MINERALOGICAL MAGAZINE, JUNE 1969, VOL. 37, NO. 286

Subsolidus crystallization behaviour in the system $KAlSi_3O_8$–$NaAlSi_3O_8$–H_2O

IAN PARSONS, B.SC., PH.D.
Department of Geology and Mineralogy, Marischal College, Aberdeen AB9 1AS

SUMMARY. When gels and glasses of alkali feldspar composition are crystallized hydrothermally below their solidus the crystals present when crystallization is incomplete do not have the same Na:K ratio as the starting material but bear a relation to the starting material analogous to that between crystals and liquids coexisting at the liquidus. This effect has been investigated in the temperature range 700–850 °C at water-vapour pressures between 5000 lb/in.^{2} and 30 000 lb/in.^{2} Fractionation and normal zoning of crystals may, in principle, occur within fixed bulk compositions held under isothermal, isobaric conditions.

WHEN gels or glasses of alkali feldspar compositions (i.e. between $NaAlSi_3O_8$ and $KAlSi_3O_8$) are crystallized below their solidus the crystals present while the crystallization process is incomplete, do not, in most cases, have the Na:K ratio of the starting material. Crystals with a different Na:K ratio to that of the starting material coexist with a residual glass, also of different composition to the starting material, and only when the charge is wholly crystalline do the crystals have the same composition as the starting material. This process of compositional equilibration was noticed and investigated during the course of a recently described series of experiments on the Al–Si ordering process in sodium-rich alkali feldspars (Parsons, 1968*b*). Even under hydrothermal conditions complete crystallization may take some appreciable time, and since the X-ray diffraction patterns of alkali feldspars are sensitive both to composition and to the degree of Al–Si order, it was necessary to investigate the manner in which compositional (as distinct from structural state) equilibrium was attained. The results of this study are presented here. They have certain general petrological implications that may not be widely familiar.

Synthesis technique. The hydrothermal apparatus used and the method of preparing starting materials are described fully elsewhere (Parsons, 1968*b*). Runs were carried out in 'cold seal' bombs in welded gold capsules containing about 20 mg of starting material together with up to 5 mg of deionized water. The basic starting materials were stoichiometric dehydrated gels made up at 5 wt % intervals over the alkali feldspar compositional range. The size of the particles in these crushed gels was variable within individual compositions and included large particles 0·1–0·2 mm in size, although most grains were much finer. These materials will be referred to as 'coarse' gels. The gels used in the ordering study ($Ab_{95}Or_5$ and $Ab_{90}Or_{10}$, Parsons, 1968*b*), were more carefully crushed to < 0·05 mm. Portions of some of the gels were further crushed to < 0·025 mm and will be called 'fine' gels. Some gel compositions were converted to hydrous glass by holding them above their liquidus at 900 °C and a water-vapour pressure of 15 000 lb/in.^{2} for five hours. This material was then crushed to < 0·025 mm and crystallized at a lower temperature in the presence of some additional water. These materials will be referred to as 'hydrous glass'.

Many of the runs involved are very short (two hours) and the warming up period when a pressure vessel is first placed in a furnace will have some effect on the products of the runs. No particular precautions were taken to ensure that the different runs attained their intended temperatures with equal rapidity and some of the scatter of results is probably caused by this. This factor in no way affects the general validity of the results obtained. The quench period was short, cooling to room temperature in a few minutes in a compressed air stream.

X-ray technique. The Na:K ratio of the alkali feldspars was obtained from the position of the $20\bar{1}$ reflection on X-ray diffractometer traces. Measurement techniques are given elsewhere (Parsons, 1968*b*), and the values given in table I are believed to be accurate to $\pm 0{\cdot}004^\circ$ 2θ. A new working curve relating the feldspar $20\bar{1}$ reflection and the 101 of $KBrO_3$ used as an internal standard (Orville, 1958) was applied in the present study. Some of the points on this curve have been shown in a previous paper (Parsons, 1968*a*) and it is closely similar to that given by Tuttle and Bowen (1958). It differs from that of Orville (1963) by a maximum of 2 wt % Or.[1] The small effect of Al–Si order–disorder on $20\bar{1}$ can be ignored in the present study because the runs are either at high temperatures or very short and there is good reason to believe that all alkali feldspars will form initially as disordered crystals and will take some days to achieve even partial order at 700 °C and below (MacKenzie, 1957; Parsons, 1968*b*).

Results

General considerations. Fig. 1 shows the composition of feldspars coexisting with a residuum that is optically isotropic and amorphous to X-rays after a two-hour period at the stated temperatures and water-vapour pressures, plotted against the composition of the starting material, which was in each case 'coarse' gel. Clearly, after this short period of crystallization the crystals do not possess the same Na:K ratio as the starting material although they are growing at least 100 °C below the solidus of each composition (the amount of undercooling may be estimated from the data of Bowen and Tuttle, 1950). The residuum will be referred to as 'glass', although how the physical condition of this material compares to the initial gel is not known. It seems that in many cases flow of the starting material has occurred, since the charge is removed in a partly fused condition. If crystallization is continued for a longer period the composition of the crystals changes until, when the charge is wholly crystalline, the crystals lie on the straight line shown. Fig. 1 compares the distribution of the compositions of these early formed crystals, which are *not* in equilibrium with glass, to the curves obtained when the composition of liquids at the liquidus is plotted against the composition of crystals in equilibrium with those liquids, the composition of the liquid in this case being plotted as the 'bulk composition'. The water-vapour pressures stated apply for both types of curve, but the equilibrium curves are not isothermal and were constructed from the data of Bowen and Tuttle (1950). The broad similarity between the two types of curve is obvious, although the detailed similarity in shape is fortuitous. The subsolidus points do not represent equilibrium compositions and their exact location will depend on the rate of attainment of equilibrium in each composition. The subsolidus experiments are not reversible and the

---

[1] Details can be supplied on request.

TABLE I. *Separation of alkali feldspar 20$\bar{1}$ reflection and 101 reflection of* $KBrO_3$ *after short periods under various conditions*

Conditions	Run no.	Ab*	$\Delta 2\theta_{20\bar{1}}$ Cu-$K\alpha$	Quality of reflection
‘Coarse’ gel for 2 hours at 850 °C and P_{H_2O} = 5000 lb/in.²	96	95	1·762°	
	100	90	1·719	
	107-1	85	1·699	
	211-1	80	1·678	
	107-2	75	1·635	
	107-3	70	1·578	
	211-2	65	1·450	v. weak
	211-3	60	1·226	weak
	108-1	50	1·045	
	251-2	35	0·975	
	108-3	25	0·882	
	251-1	10	0·796	weak
‘Coarse’ gel for 2 hours at 700 °C and P_{H_2O} – 5000 lb/in.²	270-1	75	1·591	
	253-2	70	1·541	
	258-1	60	1·178	v. weak
	254-3	50	1·012	
As above for 5 hours	276-1	75	1·542	
	279-1	75	1·542	
	279-2	70	1·510	
	275-2	55	1·135	
	275-3	50	1·150	
As above for 10 hours	280-2	65	1·431	
	283-3	60	1·335	
‘Fine’ gel for 2 hours at 850 °C and P_{H_2O} – 5000 lb/in.²	288-1	75	1·541	
	288-2	65	1·430	
	288-3	55	1·251	
	289-1	45	1·087	
	289-2	35	0·972	
	266-3	35	0·940	
	289-3	25	0·970	
	266-2	25	0·970	
‘Coarse’ gel for 2 hours at 700 °C and P_{H_2O} = 15 000 lb/in.²	74	90	1·724°	
	247-2	85	1·672	
	250-3	80	1·645	
	245-1	75	1·553	
	243-1	70	1·491	
	244-3	65	1·402	weak
	244-1	60	1·330	v. diffuse
	247-3	55	1·166	diffuse, asym.
	243-2	50	1·095	
	250-2	45	1·115	
	250-1	35	0·996	
	243-3	25	0·919	
As above at P_{H_2O} = 30 000 lb/in.²	268-3	80	1·650	
	257-1	75	1·552	
	268-2	75	1·565	
	268-1	70	1·491	
	257-2	65	1·203	v. weak
	269-1	65	1·218	v. weak
	259-1	60	1·275	asym.
	269-2	60	1·334	v. diffuse
	269-3	55	1·172	diffuse, asym.
	259-3	50	1·029	
As above for 5 hours	282-1	75	1·553	
	281-2	70	1·506	
	281-1	60	1·280	
	282-2	55	1·151 1·318 1·492	K-phase Mean Na-phase
	281-3	50	1·054	v. weak
‘Hydrous glass’ for 2 hours at 850 °C and P_{H_2O} – 5000 lb/in.²	284-1	75	1·528	
	285-2	70	1·490	
	284-3	65	1·438	
	284-2	55	1·273	
	285-3	50	1·202	

* Bulk composition, wt % Ab.

line drawn through these points serves only to emphasize the general disposition of crystal compositions.

The $20\bar{1}$ reflections used to obtain these points were, in the main, sharp and intense, except for certain compositions; 2θ values and comments on the quality of the reflections are given in table I. By no means all runs of equal length under particular conditions yielded X-ray diffraction patterns even though crystals could be detected optically. This was particularly true of the compositions $Ab_{65}Or_{35}$, $Ab_{60}Or_{40}$, and $Ab_{55}Or_{45}$. Only runs that gave X-ray diffraction patterns are tabulated here, and in some cases reflections for these three starting compositions were of poor quality.

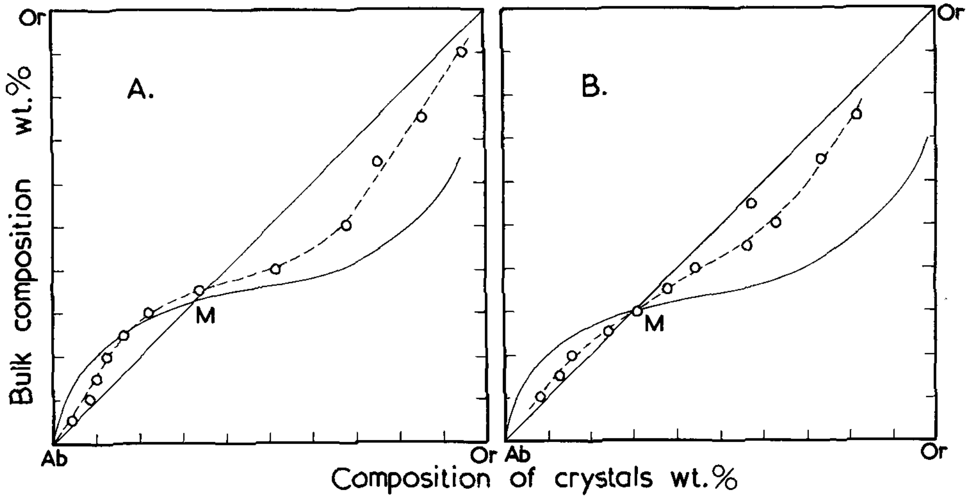


FIG. 1. Plots of bulk composition of starting material against composition of feldspar crystals present together with glass after two hours at: A, 850 °C and $P_{H_2O} = 5000$ lb/in.^{2}; B, 700 °C and $P_{H_2O} = 15\,000$ lb/in.^{2} The broken curves emphasize the general similarity between the distribution of these compositions and the solid curves, which represent the compositions of crystals in equilibrium with liquid at the liquidus, the liquid composition being the bulk composition for these curves. The solid curves refer to the same water-vapour pressures as the broken curves in each case and were constructed from the data of Bowen and Tuttle (1950). The point M is the binary minimum at each pressure.

The data show that when these gels are crystallized under isothermal, isobaric conditions below their solidus, the crystals that form at first do not instantaneously possess the bulk composition of the starting material, but bear a relationship to the bulk composition like that exhibited by first-formed crystals in a cooling liquid intersecting the liquidus. Only in three unique compositions do the crystals always possess the composition of the starting material: these are the end members and an intermediate composition that corresponds closely to the minimum-melting composition in the binary system at any particular water-vapour pressure found by Bowen and Tuttle, 1950. Figs. 1A and 1B show that this unique composition behaves similarly to the binary minimum-melting composition by moving towards albite with increasing water-vapour pressure. On the albite side of this composition early-formed crystals will be more albitic than the bulk composition and will react with glass as crystallization proceeds, becoming more potassic until the charge is wholly crystalline. The converse will apply for bulk compositions on the orthoclase side of the unique composition. Compositions close to and to the orthoclase side of this compositional point were consistently slow to crystallize (table I). The relevance of these compositional changes to the identification of the ordering process in anorthoclases has been described elsewhere (Parsons, 1968*b*).

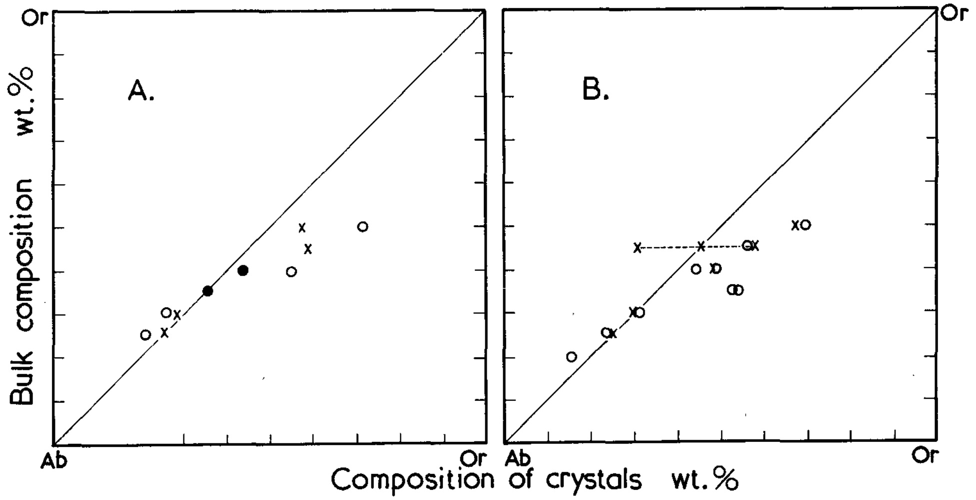
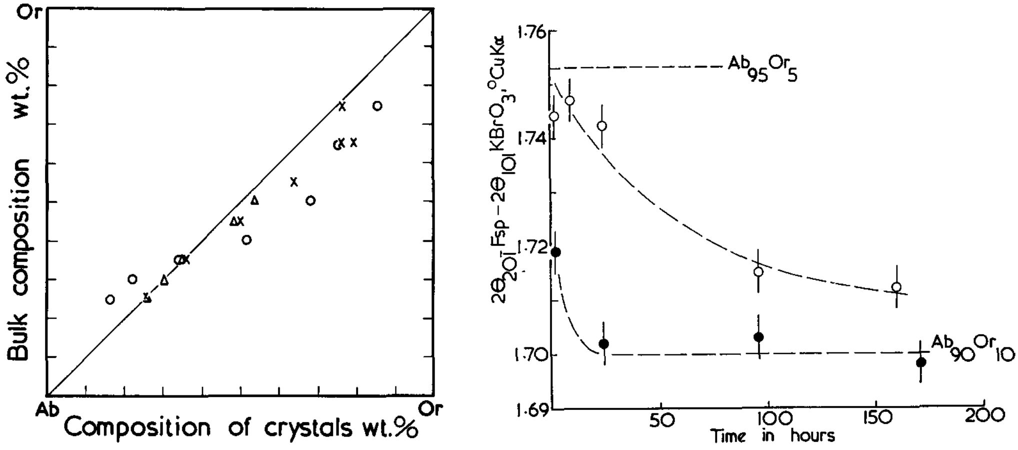


FIG. 2. Plots of bulk composition of starting material against compositions of feldspar crystals present together with glass after various periods of time at 700 °C and A, P_{H_2O} = 5000 lb/in.^{2}; B, P_{H_2O} = 30 000 lb/in.^{2} Duration of experiments: open circles, 2 hours; crosses, 5 hours; solid circles, 10 hours.

Effect of pressure. The effect of different water-vapour pressures was further investigated at 700 °C. Runs were carried out at 30 000 lb/in.^{2}, 15 000 lb/in.^{2}, and 5000 lb/in.^{2} on gels between $Ab_{75}Or_{25}$ and $Ab_{50}Or_{50}$, and compositions of the crystals present after various periods of time are plotted on fig. 2. $20\bar{1}$ spacings are given in table I. The composition $Ab_{65}Or_{35}$ was difficult to crystallize at 5000 lb/in.^{2} and a diffraction pattern was obtained only after a ten-hour run. At 30 000 lb/in.^{2} this composition was again difficult to crystallize and the very weak reflections present after two hours in two runs gave the aberrant compositions indicated. Further, at the latter water-vapour pressure, the $20\bar{1}$ reflection of crystals forming in the gel of $Ab_{60}Or_{40}$ composition was asymmetrical with a diffuse tail extending towards albite. The reflections given by the partially crystallized $Ab_{55}Or_{45}$ gel were very broad, and, after a five-hour run, two distinct peaks appeared at the extremities of this broadened reflection. The compositions corresponding to the mean peak position and to these two phases appear on fig. 2B. These effects would appear to be due to proximity to the alkali feldspar solvus, although these conditions are at a temperature some 30 °C above the solvus obtained by Luth and Tuttle (1966) on a stoichiometric $Ab_{60}Or_{40}$ gel.

Fig. 2 shows that the general disposition of points given in fig. 1 persists under these different conditions, although feldspars forming at 700 °C and 5000 lb/in.^{2} water-vapour pressure were about 250 °C below their solidus at this pressure. Equilibrium would seem to be attained more rapidly at 15 000 lb/in.^{2} than 5000 lb/in.^{2}, but at 30 000 lb/in.^{2} the additional complexities outlined preclude simple comparison.

Effect of variation in starting material. The rate of attainment of equilibrium is influenced by grain size and in all probability by the structure of the starting material.



FIGS. 3 and 4: FIG. 3 (left). Plot of bulk composition of starting materials of different types against composition of feldspars present after 2 hours at 850 °C and P_{H_2O} = 5000 lb/in.^{2} Open circles, 'coarse' gels; crosses, 'fine' gels; triangles, 'hydrous glasses'. FIG. 4 (right). Plot of $2\theta_{20\bar{1}}$ Feldspar $-2\theta_{101}$KBrO$_3$ of crystals formed from gel of $Ab_{90}Or_{10}$ composition after various periods of time at 850 °C. The bars on each symbol indicate the probable error associated with each measurement. Open circles, P_{H_2O} = 15 000 lb/in.^{2}; solid circles, P_{H_2O} = 5000 lb/in.^{2} The final value of $20\bar{1}$ for crystals of composition $Ab_{95}Or_5$ is also shown.

Fig. 3 compares the compositions of crystals present after holding the 'coarse' and 'fine' gel materials at 850 °C, 5000 lb/in.^{2} water-vapour pressure for two hours, together with results for the finely crushed 'hydrous glasses'. The latter material equilibrates most rapidly and the 'fine' gel a little more rapidly than the 'coarse' gel, although the compositional difference between crystals and starting material persists for compositions less albitic than $Ab_{60}Or_{40}$. More albitic compositions were effectively wholly crystalline after two hours.

Rate of attainment of equilibrium in $Ab_{90}Or_{10}$. During the course of the experiments on Al–Si ordering described elswhere (Parsons, 1968*b*) the composition $Ab_{90}Or_{10}$ was investigated at 850 °C at two water-vapour pressures, 15 000 lb/in.^{2} and 5000 lb/in.^{2} The former conditions are very close to the solidus for this composition (about 10° below) whilst the latter conditions are about 100 °C below the solidus. Fig. 4 shows the change in $20\bar{1}$ spacing with time for crystals forming from the $Ab_{90}Or_{10}$ gel. At the high water-vapour pressure, glass could be detected optically in the charge even after 171 hours and the $20\bar{1}$ spacing suggests that the crystal compositions are different from the final value even after this period. At the lower pressure a $20\bar{1}$ value from which no significant change occurred was reached in less than 24 hours. In the immediately subsolidus region it appears that compositional differences between glass and crystals may persist for appreciable periods.

Discussion

The subsolidus crystallization phenomena investigated do not appear previously to have been described as such and clearly the experiments merely touch at the general principles of a complex process that involves rates of nucleation and crystal growth, glass viscosity, and rates of alkali ion exchange between crystals and glass, all of which may vary with *P–T* conditions, composition, and water content, and with the prior heat-treatment of starting materials. The familiar reference to subsolidus crystallization in a binary silicate system with continuous solid solution is that given by Bowen, 1928 (and frequently incorporated in later textbooks), which concerns subsolidus crystallization of plagioclases of which it is said: 'With very quick chilling, such that crystallization took place from a somewhat undercooled condition, the result would be homogeneous mix crystals or solid solutions having the total composition of the original liquid. In this case there would be no change in composition of liquid during crystallization.' This is manifestly not the case in the alkali feldspar series and experiments by Kudo and Weill (1967) suggest that it may not be the case in the plagioclase series. In the latter experiments glasses made from natural acid rocks were held at constant temperature in their melting interval; Ca-rich plagioclase nucleated rapidly but then took 2 to 3 weeks to yield a more sodic equilibrium composition. These plagioclases were thus behaving in a manner similar to that demonstrated for the alkali feldspars.

It seems worthwhile to enlarge on certain general implications of the behaviour found for the alkali feldspars that may have petrological significance. The observations of Kudo and Weill (1967) suggest that similar considerations may apply to plagioclase feldspars.

Firstly, the presence of alkali feldspar crystals in a glass having a different Na:K ratio to the crystals in no way presumes that those crystals formed at the liquidus or in the melting interval.

Secondly, depending on the relative rates of crystal framework growth and alkali-ion exchange between crystals and undercooled melt, subsolidus crystallization could follow an 'equilibrium' course or a 'fractionation' course. If it were possible for early formed crystals to be continuously subtracted from the melt a 'perfect fractionation' course could be followed differing only from perfect fractionation at the liquidus in that fractionation is not restricted by the need for falling temperature to maintain the composition of the liquid on or below the liquidus. Subsolidus fractionation could occur under isothermal isobaric conditions, and would be restricted only by the impossibility of passing the unique composition that is analogous to the binary minimum (point *M* of fig. 1). It should be remembered that the viscosity of silicate liquids does not suddenly increase at the temperature of the solidus of the crystals to which they give rise (e.g. Shaw, 1963).

Thirdly, it seems possible that some degree of normal (but not reversed or oscillatory) zoning may develop in crystals forming under certain favourable subsolidus, isothermal, isobaric, constant-bulk-composition conditions. Crystal framework growth may exceed the rate at which Na and K can redistribute themselves to give unzoned crystals (this is not impossible, despite the mobility of Na and K, since zoned alkali feldspars do occur in nature). Indeed the asymmetry of some of the $20\bar{1}$ diffractometer peaks seems to suggest that compositional variations do exist in the crystals. A zonal arrangement of extinction angles may be seen in some crystals under the microscope. Crystal homogenization would probably be hindered in plagioclase and ternary feldspars by the necessity of redistributing Al in the structure, so that if, as the work of Kudo and Weill (1967) suggests, Ca-bearing feldspars behave in the same manner as the binary alkali feldspars described in the present paper, there might be a wider range of circumstances favourable to development and preservation of zoning. Changing temperature, pressure, or bulk composition do not appear to be necessary prerequisites for the development of normal zoning in feldspars.

Acknowledgements. This work was in part aided by an N.E.R.C. Research Grant. Thanks are due to R. J. Clark for technical assistance and to Professor W. S. MacKenzie for discussion on aspects of this study.

REFERENCES

Bowen (N. L.), 1928. *The Evolution of the Igneous Rocks.* Princeton University Press.
—— and Tuttle (O. F.), 1952. *Journ. Geol. Chicago,* **58,** 489.
Kudo (A. M.) and Weill (D. F.), 1967. *Progr. Abstr. Geol. Soc. Amer. Meeting,* 124.
Luth (W. C.) and Tuttle (O. F.), 1966. *Amer. Min.* **51,** 1359.
MacKenzie (W. S.), 1957. *Amer. Journ. Sci.* **255,** 481.
Orville (P. M.), 1958. *Ann. Rep. Dir. Geophys. Lab. Carnegie Inst. Washington,* 206.
Parsons (I.), 1968*a*. *Min. Mag.* **36,** 797.
—— 1968*b*. Ibid., 1061.
Shaw (H. R.), 1963. *Journ. Geophys. Res.* **68,** 6337.
Tuttle (O. F.) and Bowen (N. L.), 1958. *Geol. Soc. Amer. Mem.* **74.**

[*Manuscript received 31 October 1968*]