900 °C 5000 lb/in.^{2}		
237–1	114	1·868
237–2	114	1·868
550 °C 15 000 lb/in.^{2}		
219–3	21½	1·821°
236–1	46	1·805
203–1	67	1·808
228–1	120	1·780
209–2	171	1·769
201–1	174	1·759
201–2	174	1·780
200–1	474	1·751
200–2	474	1·776
199–1	690	1·743
199–2	690	1·745
700 °C 15 000 lb/in.^{2}		
187–2	10	1·861
185–2	18	1·845
184–2	23½	1·826
184–3	23½	1·832
174–2	26	1·818
174–3	26	1·824
151–2	41	1·822
189–2	48	1·816
189–3	48	1·816
153–3	65	1·816
147–2	93	1·805
156–2	113	1·806
156–3	113	1·805
170–2	287	1·794
170–3	287	1·793
198–3	432	1·775
176–2	960	1·758
176–3	960	1·754
173–2	1843	1·760
173–3	1843	1·769
850 °C 15 000 lb/in.^{2}		
196–2	2	1·893
194–2	9	1·900
194–3	9	1·890
191–2	24	1·869
191–3	24	1·876
193–2	47	1·882
193–3	47	1·864
177–3	90	1·854
223–1	95	1·851
180–2	160	1·850
180–3	160	1·849
950 °C 3000 lb/in.^{2}		
213–1	5	1·915
204–1	48	1·881

* See text, p. 1064.

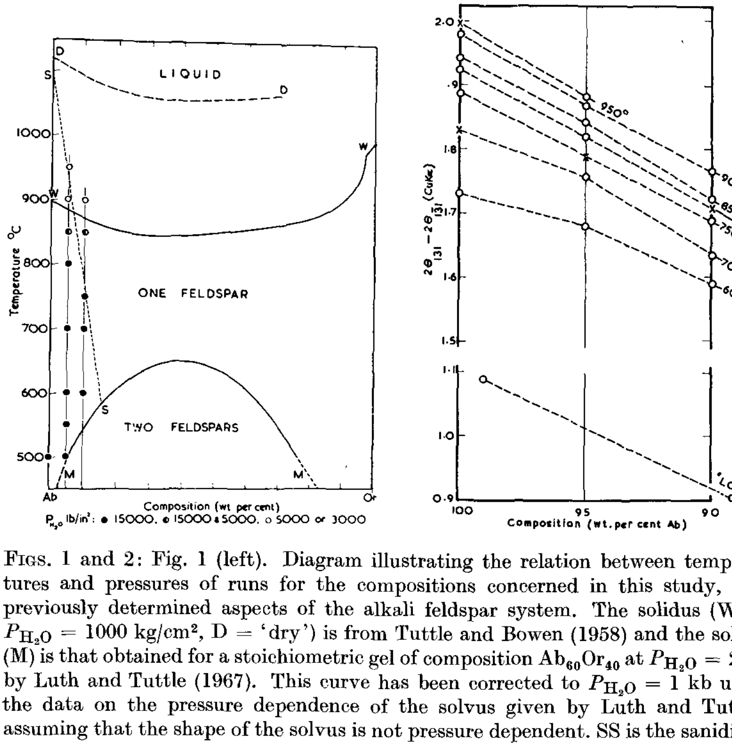
TABLE II. Values of $2\theta_{131}-2\theta_{1\bar{3}1}$ (Cu-$K\alpha$ radiation) for $\mathrm{Ab_{90}Or_{10}}$ (wt. %) crystallized for different lengths of time (in hours) at various temperatures and water vapour pressures.

Run no.	*Time*	$2\theta_{131}-2\theta_{1\bar{3}1}$
600 °C 15 000 lb/in.²		
188–1	10	1·777°
183–1	23	1·734
163–4	23	1·752
148–1	92	1·721
158–1	167	1·685
169–1	235	1·681
166–1	331	1·675
167–1	331	1·670
167–2	331	1·689
157–2	333	1·670
157–3	333	1·678
205–2*	883	1·631
139–2	940	1·624
171–1	1002	1·632
152–1	1333	1·627
152–2	1333	1·618
205–1*	1885	1·592
750 °C 15 000 lb/in.²		
128–2	2095	1·693
850 °C 5000 lb/in.²		
100	2	1·815
62	24	1·723
134–2	64	1·723
115–3	96	1·722
63	171	1·733
700 °C 15 000 lb/in.²		
74	2	1·791°
187–1	10	1·756
164–1	10½	1·739
164–2	10½	1·752
184–1	23½	1·742
64	24	1·747
174–1	26	1·729
151–1	41	1·710
189–1	48	1·704
147–1	93	1·694
156–1	113	1·691
65	168	1·693
170–1	287	1·683
111	504	1·646
176–1	960	1·640
67	1506	1·636
173–1	1843	1·651
850 °C 15 000 lb/in.²		
196–1	2	1·838
194–1	9	1·829
191–1	24	1·813
177–1	96	1·761
180–1	160	1·739
900 °C 5000 lb/in.²		
70	328	1·763

* See text, p. 1064.

present. As indicated by fig. 1 the latter conditions are very close to the solidus and the gel starting materials used crystallized very slowly in this region. For the composition $\mathrm{Ab_{90}Or_{10}}$ the curves of $2\theta_{131}-2\theta_{1\bar{3}1}$ against time for the two water-vapour pressures at 850 °C are quite different (see fig. 4) solely because crystallization was very much more rapid at 5000 lb/in.² than at 15 000 lb/in.², so that the form of the latter curve reflects these slow changes in composition, as well as changes due to ordering. The runs at 850 °C, 15 000 lb/in.² were undertaken in an endeavour to provide a $2\theta_{131}-2\theta_{1\bar{3}1}$/time curve isobaric with the curves at lower temperatures, with a view to investigating the rate of attainment of equilibrium with respect to ordering, but clearly crystallization of amorphous starting materials is not a satisfactory method under these conditions. The tendency for the curves at both water-vapour pressures to approach similar final limiting values can be seen, however.

MacKenzie's (1957) data shows that larger final values of $2\theta_{131}-2\theta_{1\bar{3}1}$ are obtained at lower pressures, but the present data is inadequate to evaluate this small effect for the compositions studied.



FIGS. 1 and 2: Fig. 1 (left). Diagram illustrating the relation between temperatures and pressures of runs for the compositions concerned in this study, and previously determined aspects of the alkali feldspar system. The solidus (W at P_{H_2O} = 1000 kg/cm², D = 'dry') is from Tuttle and Bowen (1958) and the solvus (M) is that obtained for a stoichiometric gel of composition $Ab_{60}Or_{40}$ at P_{H_2O} = 2 kb by Luth and Tuttle (1967). This curve has been corrected to P_{H_2O} = 1 kb using the data on the pressure dependence of the solvus given by Luth and Tuttle, assuming that the shape of the solvus is not pressure dependent. SS is the sanidine–anorthoclase displacive transformation (MacKenzie, 1952). This does not influence the results in the present study since all measurements were made at room temperature. Fig. 2 (right). Final values of $2\theta_{131}-2\theta_{1\bar{3}1}$ at various temperatures estimated from figs. 3 and 4 plotted against composition. The data for albite is from MacKenzie (1957). Circles are determined points, crosses are interpolated from fig. 5. The line marked 'low' is for the forms intermediate between low-albite and microcline made by Orville (1967).

Although in all other runs described the amount of glass was extremely small, it may account in part for the scatter of $2\theta_{131}-2\theta_{1\bar{3}1}$ values found for repeated runs on the same composition at fixed temperatures and pressures and for equal periods of crystallization. This is a little larger than that found by MacKenzie (1957) for pure albite. He also observed small amounts of glass after long runs, and ascribed the scatter of $2\theta_{131}-2\theta_{1\bar{3}1}$ values to variations in grain size of the starting materials causing different rates of approach to the ordered forms. Both factors may be influencing the $2\theta_{131}-2\theta_{1\bar{3}1}$ values obtained in the present study. The $2\theta_{131}-2\theta_{1\bar{3}1}$ differences exist both between the products of pairs of runs carried out simultaneously in one pressure vessel, and between runs carried out on different occasions, and cannot be due to inadequate temperature or pressure control. Attention is drawn (Tables I and II) to the four- and five-times repeated runs on both compositions at 600 °C for 331–3 hr. These were undertaken to establish the magnitude of this scatter, which covers a range of about 0·020° for both compositions, at least four times the standard error of the X-ray measurements.

The lowest temperatures at which runs were carried out were close to the previously determined position of the alkali feldspar solvus (see fig. 1). Since it may well be that the solvus for ordered feldspars falls outside that for disordered feldspars it is essential to consider, in the interpretation of $2\theta_{131}-2\theta_{1\bar{3}1}$ values, the possible effect of unmixing following crystallization of one homogeneous feldspar phase, or of the initial direct crystallization of two feldspar phases. For these sodium-rich compositions unmixing or subsolvus crystallization would lead to diffraction patterns appropriate to more albitic compositions and the small amount of potassium feldspar would be undetectable by X-ray means. Small changes in composition will be indistinguishable by X-ray means from changes due to ordering because all alkali feldspar lattice parameters are to some extent sensitive to both composition and structural state (Orville, 1967). In the discussion that follows good reasons will be given for believing that the form of the $2\theta_{131}-2\theta_{1\bar{3}1}$ v. time curves at low temperatures is dominantly due to changes in degree of order, but it is important to be aware of the possibility that unmixing is influencing the $2\theta_{131}-2\theta_{1\bar{3}1}$ values.

Discussion of results. In figs. 3 and 4 the $2\theta_{131}-2\theta_{1\bar{3}1}$ values obtained after different lengths of time at different temperatures are plotted and compared to the results of MacKenzie (1957) for pure albite. Final values of $2\theta_{131}-2\theta_{1\bar{3}1}$ estimated from figs. 3 and 4 are plotted against composition on fig. 2 and against temperature on fig. 5. The two potassium-bearing compositions show, at temperatures including 700 °C and above, final values of $2\theta_{131}-2\theta_{1\bar{3}1}$ related to each other in a very similar manner to the final values of albite, with the differences between the final forms of the various temperatures diminishing with increasing temperature. Further, the forms of the curves of $2\theta_{131}-2\theta_{1\bar{3}1}$ with time (figs. 3 and 4) are remarkably similar for all three compositions. Both the magnitude of the changes from early formed to final crystals and the time taken to attain the final forms are similar (with the proviso, already discussed, that the curves at 850 °C, 15 000 lb/in.², reflect compositional changes due to slow crystallization). There seems every reason to accept that the process involved in the changes evidenced in these curves is the same as that producing the changes in albite, namely Al–Si ordering, and that an equilibrium degree of order is gradually approached at the various temperatures.

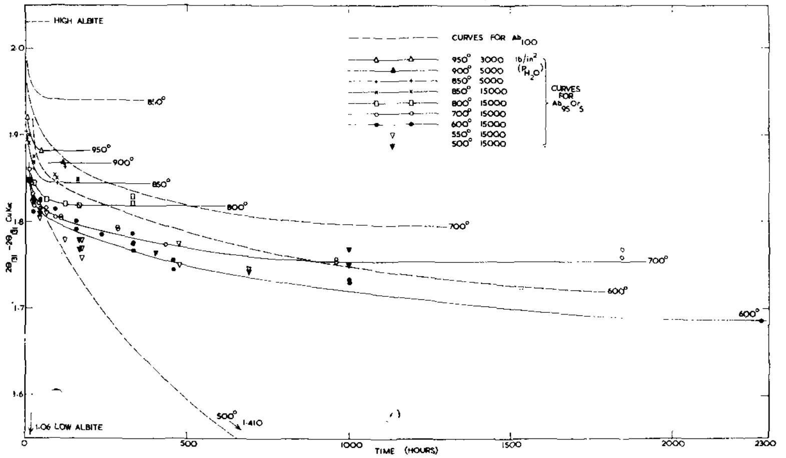


FIG. 3. Change in $2\theta_{131}-2\theta_{1\bar{3}1}$ with time of crystallization for the composition $Ab_{95}Or_5$. Curves for Ab_{100} from MacKenzie (1957) are shown for comparison. No curves have been drawn through the limited data on $Ab_{95}Or_5$ at 550 and 500 °C, but the wide difference in behaviour between this composition and albite at these temperatures may be seen. Two additional data points at 500 °C lie off the diagram at 2777 hrs with values of 1·716 and 1·704.

The $2\theta_{131}-2\theta_{1\bar{3}1}$ v. time curves (figs. 3 and 4) at 600 °C differ only slightly from those for albite, but those at 550 and 500 °C differ strikingly from the albite curves. The 600 °C curves for both anorthoclases overlap the 700 °C curves over much of their length for runs of shorter duration, and this overlap is more extensive for $Ab_{90}Or_{10}$ than for $Ab_{95}Or_5$. The 600 and 700 °C curves for albite are distinct over their whole lengths. Figs. 2 and 5 show that the final values of $2\theta_{131}-2\theta_{1\bar{3}1}$ at 600 °C do not differ from the 700 °C final values as much in the anorthoclases as in albite, so that at lower temperatures the curves showing the final values converge. The runs at 600 °C were not long enough to be quite certain that further $2\theta_{131}-2\theta_{1\bar{3}1}$ changes would not occur, but these are unlikely to be of sufficient magnitude to remove this convergence.

A pronounced change in behaviour is shown by the values obtained at 550 and 500 °C on $Ab_{95}Or_5$. These do not differ greatly from the 600 °C values on this composition, and they contrast in a marked way to the behaviour of albite at these low temperatures. This cannot be an effect of change of composition produced by unmixing, because the 550 and 500 °C results all lie *above* the $2\theta_{131}-2\theta_{1\bar{3}1}$ v. time curves for albite at these temperatures, (fig. 3) (MacKenzie (1957) shows data for 500 °C, which is plotted on fig. 3, and McConnell and McKie (1959) present additional data at 550 °C supplied by MacKenzie). All the curves at higher temperatures lie systematically *below* those for albite. If unmixing had occurred the $2\theta_{131}-2\theta_{1\bar{3}1}$ values would indeed tend towards those of albite, but if equivalent changes due to ordering had also occurred in some feldspar between $Ab_{95}Or_5$ and Ab_{100}, the $2\theta_{131}-2\theta_{1\bar{3}1}$ values must lie *below* the albite curves. It cannot be stated on the basis of the techniques adopted here, that no unmixing has occurred but it can be deduced with certainty that any changes in $2\theta_{131}-2\theta_{1\bar{3}1}$ due to ordering must be radically less than those observed in albite below 600 °C.

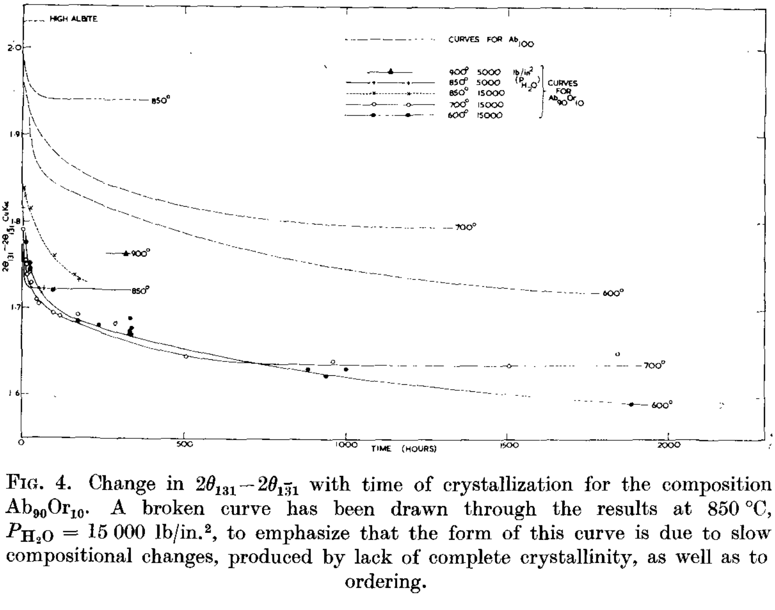
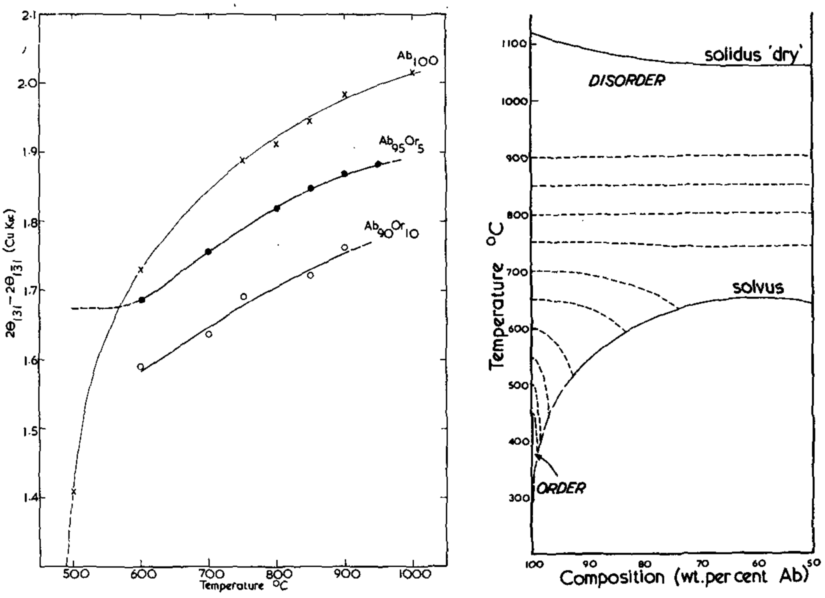


FIG. 4. Change in $2\theta_{131}-2\theta_{1\bar{3}1}$ with time of crystallization for the composition $Ab_{90}Or_{10}$. A broken curve has been drawn through the results at 850 °C, $P_{H_2O} = 15\,000$ lb/in.², to emphasize that the form of this curve is due to slow compositional changes, produced by lack of complete crystallinity, as well as to ordering.

To check that the different behaviour of $Ab_{95}Or_5$ below 600 °C was not due to some special peculiarity of the gel starting materials used, a few runs were undertaken on a gel of composition Ab_{100}, at 500 °C. Although the intermediate results on this were not identical to MacKenzie's figures, this would not be expected for a different starting material, since grain size and porosity will effect the rate of attainment of equilibrium, and the runs in the present study were not extensive enough to compare the probable final equilibrium values. The values on the Ab_{100} gel, however, lie reasonably close to MacKenzie's curve and plot on fig. 3 well below the values for $Ab_{95}Or_5$ at 500 °C. The radical difference in behaviour of $Ab_{95}Or_5$ below 600 °C may be interpreted as indication of a change in the ordering behaviour of $Ab_{95}Or_5$ relative to albite in this temperature range.



FIGS. 5 and 6: FIG. 5 (left). Final values of $2\theta_{131}-2\theta_{1\bar{3}1}$ estimated from figs. 3 and 4 plotted against temperature of crystallization. The curve for albite is from MacKenzie (1957). The change in curvature of the $Ab_{95}Or_5$ curve below 600 °C is intended to show that the values for this composition may plot above those for albite at 550 and 500 °C, although the final equilibrium values have not been obtained. FIG. 6 (right). Diagram showing the possible relation between equilibrium degree of ordering, temperature, and composition in sodic alkali feldspars. The broken curves are intended to indicate equal degrees of order to albite, the degree of order being unspecified. The solvus is that used in fig. 1, but it should be noted that an equilibrium solvus for the possible equilibrium degrees of ordering implied has not been obtained.

Interpretation of results

The simplest interpretation that may be placed on the results for the anorthoclases is to compare them directly to the results obtained by MacKenzie (1957) for albite, and to accept that differences in $2\theta_{131}-2\theta_{1\bar{3}1}$ within one composition between different temperatures are equivalent to equal differences in degree of order. Support for this argument is given by the great similarity between the $2\theta_{131}-2\theta_{1\bar{3}1}$ v. time curves (figs. 3 and 4) at 700 °C and above, and the parallelism of the final value curves (figs. 2 and 5) in this temperature range. In agreement is Orville's (1967) data for a range of synthetic metastable alkali feldspars made by alkali ion-exchange with natural low-albite and maximum microcline end-members. Orville (p. 82) gives reason to believe that his intermediate Na–K feldspars have retained, with little disordering, the highly ordered Al–Si frameworks of the parent natural crystals, and if this is so they represent feldspars that might exist if unmixing did not occur in alkali feldspars and if the high degree of order that exists in low albite and maximum microcline could be achieved in such mixed crystals. Natural low albite has a considerably smaller $2\theta_{131}-2\theta_{1\bar{3}1}$ value than the lowest temperature form produced by MacKenzie, and similarly Orville's 'low-temperature' form close to $Ab_{90}Or_{10}$ has a far smaller $2\theta_{131}-2\theta_{1\bar{3}1}$ value than any of the forms synthesized by the writer. Fig. 2 compares Orville's $2\theta_{131}-2\theta_{1\bar{3}1}$ values for his 'low-temperature' forms to the present data for higher temperatures. Change in $2\theta_{131}-2\theta_{1\bar{3}1}$ with composition in the 'low-temperature' forms is effectively the same as that in the synthetic high-temperature forms above 700 °C.

Viewed in this light it will be seen that the 600 °C final $2\theta_{131}-2\theta_{1\bar{3}1}$ values are closer to the 700 °C values than might be expected, and this gives rise to a convergence of the $2\theta_{131}-2\theta_{1\bar{3}1}$ v. temperature curves of fig. 5 and the $2\theta_{131}-2\theta_{1\bar{3}1}$ v. composition curves of fig. 2. It seems likely that the equilibrium forms at 600 °C are less well ordered than albite at this temperature. Although the data on $Ab_{95}Or_5$ at 550 and 500 °C are not conclusive, the radical difference in behaviour relative to albite is consistent with a wide difference in the equilibrium degree of order relative to albite, and this drastic change in the ordering behaviour occurs in the range 550–600 °C. It is possible that the 550 °C results indicate a pronounced slowing down in the rate of attainment of equilibrium but there seems no forewarning of this in the 600 °C curves (fig. 3) whereas there is some indication that at 600 °C the stable form of $Ab_{95}Or_5$ is less well ordered than albite at this temperature. We may reasonably conclude that the equilibrium forms of this alkali feldspar have approximately the same degree of order as albite above 700 °C, but that at lower temperatures the relative degree of order becomes less, falling sharply in the range 600–550 °C.

The rate of attainment of the equilibrium forms at various temperatures can be assessed by inspection of figs. 3 and 4. There seems no significant difference in the time taken to attain equilibrium for any of the three compositions concerned, at least at 600 °C and above. This is not consistent with the observations reported by Eberhard (1967).

A feature of the $2\theta_{131}-2\theta_{1\bar{3}1}$ v. time curves (figs. 3 and 4) of the anorthoclases that differs from the behaviour of albite is the apparent overlap of the curves over the early part of their lengths, in particular of the 700 °C and 600 °C curves. The degree of overlap appears to increase from $Ab_{95}Or_5$ to $Ab_{90}Or_{10}$. It seems possible that the early stages of incomplete crystallinity, and ordering developed in the crystals before the whole charge was crystalline, may be the cause of this behaviour. Evidence has already been presented that at 850 °C and P_{H_2O} of 15 000 lb/in.^{2} Al–Si ordering may be much more rapid than crystal growth, and since the largest changes in $2\theta_{131}-2\theta_{1\bar{3}1}$ take place in the first few hours of crystallization at all temperatures it is certain that some at least of the ordering will take place in crystals with a different Na:K ratio to the final product. We have no knowledge as to the homogeneous distribution or otherwise of Na and K after this early period of crystallization. It seems possible that, particularly at low temperatures in the vicinity of the solvus, once Na-rich and K-rich regions of structure had developed during crystallization the attainment of a homogeneous Na–K distribution might be a slow process. The evidence of the present experiments appears to be that at low temperatures, below 600 °C, the equilibrium form of albite is more ordered than the potassium-bearing compositions. Thus a crystalline product with an inhomogeneous Na–K distribution might also have variable degrees of order, which, in turn, would further inhibit the homogenization process. In this context it is perhaps relevant to note that at 600 °C, and particularly at 500 °C, the X-ray diffraction patterns of the feldspars produced in the present study were noticeably more diffuse than those at higher temperatures, and occasional large crystals showed a distinct zonal arrangement of extinction angles under the microscope. This diffuseness was not observed in the albites synthesized at 500 °C. Because of these possible co-operative effects, and the large scatter of experimental points, it would not be appropriate, in the writer's view, to subject the results on $Ab_{95}Or_5$ and $Ab_{90}Or_{10}$ to a kinetic analysis as carried out by McConnell and McKie (1959) for albite. The effect shown by them, using MacKenzie's data, of a relative increase in the rate of change of $2\theta_{131}-2\theta_{1\bar{3}1}$ with time below about 600 °C is masked, in the anorthoclases, by the pronounced change in behaviour below 600 °C. This is certainly a change of a type different to the smeared transformation that McConnell and McKie believed they had detected.

Conclusions

Whilst the preceding deductions may be unduly naïve in view of the possible complexities of ordering in alkali feldspars it is worthwhile to restate the aspects of the present work that appear to be capable of clear interpretation, and to tentatively suggest how these may be represented by an alkali feldspar 'phase diagram'. It should be noted that the X-ray properties of the feldspars that form the basis of this work were measured at room temperature and the values obtained would be quite different if measured at the temperatures of synthesis. One cannot, therefore, give a diagram showing $2\theta_{131}-2\theta_{1\bar{3}1}$ values of the crystals in the temperature ranges in which they are the stable forms or a diagram showing the change from monoclinic to triclinic symmetry for the stable forms. Furthermore, because of the absence of sufficiently large crystals of intermediate albites for structure determinations, the relation between $2\theta_{131}-2\theta_{1\bar{3}1}$ and degree of order is by no means clear. MacKenzie and Smith (1961) accept that $2\theta_{131}-2\theta_{1\bar{3}1}$ is directly proportional to degree of order, so that MacKenzie's (1957) data (reproduced in fig. 5) suggest an asymptotic approach to complete disorder. Laves (1960) favours an indirect relation between $2\theta_{131}-2\theta_{1\bar{3}1}$ and degree of order, suggesting an asymptotic approach to complete order with falling temperature, the situation observed in alloys. Fig. 6, therefore, compares the equilibrium degrees of order in the potassium-bearing feldspars to those of albite at each temperature.

At the temperatures above 600 °C there seems no appreciable difference in the ordering behaviour of the anorthoclases and albite. If we can accept that equal variation in $2\theta_{131}-2\theta_{1\bar{3}1}$ with temperature between the different compositions is equivalent to similar relative degrees of order, then the addition of 10 % Or to the albite structure does not appear to affect Al–Si ordering at 700 °C and above. This is at variance with the hypothesis advanced by MacKenzie and Smith (1961), that the presence of K would tend to promote disorder, and suggests the horizontal lines of equal disorder shown on fig. 6. (Compare with fig. 3 of MacKenzie and Smith, 1961.) At lower temperatures, however, at 600 °C a somewhat lower degree of order appears to hold relative to albite, and at 550 °C the degree of order in $Ab_{95}Or_5$ may be very similar to the degree of order in this composition at 600 °C, and seems certainly to be much less than in albite at this temperature. This suggests that relative to albite disorder becomes pronounced as the solvus is approached. The equal-disorder curves of fig. 6 are arranged to fit the present data. It seems that the effect postulated by MacKenzie and Smith, that substitutional disorder of Na and K would promote positional disorder of Al and Si, only becomes important at lower temperatures in the region of the solvus. This is not an unreasonable hypothesis, since it is distortion of the Al–Si framework produced by the alternation of large K and relatively small Na atoms that leads to unmixing, and it may be that the effect of these distortions on Al–Si order increases rapidly with falling temperature, particularly close to the solvus where slight lowering of temperature would lead to unmixing.

This hypothesis is consistent with the observed variation of natural specimens of albitic feldspars, low-albite specimens always being close to pure albite in composition. The $\alpha^*\gamma^*$ plot of MacKenzie and Smith (1962) shows that as these lattice parameters approach the disordered high-albite to sanidine series, they may also tend towards values for potassium-bearing feldspars. Ordering in sodic alkali feldspars can only proceed so long as unmixing also occurs, and a stable equilibrium solvus will presumably exist along which ordering and unmixing are everywhere in step. Whereas, however, a disordered feldspar may unmix, a feldspar that has not unmixed may not order, and to this extent it is composition that is the primary control of structural state in albitic feldspars.

It does not seem unlikely that similar relations hold for potassium feldspars, and MacKenzie and Smith (1961) have explained the common persistence of orthoclase in rocks in which microcline has been later formed, as a result of compositional differences. Petrological studies (Parsons, 1965) suggest that this is not the only reason for this effect, and ordering in the hypersolvus region was postulated in the latter paper. The present experiments indicate that ordering will indeed occur in this region, and, following the experimental indications that the presence of potassium does not prohibitively slow down the ordering process, experiments are in hand to investigate ordering in more potassic compositions.

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