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THE ALKALI FELDSPARS: IV. THE COOLING HISTORY OF HIGH-TEMPERATURE SODIUM-RICH FELDSPARS*

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AND

ABSTRACT

A redetermination of part of the alkali feldspar solvus has been made using single crystal x-ray methods to obtain the composition of the sodium-rich phase of a natural cryptoperthite subjected to various heat treatments. This solvus differs considerably from that previously determined by Bowen and Tuttle for synthetic feldspars. The discrepancy is believed to be caused by errors in the determination from powder patterns of the compositions of the separate phases of perthites and by metastability of the synthetic feldspars in the temperature range of the solvus.

Single crystal x-ray photographs of some natural sodium-rich high-temperature alkali feldspars revealed several different orientations for the twinned components and the perthitic units of unmixed crystals. Interpretation of the x-ray photographs in the light of the position of the monoclinic-triclinic inversion and the revised position of the solvus has given information on the cooling history of these specimens.

INTRODUCTION

Bowen and Tuttle (1950) made one of the most significant advances in the study of the feldspars when they determined experimentally the position of the solvus for synthetic alkali feldspars. Although evidence for exsolution in the alkali feldspar series had been available from a number of previous studies, the experimental proof of its existence and the determination of its position were of the greatest importance. The amount of calcium in most natural alkali feldspars, with the exception of some sodium-rich specimens, is sufficiently small for the effect of calcium in raising the temperature of the solvus to be neglected: in addition it was shown that the position of the solvus is virtually independent of pressure (O. F. Tuttle, personal communication). For these two reasons it appeared that this was a very valuable geologic thermometer and a number of investigators have attempted to use it as such. However, many perthitic feldspars (orthoclase and microcline perthites) cannot be homogenized except by heating at temperatures well above the crest of the experimentally determined solvus (660° C.) and the position of the solvus must, therefore, be affected by the Si, Al arrangement in the unmixed components. Since the synthetic feldspars used by Bowen and Tuttle (1950) to determine the position of the solvus are almost certainly metastable in the temperature range 500°-670° C., and natural feldspars belonging to

the sanidine-anorthoclase series (Tuttle, 1952) are probably closer to the stable form of the feldspar at this temperature range, a more reliable measurement of the position of the stable solvus should be obtainable from natural high-temperature specimens.

This paper presents the results of a new determination of part of the alkali feldspar solvus obtained from a study of the change in composition of the sodium-rich phase of a natural crypto-perthite subjected to various heat treatments. In addition, information on the cooling history of a number of sodium-rich alkali feldspars has been obtained by interpretation of the crystallographic relations found in single-crystal x-ray patterns and in the light of the revised position of the solvus.

An optical and x-ray study of a series of natural alkali feldspars obtained mainly from volcanic rocks was given in paper III of this series (MacKenzie and Smith, 1956). These quickly cooled specimens were found to have retained their high-temperature structure and with two exceptions belong to the sanidine-anorthoclase series. Specimens in the composition range Or_{66}(Ab+An)_{34} to Or_{25}(Ab+An)_{75} were found to be unmixed but could be rendered homogeneous by heating at 700° C. for a few hours. When homogeneous, specimens more sodium-rich than Or_{37}(Ab+An)_{63} are triclinic, whereas more potassium-rich specimens are monoclinic.

Because the high-temperature albite structure can accommodate both potassium and calcium, it is desirable at this stage to make a clear distinction between a high-temperature plagioclase, an anorthoclase and a sanidine. For this purpose the compositional properties of the monoclinic-triclinic inversion may be utilized. Those homogeneous triclinic high-temperature feldspars which invert reversibly to monoclinic symmetry before beginning to melt are called anorthoclases, those which begin to melt before acquiring monoclinic symmetry are plagioclases and those high-temperature feldspars which are monoclinic are called sanidines. The compositional fields of these three types are shown in Fig. 1 (modified slightly from MacKenzie, 1952). Upon heating, the boundary between the triclinic and monoclinic high-temperature sodium-rich feldspars changes and an attempt to delineate the change with temperature has been made in Fig. 1 on the basis of the limited data at present available. Thus all anorthoclases invert to sanidines at elevated temperatures but high-temperature plagioclases do not. In petrography no confusion in nomenclature should arise since observations are normally made at room temperature.

The alkali feldspar solvus

Bowen and Tuttle (1950) determined the position of the alkali feldspar solvus by crystallizing homogeneous glasses of composition Or_{50}Ab_{50};
OrrsAbsr and OrrsAbeo at temperatures below 660° C. They obtained two feldspars, the compositions of which were estimated from the diffraction angles of the 201 planes in x-ray powder diffraction patterns. They were also able to unmix a previously crystallized homogeneous feldspar of composition OrrsAb60 by holding it at 530° C. in the presence of water vapor under pressure. Bowen and Tuttle emphasized that these syn-

![Triangular diagram showing the composition fields of high-temperature ternary feldspars (modified from MacKenzie, 1952). The compositions of some natural and synthetic feldspars are plotted and the temperature of the monoclinic-triclinic inversion is given for each point plotted. Isotherms of the monoclinic-triclinic inversion temperatures are drawn, the data (MacKenzie, 1952; Laves, 1952, being very limited where the lines are dashed. The boundary between the fields of one feldspar and of two feldspars is arbitrarily drawn through OrrsAb60An10, OrrsAb60An20 and OrrsAb60An10.

The one feldspar field has been divided into the fields of sanidine, anorthoclase, and high-temperature plagioclase by the line XY and the line from Ab to Z. Homogeneous high-temperature feldspars in the plagioclase field are triclinic at all temperatures. Triclinic feldspars in the field Ab Z X Y are called anorthoclases. All anorthoclases become monoclinic at a particular temperature that varies with the composition as shown by the isotherms. All monoclinic high-temperature feldspars are called sanidine. The extent of the sanidine field varies with temperature, gradually taking over the anorthoclase field as the temperature is raised.

Fig. 1. Triangular diagram showing the composition fields of high-temperature ternary feldspars (modified from MacKenzie, 1952). The compositions of some natural and synthetic feldspars are plotted and the temperature of the monoclinic-triclinic inversion is given for each point plotted. Isotherms of the monoclinic-triclinic inversion temperatures are drawn, the data (MacKenzie, 1952; Laves, 1952, being very limited where the lines are dashed. The boundary between the fields of one feldspar and of two feldspars is arbitrarily drawn through OrrsAb60An10, OrrsAb60An20 and OrrsAb60An10. The one feldspar field has been divided into the fields of sanidine, anorthoclase, and high-temperature plagioclase by the line XY and the line from Ab to Z. Homogeneous high-temperature feldspars in the plagioclase field are triclinic at all temperatures. Triclinic feldspars in the field Ab Z X Y are called anorthoclases. All anorthoclases become monoclinic at a particular temperature that varies with the composition as shown by the isotherms. All monoclinic high-temperature feldspars are called sanidine. The extent of the sanidine field varies with temperature, gradually taking over the anorthoclase field as the temperature is raised.
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thetic feldspars retain the characteristics of high-temperature feldspars. The same authors also determined the composition of the separate phases in a number of perthitic feldspars both in their natural state and after the various heat treatments, and they very kindly placed their results and the heated samples at our disposal.

Using single crystal x-ray methods we have made a new determination of the sodium-rich part of the alkali feldspar solvus and we believe that this represents more closely the equilibrium solvus than that previously determined. The material selected for this purpose was a sanidine-cryptoperthite from Korea (Or$_{47.4}$Ab$_{52.6}$An$_{0.8}$) described by Spencer (1937) and denoted as specimen P. This specimen was chosen because of its low calcium content and because of the relatively simple pattern given by single crystal x-ray diffraction. The effect of heat treatment of the sodium-rich phase was studied by measuring the reciprocal lattice angles $\alpha^*$ and $\gamma^*$ of the pericline twinned sodium-rich phase from single crystal x-ray photographs using the method described in paper II of this series (Smith and MacKenzie, 1955) and from these angles determining the chemical composition of the sodium-rich phase using the data of Donnay and Donnay (1952). After each period of heat treatment an x-ray photograph was taken and the reciprocal lattice angles $\alpha^*$ and $\gamma^*$ measured, the data are set down in Table 1. In Fig. 2 curves are drawn of the variation in $\alpha^*$ and $\gamma^*$ with chemical composition for anorthoclases and high-temperature albite using the values determined by Donnay and Donnay (1952) for synthetic feldspars of composition Or$_{30}$Ab$_{70}$, Or$_{20}$Ab$_{80}$, Or$_{10}$Ab$_{90}$ and the value determined for high-temperature albite by Smith

Table 1. Reciprocal Lattice Angles of the Sodium-Rich Phase of Specimen P. (Or$_{47.4}$Ab$_{52.6}$An$_{0.8}$)

<table>
<thead>
<tr>
<th>Number of crystal</th>
<th>Heat treatment</th>
<th>$\alpha^*$</th>
<th>$\gamma^*$</th>
<th>Or content (from Fig. 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>unheated</td>
<td>87°56'</td>
<td>89°0'</td>
<td>25.5%</td>
</tr>
<tr>
<td>1</td>
<td>then 17 hrs. at 433° C.</td>
<td>87°43'</td>
<td>88°59'</td>
<td>24.0%</td>
</tr>
<tr>
<td>1</td>
<td>then 23 hrs. at 470° C.</td>
<td>87°51'</td>
<td>89°2'</td>
<td>25.5%</td>
</tr>
<tr>
<td>1</td>
<td>then 16 hrs. at 490° C.</td>
<td>88°9'</td>
<td>89°5'</td>
<td>27.5%</td>
</tr>
<tr>
<td>1</td>
<td>then 16 hrs. at 515° C.</td>
<td>88°17'</td>
<td>89°7'</td>
<td>28.5%</td>
</tr>
<tr>
<td>1</td>
<td>then 20 days at 525° C.</td>
<td>88°42'</td>
<td>89°14'</td>
<td>30.5%</td>
</tr>
<tr>
<td>2</td>
<td>105 days at 400° C.</td>
<td>87°20'</td>
<td>88°45'</td>
<td>20.5%</td>
</tr>
<tr>
<td>3</td>
<td>95 days at 500° C.</td>
<td>88°30'</td>
<td>89°19'</td>
<td>30.5%</td>
</tr>
<tr>
<td>4</td>
<td>8 days at 425° C.</td>
<td>88°1'</td>
<td>89°0'</td>
<td>26.0%</td>
</tr>
<tr>
<td>5</td>
<td>8 days at 450° C.</td>
<td>88°1'</td>
<td>88°57'</td>
<td>26.0%</td>
</tr>
<tr>
<td>6</td>
<td>8 days at 475° C.</td>
<td>88°14'</td>
<td>89°0'</td>
<td>28.0%</td>
</tr>
<tr>
<td>7</td>
<td>8 days at 560° C.</td>
<td>90°0'</td>
<td>90°0'</td>
<td>≥37.0%</td>
</tr>
</tbody>
</table>
Feldspars more potassic than Or$_{37}$Ab$_{63}$ are monoclinic and so have $\alpha^* = \gamma^* = 90^\circ$. The values of $\alpha^*$ determined for the sodium-rich phase of each of the heat-treated crystals are joined by a vertical line to the determined values of $\gamma^*$ and the position of the vertical line adjusted so that the deviations of $\alpha^*$ and $\gamma^*$ from the reference curves are equal. The ends of the lines all fall close to the two reference curves and if the error in the chemical composition depends only on the error in determining the reciprocal lattice angles the predicted composition should be accurate to $\pm 1\frac{1}{2}$\% Or. There are, however, other errors to be considered and these will be discussed below.

Before heating, the sodium-rich phase of specimen P had lattice angles which indicated a composition Or$_{35.5}$(Ab + An)$_{74.5}$. Heating for several
hours between 400° C. and 500° C. produced no appreciable change in the lattice angles, but longer periods led to significant changes. Heating for 105 days at 400° C. decreased $\alpha^*$ and $\gamma^*$ whereas treatment at 500° C. for 95 days increased them, from which it may be deduced that specimen P is in a state that would be stable at some temperature between 400° C. and 500° C. Heating for 20 days at 525° C. produced little change over that achieved at 500° C., but on heating at 560° C. for 8 days the sodium-

![Graph showing composition changes](image)

Fig. 3. Plot of the composition of the sodium-rich phase of heat treated samples of specimen P against temperature. The estimated error in the determination of chemical composition (13% Or) is marked for the runs of longer duration. The curve of best fit is drawn through the points with a strong bias towards the runs of longer duration.

feldspar component became monoclinic giving a two-sandine perthite. As the composition of the symmetry change is Or$_{37}$(Ab+An)$_{63}$ the solvus should pass through this composition at some temperature not higher than 560° C. The data are given in Table 1 and plotted in Fig. 3 in which a curve is drawn as close as possible to the points representing the longer periods of heating. This curve is believed to give a good representation to the sodium-rich boundary of the solvus in the range 400°–550° C.

In Fig. 4 three solvi are shown. Curve A represents the solvus deter-
The curve showing the relation between chemical composition and temperature of the symmetry change in anorthoclases is reproduced from MacKenzie (1952).

The curve showing the relation between chemical composition and temperature of the symmetry change in anorthoclases is reproduced from MacKenzie (1952).

It is obvious that there are large discrepancies to be explained. The discrepancy between the two sets of results on specimen P can be explained if either or both of the methods give an incorrect estimate of the
composition. It is now well known that the 201 method is inaccurate for perthitic materials because Laves (1952), Coombs (1954) and MacKenzie and Smith (1956) have noted that impossible results are commonly obtained for the compositions of the separate phases of orthoclase perthites. The error is believed to result from the lattice distortion caused by strain between the unmixed components. Despite this evidence for lattice distortion we believe that the lattice angles $\alpha^*$ and $\gamma^*$ give a good estimate of the composition of the sodium-rich phase for the following two reasons. First, the values of $\alpha^*$ and $\gamma^*$ for the soda-rich phases in orthoclase, sanidine and anorthoclase perthites have all been reasonable and not in conflict with the values obtained from homogeneous sodic feldspars (Donnay and Donnay, 1952, Mackenzie and Smith, 1955, 1956). Secondly, the heating experiments of specimen P showed that ionic movement was becoming sluggish at 400°C. and consequently the boundaries between homogeneous and unmixed volcanic specimens would be expected to be near the positions of the solvus at this temperature. The observed sodic boundary, $\text{Or}_{30}(\text{Ab}+\text{An})_{70}$ (paper III), agrees well with the solvus determined from $\alpha^*$ and $\gamma^*$ but disagrees strongly with the solvus determined from the (201) spacing. Additional confirmation of the validity of the $\alpha^*$ and $\gamma^*$ angles is given by agreement of the boundary composition with the compositions $\text{Or}_{10}$ to $\text{Or}_{20}$ determined from the $\alpha^*$ and $\gamma^*$ angles of the exsolved sodic phases of sanidine perthites (paper III).

The position of the crest of the solvus would be unaffected by errors in $\alpha^*$, $\gamma^*$ and the (201) spacing and the discrepancy between the crests for the specimen P and the synthetic feldspar probably must be ascribed to some structural difference, the most likely variation being in the Si, Al arrangement.

It seems certain that both factors have contributed to differences in the position of the solvi shown in Fig. 4, and we believe that the small part of the solvus determined by us is more applicable to natural feldspars and is probably closer to the equilibrium solvus than that determined by Bowen and Tuttle.

**Twinning in Triclinic Feldspars**

Laves (1950) made an important contribution to our knowledge of twinning in feldspars when he discovered that in the cross-hatched twin structure of microcline the twin axis $b$ of the pericline twins was normal to the twin plane (010) of the albite twins. He noted that this arrangement would not be expected if twinning occurred while the microcline were triclinic for there is no simple crystallographic relationship, based on the triclinic unit cell, between the $b$ axis and the (010) plane. How-
ever, the arrangement could be readily understood if twinning had occurred as the result of inversion from a monoclinic phase, for parts of the crystal could retain the diad axis and other parts the plane of symmetry. The validity of the argument was strengthened when Laves (1952) found a similar twin structure in some anorthoclases, for in this case it can be shown in the laboratory that anorthoclases acquire monoclinic symmetry on heating and revert to triclinic symmetry on cooling.

Laboratory studies have shown that, except possibly for pure albite, plagioclase feldspars do not acquire monoclinic symmetry on heating and must crystallize directly as triclinic crystals (MacKenzie, 1952). Thus we should not expect to find the twin axis of the pericline twins lying normal to the twin plane of the albite twins. Single crystal x-ray photographs of plagioclase crystals twinned on both laws generally show that there are three components which may be denoted A, B, and C: B is related to A by the albite law and to C by the pericline law. The $b$ axis and the 010 plane of unit B are not perpendicular and the crystallographic relations of the twin structure are consistent with the triclinic symmetry. Sometimes more than three components occur, say A, B, C, D, E, ... In this case alternate pairs AB, CD, EF, ... are related by one twin law and BC, DE, ... by the other. Laves (1952, p. 558) has noted that it is geometrically impossible for the fourth unit in sequence to be related to the first unit by a twin relation. [This repeated twinning may explain some of the discrepancies commonly noted in angular measurements of plagioclase twins, discrepancies which have led to the postulation of vicinal faces and compositional differences in the twin components among other things (see Barber, 1935, for example), for it is possible that angular comparison may unwittingly be made between units A and D of a sequence of albite and pericline twins.] For convenience, the two types of twin relationship will be designated 'M' and 'T'; for the remainder of the paper these will be understood to have a genetic significance indicating that twinning occurred either during inversion from a monoclinic crystal (M type) or directly in a triclinic crystal (T type).

The different origins of the twinning lead to characteristic optical differences. Although the twin lamellae sometimes intersect in plagioclases it is more common to find an area which is pericline twinned and an adjacent area which is albite twinned. In anorthoclases the two sets of twin lamellae can be seen in a suitable orientated section to intersect very frequently, giving an appearance that has variously been described by the adjectives cross-hatched, tartan or quadrille. One exception has been noted, an anorthoclase from Mt. Franklin which has the plagioclase type of twinning. X-ray study to be described later in this paper
shows that it has the T-type twinning and presumably twinned while triclinic. Thus the presence of cross-hatching can be used to characterize an anorthoclase, but the presence of the first type of twinning does not necessarily indicate a plagioclase, though the inference is strong. Twinned microclines generally show the cross-hatched or quadrille twin structure but the lamellae are frequently spindle-shaped in contrast to the parallel sides of the anorthoclase lamellae. The difference is probably caused by the different character and velocity of the monoclinic-triclinic inversions: the sanidine-anorthoclase inversion is displacive and almost instantaneous whereas the sanidine-microcline inversion is caused by order-disorder of Si and Al atoms and is extremely sluggish.

From a study of the crystallographic relations between twin components and unmixed phases of anorthoclase perthites, it should be possible to deduce something about the crystallization history of the containing rock, and such attempts have been made in the next section for several specimens.

THE CRystALLIZATION HISTORY OF SOME HIGH-TEMPERATURE ALKALI FELDSPARS

A detailed study of the single crystal x-ray photographs of a few of the sanidine and anorthoclase-cryptoperthites described in paper III of this series (MacKenzie and Smith, 1956) has been made and a brief description of four of these specimens is given below. Each of the x-ray photographs was taken in the standard orientation used by the present authors, i.e. a 15° oscillation about the morphological b-axis of the crystal, the (001) plane being set in the center of the arc of oscillation.\(^1\) By using this one orientation, interpretation of the photographs is simplified as they can be directly compared with one another.

In Fig. 4, in addition to the three solvi represented by curves A, B, and C, the curve showing the relation between composition and temperature of the change in symmetry in the anorthoclases is reproduced (MacKenzie, 1952). This diagram will be referred to in discussing the sequence of changes in the cooling of alkali feldspars.

a) Sanidine cryptoperthite from Cebolla Creek (Or\(_{40.3}\)Ab\(_{57.6}\)An\(_{2.1}\)).

This specimen consists of a monoclinic potassium phase and a four-component triclinic sodium phase twinned on the albite and pericline laws such that the relation is of the M type. The x-ray oscillation photograph is reproduced in Fig. 5 and a key to its interpretation is

\(^1\) Because cryptoperthites consist of more than one phase and commonly have albite or pericline twinning of the triclinic phase, the simplest method of specifying the axis of oscillation is to refer to the morphological axis of the crystal. Generally when a monoclinic potassium phase is present its orientation is that of the morphology of the crystal.
Fig. 5. Sanidine cryptoperthite from Cebolla, Creek, $b$ axis oscillation photograph with the $x$-ray beam parallel to (001) in the center of a 15° oscillation. The inset diagram in the bottom left hand corner provides a key for the interpretation of the reflections enclosed in the small rectangle in the upper left. There are five components: $A_1A_2$ and $P_1P_2$ are albite and pericline twins of the soda-rich phase and $M$ is the monoclinic potash phase. The components are related by the $M$ type of association because reflections $P_1$ and $P_2$ lie on the same layer lines whereas reflections from $A_1$ and $A_2$ lie on bent layer lines symmetrically related to the $P_1P_2$ layer lines. The $b$ twin axis, therefore, is perpendicular to the (010) twin plane. The $M$ reflections lie on the same layer lines as the $P_1P_2$ reflections indicating unmixing from an original homogeneous monoclinic phase.

given as an inset. The twin elements of the sodium-rich phase are coincident with the symmetry elements of the potassium-rich phase and this relation indicates that the unmixing took place from a monoclinic crystal: it also indicates that the twinning of the sodium-rich phase took place on inversion from monoclinic to triclinic symmetry. Most sanidine cryptoperthites show only pericline twinning of the sodium-rich phase but those which show both albite and pericline twinning will be expected to have this special orientation.

If this specimen cooled under equilibrium conditions it would have begun to unmix at 560° C. (see Fig. 4) and the two monoclinic phases would have changed in composition along the solvus until at about 400° C the sodium-rich phase of composition $Or_{31}(Ab+An)_{70}$ changed to triclinic symmetry and adopted the $M$ type twinning. From measurements of $\alpha^*$ and $\gamma^*$ (Table 2), the composition of the sodium-rich phase was estimated to be $Or_{31}(Ab+An)_{70}$, and it appears that unmixing has not proceeded below the inversion temperature: if unmixing had occurred below this temperature, additional reflections, as in the photographs of the next specimen, would have been expected.
b) Anorthoclase cryptoperthite from Grande Caldeira, Azores (O\textsubscript{T}3\textsubscript{1},\textsubscript{7}A\textsubscript{b}6\textsubscript{.5}A\textsubscript{m}1,\textsubscript{8}).

Some of the crystals show the M type of relation between the albite and pericline twins of the sodium phase together with a potassium phase which gives three sets of x-ray reflections (see Fig. 6). (Other crystals show only one twin law.) One set of reflections from the potassium phase has its $b$ axis parallel to the $b$ axis of the pericline twinned units of the

![Fig. 6. Anorthoclase cryptoperthite from Grande Caldeira, b axis oscillation photograph with the x-ray beam parallel to (001) in the center of a 15° oscillation. The inset diagram at the bottom left provides a key for the interpretation of the reflections enclosed in the rectangle at the upper left. There are seven components: $A_1A_2P_1P_2$ are albite and pericline twins of an anorthoclase showing the M type of association; $M_1M_2M_3$ are three potassic components. The reflections from $M_1$ and $M_3$ lie in the same bent layer lines as the reflections from $A_1$ and $A_2$, and the reflections from $P_1P_2$ and $M_2$ also lie on the same layer lines. Hence $M_1A_1$, $M_3A_2$, $P_1P_2M_2$, respectively, have parallel $b$ axes.](image-url)
sodium phase, while the other two have their $b$ axes parallel, one each, to the $b$ axes of the albite twins of the sodium phase. This arrangement would be expected from a specimen which unmixed after inverting from monoclinic to triclinic symmetry: on inversion the $M$ type twinning was produced and from each of the four twinned units a potassium-rich unit exsolved with its $b$ axis constrained to be parallel to the $b$ axis of the host; since the $b$ axes of the pericline twinned units are identical there are three sets of reflections for the potassium-rich phase. However, it is possible that some unmixing occurred before the inversion temperature was attained: in this case, unmixing would have continued after the inversion had occurred in the sodic component.

Reciprocal cell angle measurements (Table 2) indicate that the composition of the sodium-rich phase is $Or_{29}(Ab+An)_{71}$ so that the unmixing has not proceeded very far. If no unmixing had occurred before inversion, the specimen would have become monoclinic at $100^\circ$ C. (Mackenzie, 1952): if unmixing had occurred before inversion the sodic component could have inverted at a temperature not higher than $200^\circ$ C. Under equilibrium conditions unmixing would have begun at $525^\circ$ C. It may be concluded that the lava in which these crystals occur was extruded and quenched at some temperature above $525^\circ$ C. and that most, if not all, of the unmixing now observed took place at a very low temperature near $100^\circ$ C., probably over an extended period of time.

c) Anorthoclase cryptoperthite from Mt. Franklin ($Or_{24.9}Ab_{67.3}An_{7.8}$).

This specimen was described as a homogeneous anorthoclase in paper III of this series but some crystals have now been found to be unmixed. This difference in crystals from the same sample indicates that cooling of the feldspar in the temperature range in which unmixing took place has been too rapid for the attainment of equilibrium. The photograph in Fig. 7 shows the x-ray diffraction pattern obtained from an unmixed crystal of this sample, and a key to the interpretation of the photograph is given as an inset. The sodium-rich phase shows three sets of reflections ($A$, $B$, and $C$) and the potassium-rich phase two sets of reflections ($D$ and $E$). $A$ and $B$ are albite twinned and $B$ and $C$ are pericline twinned so that this is an example of $T$ type twinning in an anorthoclase indicating that twinning was acquired from a triclinic untwinned crystal.

From the x-ray photograph it can be seen that the sets $B$, $C$ and $E$ have parallel $b$ axes and also that $A$ and $D$ have parallel $b$ axes (reflections D cannot be seen clearly except on the original film). Thus the unmixing must have occurred after the twinning was adopted and it is known that the twinning did not form on inversion to triclinic symmetry (assuming that the crystal was originally monoclinic). An approximate value of
Fig. 7—Anorthoclase cryptoperthite from Mt. Franklin, $b$ axis oscillation photograph with the $x$-ray beam parallel to (001) in the center of a 15° oscillation. The inset diagram provides a key to the reflections occurring in the small rectangle. The soda-rich phase gives three sets of reflections, ABC: reflections from B and C lie on the same layer lines so B and C are pericline twinned; reflections from A and B lie on the same row lines so A and B are albite twinned. This is the T type of association and is readily recognized from the groups of three reflections lying at the corners of a numeral 7. The D and E reflections have their $b$ axes parallel to A and BC respectively. The extent of unmixing has been slight, for the reflections from D and E are weak and diffuse, so weak in fact that they are only barely visible on the reproduction of the x-ray photograph.

500° C. for the temperature of the monoclinic triclinic inversion for this specimen may be obtained from Fig. 1, and since the twinning did not occur as a result of this inversion, the bulk of the unmixing occurred at a much lower temperature. A feldspar of composition Or$_{25}$Ab$_{75}$ would begin to unmix at about 450° C. (see Fig. 4) and this specimen with 7.6% An should, under equilibrium cooling, begin to unmix at a considerably higher temperature. It is not surprising to find some homogeneous crystals as well as unmixed crystals in the same sample since the unmixing has occurred metastably at low temperature.

d) Anorthoclase-cryptoperthite from Victoria, Australia (Or$_{23.3}$Ab$_{75.5}$-An$_{1.2}$).

This specimen was described in some detail in paper III but the evidence from the x-ray photograph and from the other data available were somewhat conflicting. In the light of the new determination of the solvus these difficulties can be resolved. The x-ray photograph of this crystal is reproduced in Fig. 8 and the feldspar can be seen to consist
Fig. 8. Anorthoclase cryptoperthite from Victoria, $b$ axis oscillation photograph with the x-ray beam parallel to (001) in the center of a 15° oscillation. There are four components, two soda-rich and two potash-rich. The reflections occur in groups of four lying at the corners of a trapezium, the trapezium being outlined by diffuse streaks linking the corners. Both pairs of components are in the positions required for albite twinning, the apparent deviation from monoclinic geometry of the potassic phase being smaller than that for the sodic phase.

of two phases. The sodium-rich phase is albite twinned and the potassic-rich phase consists of two units, the $b$ axes of which lie between the positions required for monoclinic symmetry and for parallelism with the $b$ axes of the albite twinned sodium phase. Since only albite twinning of the sodium phase is present it cannot be stated whether the twinning was formed from a triclinic or monoclinic crystal. The bulk chemical composition of this specimen corresponds very closely to that of the intersection of the solvus and the monoclinic-triclinic inversion curve, and it is likely that the process of unmixing began just after the specimen had turned into an anorthoclase. From each of the albite twin lamellae unmixing occurred and the potassium-rich component ‘adopted’ the $b$ axis of the dominant sodium-rich component. The strain between the unmixed phases has resulted in triclinic symmetry of the potassium-rich phase as is shown by the difference in intensity of the $(hkl)$ and $(k\bar{h}l)$ reflections. The streaks connecting the corresponding reflections of the sodium and potassium phases are in harmony with the above interpretation.

This is the same material as that investigated by Tuttle (1952) who found that the crystals of this specimen were optically monoclinic in their natural state but after heating until homogeneous and then cooling they were distinctly triclinic. The optically monoclinic symmetry in
this material may be due either to the sub-microscopic albite twinning or to the cryptoperthitic unmixing or to a combination of both of these factors. It is possible that the optical symmetry of this specimen in the unmixed state may be related to its bulk composition but until other anorthoclases of similar composition are investigated such a suggestion must be considered very tentative.

CONCLUSIONS

From the observations reported here it is clear that the cooling of natural anorthoclases may be a non-equilibrium process and for this reason caution must be used in attempting to interpret the cooling history of a rock from the alkali feldspars alone.

The use of a mineral as a geologic thermometer depends on a measurable variation of some property which is temperature dependent. As has already been noted, the compositions of the unmixed phases of alkali feldspars would appear to provide an ideal thermometer since the position of the solvus is virtually independent of pressure. However, the relation between the rate of cooling and the rate at which unmixing can occur at equilibrium will determine whether the temperature is that of crystallization of the feldspar or that of final consolidation of the rock or even merely the temperature at which no further unmixing in the solid state can occur because of the slowing down of ionic movement at lower temperatures. It is believed that unmixing of an alkali feldspar of intermediate composition is sufficiently rapid to approach equilibrium in a cooling magma provided sufficient fluxes are available for fluid to exist at temperatures in the range 600° C—500° C. However, in the case of a sodium-rich or potassium-rich feldspar encountering the solvus below 450° C—500° C the rate of attainment of equilibrium may not be sufficiently great to permit an interpretation of the exact meaning of the temperature which is determined. Studies of the rates of unmixing of nephelines in the system NaAlSiO₄—KAlSiO₄ (Tuttle and Smith, 1958) have shown the strong influence of the bulk composition of the homogeneous crystal, the rate of unmixing at any particular temperature being much more sluggish for compositions near the boundaries of the solvus.

The intersection of the solvus by the monoclinic-triclinic inversion curve does increase the possible usefulness of the solvus as a temperature indicator. Thus our conclusion that the Grande Caldeira feldspar was unmixing metastably in a temperature range near 100° C could only be reached because of the existence of the monoclinic-triclinic inversion and our knowledge of the relation between temperature and composition for this inversion. Likewise the conclusion that the Mt. Franklin feldspar
did not unmix under equilibrium conditions on encountering the solvus
was based on the crystallographic evidence of the relation between the
temperature of formation of the twinning and the unmixing process.

The optical and x-ray data at present available indicate that there are
an infinite number of stable forms of both sodium and potassium feldspar
between the highest and lowest temperature forms. The most useful
phase diagram, therefore, is one showing stable equilibrium relations,
since there will be an infinite number of possible metastable equilibrium
diagrams. That part of the alkali feldspar solvus which we have rede-
termined is believed to represent stable equilibrium relations more nearly
than the previously determined solvus. It cannot be assumed that
changes in the feldspars of volcanic rocks have taken place under stable
equilibrium conditions but, provided this factor is recognized, useful
information is nevertheless obtainable. In plutonic rocks it is possible
that the changes in the alkali feldspars have often occurred under con-
ditions approaching those of stable equilibrium and in subsequent papers
we shall deal in some detail with the alkali feldspars in certain granites.

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