SUB SOLIDUS
RELATIONS IN THE PLAGIOCLASE FELDSPARS

By

P. GAY

Department of Mineralogy and Petrology,
University of Cambridge

Introduction

Almost half a century ago Bowen (1913) determined the liquidus-solidus relationships across the plagioclase feldspars series. He showed that, at least at high temperatures, a simple solid solution series probably existed over the whole range of compositions from pure albite to pure anorthite. His work was taken to confirm the view that this simple replacement series extended through the sub-solidus at all temperatures, and for about another twenty five years this assumption was not really challenged. However evidence began to accumulate in the period before the war which suggested that feldspar relationships were not so simple. An increasing number of reliable measurements showed that the optics of a feldspar of a given composition may depend on its previous geological history. The detailed and careful work of Spencer using both natural and heat treated alkali feldspars had begun to elucidate the puzzling mineralogical relationships in this series, and lent weight to the view that there were polymorphic transformations at least for the potassium-rich feldspars, and possibly for other feldspars as well. At about same time Taylor and his co-workers (1933. 1934) published the results of the first structure determinations of feldspars, which confirmed Machatschki's suggestions that all feldspars had a framework structure of linked SiO_4 or AlO_4 tetrahedral groups, and that the more obvious crystallographic differences between the alkali and plagioclase feldspars were due to the sizes of the cations which occupied interstices in the negatively-

charged framework. It was then suggested by Barth (1934) that some of the polymorphic relationships could be linked to the distribution of Si and Al atoms within the tetrahedral framework, and so the basis was laid for the Si–Al order-disorder conception which has proved fundamental to all feldspar polymorphism.

The first direct evidence that the plagioclases did not show simple replacement over the whole series came from Taylor, Darbyshire and Strunz (1934); later Chao and Taylor (1940) demonstrated that three different structural regions could be recognised. Since that time it has been found that these original structural regions are more complex than was suspected by Chao and Taylor, and in the last decade a considerable volume of work has attempted to elucidate the sub-solidus of the plagioclases. It is the purpose of this paper to review the present position of our knowledge.

General considerations

The feldspars, in particular the plagioclases, have fulfilled their early promise of becoming one of the most complicated and fascinating problems of mineralogical crystallography. Any description must be essentially crystallographic, for over the plagioclase series it is only subtle differences which distinguish one region from another. To make these distinctions, the techniques of single-crystal X-ray methods must usually be employed. Optical and X-ray powder methods, although valuable in establishing the composition and often something about the thermal history of the plagioclase, have not the resolution to identify one structural region from another.

At the outset, it should be realised that our present picture of the sub-solidus is very inexact so far as the temperature-composition fields of any structural regions are concerned. The very nature of the problems involved makes it unlikely that any progress towards an exact and definitive phase diagram will be made for some time. There has been little synthetic work done on the series, other than that on the end members, albite and anorthite; the experience of the synthetic work on albite, in particular, suggests that, with the present techniques, experimental studies of intermediate members of the series would be difficult. Most of what is known at present about the various plagioclase structures has been obtained by using natural plagioclases whose previous geological history may reasonably be inferred and by the heat

treatment of such specimens. The uncertainties inherent in such an approach, together with the lack of precision of the single-crystal X-ray method so far as temperature and composition determinations are concerned ensure that only a rudimentary phase diagram can be available at present.

Although it is not the purpose of this paper to deal with the details of plagioclase structures which have now been determined, the complexity of the sub-solidus requires some understanding of the structural features of the phenomena involved. It has now been clearly established by direct structural determination that the polymorphism shown by the feldspars can be related to order-disorder relationships, but there has been some confusion concerning the nature of these relationships. Megaw (1959) pointed out that three types of disorder could be distinguished as being relevant to feldspar structural problems, substitution disorder, position disorder and stacking disorder. In substitution disorder, crystallographically equivalent positions in the structure can be occupied at random by chemically different atoms. Historically this kind of disorder was the first that was suggested for metal alloys, and has obvious connection with the distribution of Si and Al atoms in feldspars. In position disorder, there are two (or more) sites in the structure for a particular kind of atom which are so nearly equal in energy that they may be occupied at random by such atoms. Explanations of this kind have been suggested to account for the anisotropy of some cation peaks on electron-density maps of feldspar structures. Stacking disorder implies irregularities in an ordered sequence of packing units of structure. Mistakes of this kind are particularly common among layer structures, for example among metals based on close-packed sheets of atom, whilst the best known mineralogical example is found in the polymorphism of the micas. Such disorder need not be confined to layer structures, and quite recently it has been suggested that systematic faulting of the feldspar structure can explain the diffraction phenomena which characterise some plagioclases. In considering the application of these concepts to the plagioclases, the different types of disorder cannot necessarily be considered as independent, and the order-disorder relationships will be more complex than is suggested by these simple geometrical descriptions.

To help to evaluate plagioclase sub-solidus relationships, it is also important that data should be available on the kinetics of any

polymorphic transformation. Such information is at present only available at the albite-rich end of the plagioclases, where it is agreed that the distinction between the various albite polymorphs is due mainly to changes in Si–Al distribution. Whilst the detailed mechanism of such changes is unknown, there is little doubt that it must involve some kind of diffusion process, whose rate depends both on the mobility of the ions within the structure and the surmounting of any energy barrier. The mobility of ions in the plagioclases has been demonstrated by the work of Wyart and his collaborators, although no quantitative data are yet available, whilst McConnell and McKie (1960) showed that under hydrothermal conditions, pure albite undergoes a discontinuous transformation at about 600 °C for which the activation energy is about 60 K cal/mole. The same authors have more recently shown that for the same transformation carried out by the dry heating of Amelia albite, the activation energy is significantly larger at about 74 K cal/mole; in the course of this work they showed that the transformation could proceed at reasonable rates under dry conditions at temperatures around 900°–950 °C (personal communication). Elsewhere in the series, there is at present no reliable information about these parameters, except that for very anorthite-rich materials where no change in Si–Al distribution is involved, they must be of a different order of magnitude.

We are also concerned in some plagioclases with the structural effects of exsolution. Unmixing, which again must occur by some sort of diffusion mechanism, will be peculiarly complicated in the series, for ideally the segregation of albite-rich and anorthite-rich regions involves a migration of Na and Ca ions in close association with a re-distribution of the Si and Al in the tetrahedral framework; the domains which are anorthite-rich require a higher concentration of Al atoms than either the albite-rich regions or the homogeneous crystal from which they have been exsolved. It is probably due to the complexity of such re-arrangements that the exsolution effects which are found in the plagioclases have not developed to the same clear extent as is commonly observed in the alkali feldspars. Obviously under equilibrium conditions, the actual distribution of the cations and the tetrahedrally co-ordinated silicon and aluminium will also depend on the position of the unmixing solvus with respect to the temperature interval associated with a discontinuous polymorphic transformation.

The consequences of these considerations so far as the plagioclases sub-solidus is concerned are that ideal equilibrium can be unobtainable or unrecognisable, and that there is little information concerning the stabilities of the different forms of plagioclases with the occurrence of metastable forms a common and confusing factor. In particular in systems which may be out of strict equilibrium, there may be diverse paths of structural arrangement by which they may change to one condition from another; when a specimen has been cooled under natural conditions from some temperature, and when it is returned to this temperature by heating in the laboratory, we cannot necces-sarily expect complete identity either in the paths by which the changes occur or in the structures of the initial and final material. These are the hazards of the present position, and we must be aware of them in assessing our picture of the sub-solidus.

The structural divisions

The three structural regions described by Chao and Taylor (1940) have become known as (i) anorthite structures, (ii) the intermediate structures and (iii) the albite structures. Apart from the compositional connotation of these terms, the regions are characterised by single-crystal photographs taken about the c-axis (Figure 1). Clearly the albite-structures are those for which the cell-dimension in this direction is half that of the anorthite-structures (~ 14 Å), the other two cell-edges remaining more or less similar. In the intermediate structures, the rather weak intermediate layer lines denoting the doubled repeat of the anorthite structures are replaced by pairs of weak subsidiary layer lines whose separation varies with composition of the plagioclase, and whose positions do not always correspond to rational repeat distances. It is convenient to break up discussion of the sub-solidus into these three regions.

In discussing the structures in terms of the X-ray diffraction effects, it is convenient to follow the notation of Laves and Goldsmith (1951) and Gay (1953). If reflexions are indexed on the basis of the anorthite cell, four groups can be distinguished depending on the parity of $h + k$ and l. All plagioclases show the diffraction maxima of group (a) for which both $h + k$ and l are even; such reflexions are on the average quite strong. The weaker reflexions of the other three
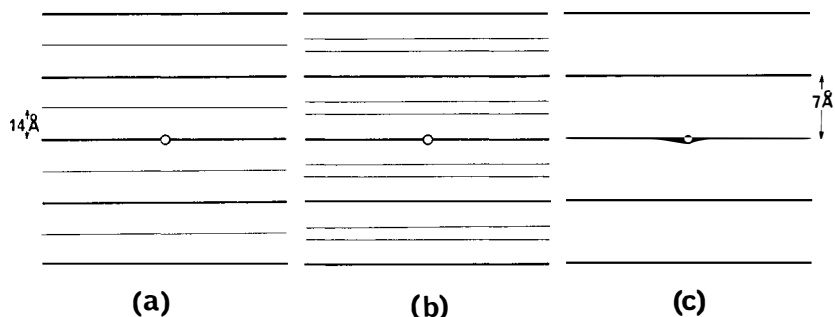
Figure 1. Schematic representation of *c*-axis oscillation photographs for (a) anorthite structures (b) intermediate structures (c) albite structures.

groups (*b*), (*c*) and (*d*), sometimes called the subsidiary or difference reflexions, are of primary importance in characterising one plagioclase structure from another. Groups (*b*), with $h+k$ odd and l odd and group (*c*) with $h+k$ even, l odd can define the weak 14 Å *c*-axis repeat of the anorthite structures; the remaining group (*d*), both few in number and very weak will fall on the layer lines due to a 7 Å repeat.

Within each structural division, we shall discuss what has been inferred about sub-solidus relations at low temperatures from the study of suitable natural materials; the effects of heat treatment on such specimens together with the results of work on natural high-temperature plagioclaes are used to infer the relations near to the solidus.

(i)   The anorthite structures

Most natural specimens with compositions approaching pure $CaAl_2Si_2O_8$ (95–100% An) show diffraction patterns characteristic of the primitive anorthite structure. All reflexions of the subsidiary groups (*b*), (*c*) and (*d*), in addition to the principal reflexions, are present as normal Bragg maxima, showing the primitive character of the anorthite cell. The only effective changes within this range with increasing albite content are very small dimensional changes as the substitution takes place. However as the anorthite content falls below about 95% An, the reflexions of groups (*c*) and (*d*) become diffuse, whilst those af (*a*) and (*b*) remain sharp. The diffuseness of these reflexions increases as the albite content rises, the (*c*) reflexions becoming elongated parallel to the b^*-axis, with the type (*d*) reflexions, which are weak and few in number, being no longer visible. Patterns of

this kind are characteristic of what is sometimes called the "transitional" anorthite structure. For many specimens within the range from 80–85% An to 70–75% An (the albite-rich limit of the anorthite structures at low temperatures), the (c) and (d) reflexions are apparently absent, giving diffraction patterns showing only the two reflexion groups (a) and (b). Such materials, although still showing the distinctive 14 Å c-axis of the anorthite structures, have a body-centred cell. However there are some materials within this range from environments which might be reasonably expected to produce low structural states for which the group (c) reflexions are still observable, although very diffuse. There is therefore some doubt as to whether body-centred anorthite is to be regarded as a stable equilibrium form at low temperatures. In the sequence of change primitive—transitional—body centred cells with increasing albite content, it is probable that at low temperatures the last stage is not reached in the range of the anorthite structures.

Synthetic $CaAl_2Si_2O_8$ crystallised near the solidus shows the transitional anorthite patterns, as do some natural specimens of almost pure anorthite composition, particularly those occurring as crystal lapilli. Indeed over the whole range, the effect of increasing temperature is to promote the change from a primitive to body-centred cell in the same way as increasing albite content. The sub-solidus relationships of the anorthite structures have been discussed by several authors (Gay, 1953, 1954; Laves and Goldsmith, 1951, 1954, 1955).

Under equilibrium conditions the stability field of the primitive anorthite structure is considered to extend from about 95% An for temperatures below about 400°–500 °C to pure anorthite for temperatures below 1100 °C. Heating experiments show that at high temperatures for the composition range 90–100% An the stable structural configurations are probably body-centred anorthite grading into transitional anorthite as pure anorthite is approached. Similar experiments for specimens in the range 70–90% An show that the low temperature structures can be transformed through the body-centred anorthite region to a configuration which shows high-albite type diffraction patterns in which all subsidiary reflexions have vanished and only the main type (a) maxima remain. These relationships are expressed schematically in Figure 2.

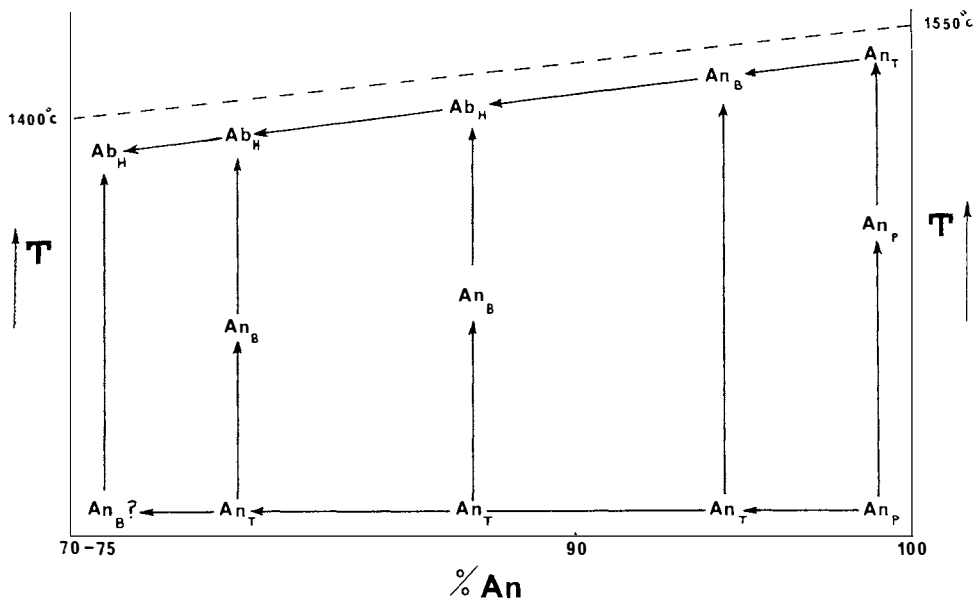It is probable that the transformation primitive—body-centred

Figure 2. Diagrammatic representation of sub-solidus relationships from 70–75 % An to 100 % An.

The dotted line represents the solidus. The various structural modifications are denoted as:—Primitive anorthite, An_P, transitional anorthite, An_T, body-centred anorthite, An_B and high albite, Ab_H.

anorthite has a low activation energy, for equilibrium seems to be rapidly established, and laboratory experiments have shown the ready reversibility of the primitive—transitional stage of the process. The change from anorthite to albite-like structures at high temperatures is not readily reversible, and must represent a transformation with different structural characteristics. It was indirectly inferred that the Si–Al distribution is ordered in all anorthite structures, and that the variations are due to cation configuration (Laves and Goldsmith, 1951; Gay and Taylor, 1953, Goldsmith and Laves, 1955); the change to the high albite type structure, however, would involve disorder in the Si–Al arrangement. The general features of this suggestion have now been confirmed by direct structural analyses (see papers by Megaw *et alia*, I.M.A. Symposium, Copenhagen, 1960), though the precise structural arrangements in the anorthites is not clear. Laves and Goldsmith (1956, 1954) first suggested that transitional anorthite

patterns were due to an "out of step" domain structure, in which the domain size is a continuous and reversible function of temperature dependent on Ca, Na-positions within the interstices of the tetrahedral framework. On the basis of later structural work, Megaw (1961) has proposed that the body-centred and primitive configurations are the only two stable structures, the former being the high temperature structure. The transitional anorthites are pictured as a two-phase region with the crystal as a whole consisting of small domains of the primitive structure separated by small domains of the body-centred structure; the higher the temperature (and presumably the greater the Ab-content) the greater is the proportion of the material in the body-centred condition. More detailed structural data are needed to confirm these ideas.

(ii)   The intermediate structure

The singular diffraction effects which characterise this region have been fully investigated in the last decade. The present position has been summarised by Bown and Gay (1958).

The equilibrium low temperature state gives diffraction patterns which show the main type (a) spots, but none of the sharp subsidiary reflexion groups (b), (c), (d); close to each (b) position, the intermediate plagioclase pattern shows a pair of maxima, symmetrically placed but of unequal intensity, which are known now as the (e) reflexions. [Formerly these were called the split (b) reflexions, and they are responsible for the pairs of weak subsidiary layer lines described by Chao and Taylor (1940)]. The indices of the (e) reflexions can then be written as $(h \pm \delta h, k \pm \delta k, l \mp \delta l)$; δh, δk and δl are positive and non-integral, and vary apparently continously and linearly over the whole composition range for which they can be observed (20–25% An to 70–75% An). For An-poor specimens, the vector in reciprocal space joining any pair of (e) maxima lies in the a^*c^* plane approximately perpendicular to $(10\bar{3})$; with increasing An content, this splitting vector decreases in magnitude and changes its orientation, so that at the An-rich limit of the field, it lies in the b^*c^* plane, approximately perpendicular to $(03\bar{2})$. The An-rich boundary is relatively sharp, with the length of the splitting vector still finite ($\sim 0.01\,\text{Å}^{-1}$). The An-poor boundary is not so well defined, because below 40–45% An the (e) reflexions tend to become more and more diffuse as the limit of the field is approached. Over the range where the (e) maxima are sharp,

their intensities seem to be independent of An-content and to bear a general relationship to those of the (b) reflexions which they replace.

In addition intermediate plagioclase patterns from specimens with more than about 50–55% An shows pairs of reflexions satellite to the type (a) reflexions. These (f) reflexions may be indexed as $(h \pm 2\delta h, k \pm 2\delta k, l \mp 2\delta l)$, so that their splitting vector is parallel to and twice the magnitude of that of the (e) reflexions. An important difference from the (e) spots is that their intensities are profoundly dependent on the An-content of the specimen decreasing sharply from the An-rich limit of the field until they have become unobservable in the region 50–55% An. We should also note that many specimens within this same region show very weak diffuse maxima in positions associated with the type (c) reflexions of anorthites.

The high temperature relationships in this composition range have been investigated by Gay and Bown (1956), who showed that a high albite type structure could be produced by heat treatment. The (e) reflexions become diffuse, forming a single diffuse region in reciprocal space which gradually weakens and disappears leaving only the type (a) reflexions; some natural specimens have also been described which show transitional or high diffraction patterns. Later Brown (1959) showed that the transformation from the intermediate structure to a high albite arrangement was slower at a particular temperature (1140 °C) the more An-rich the specimen; at this temperature, the cell dimensions after heating were those of the high structure, though this experiment does not necessarily prove that destruction of the intermediate structure is associated with a polymorphic Si–Al rearrangement. Much more experimental data are needed on the dynamics of the changes in this region, though there are considerable technical difficulties (see Gay, 1961).

The structural explanation of the unusual diffraction patterns from intermediate plagioclases has been a subject for speculation for many years. Both Chao and Taylor (1940) and Sørum (1951) proposed models based on an ordered arrangement on a very fine scale of An-rich and An-poor structural regions. Although these models failed to explain all features of the complex diffraction patterns, it was generally accepted that there was some kind of ordered unmixing on a unit-cell scale into regions of differing An-content. Later Megaw (1957) proposed a model based on an "ideal plagioclase structure" in which sets of

stacking faults occur on different planes with a probability dependent on the An-content of the plagioclase; the faults arise through site mistakes (hence their dependence on composition and the thermal history of the specimen) though the precise mechanism is unknown. These ideas have been developed in a series of papers (Megaw, 1960, a, b, c) so as to provide a complete quantitative explanation of all the features of the diffraction patterns which have been described, and apparently represent a physical solution of the problem, although there is as yet no direct evidence of the presence of such faulting in plagioclase structures. It is also suggested that this treatment not only accounts for the particular problems of the intermediate structures, but further provides the key to the understanding of such structures to the albites, on the one hand, and the various anorthite structures on the other.

The structural relationships in the intermediate composition range are shown diagrammatically in Figure 3.

(iii)   The albite structures

Tuttle and Bowen (1950) using both synthetic $NaAlSi_3O_8$ and heat treated natural specimens of albite composition clearly established the existence of a polymorphic transformation from a low to a high modification; the term "analbite" has been used by Laves and his co-workers for the latter. Both forms are triclinic with a 7 Å c-axis C face-centred cell i.e. they show only the type (a) reflexions. The high and low forms differ slightly but significantly in cell dimensions and in the intensities of corresponding reflexions.

Later it was found that at low temperatures, the albite structure can only tolerate small deviations from the ideal composition $NaAlSi_3O_8$. All specimens in the region from about 3% An to about 19% An were found to be unmixed (Laves, 1954). Single crystal patterns show two sets of type (a) spots, so that the orientation relationship between the components is that they have their b* and c* axes in common, but their a*-axes are inclined at a small angle ($\frac{1}{3}-\frac{1}{2}°$). Gay and Smith (1955), using the cell parameters of the exsolved phases showed that the co-existing components had compositions of 1–5% An and 21–25% An. More recently there have been detailed examinations of this composition field by Ribbe (1960) and Brown (1960b) which have confirmed these observations. Many unmixed specimens exhibit a characteristic bluish schiller, though this is not invariably associated
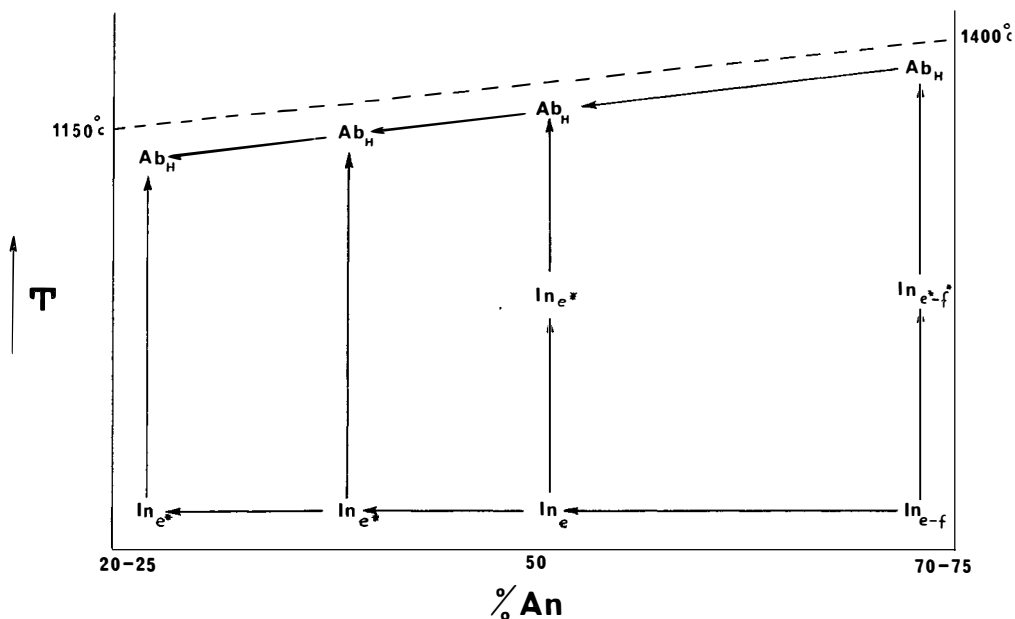
Figure 3. Diagrammatic representation of sub-solidus relationships from 20–25 % An ot 70–75 % An.

The dotted line represents the solidus. The various structural modifications are denoted as:—Intermediate plagioclase with both (e) and (f) type reflexions, In_{e-f}, intermediate plagioclase with (e) type reflexions, In_e, and high albite, Ab_H. The symbol (*) indicates that the reflexions are diffuse.

with unmixing. Such schiller effects in this region had been previously investigated by Bøggild (1924), and the term "peristerite" used to describe such specimens has now been extended to include any un-mixed specimen whether it shows schiller or not. Brown (1960b) was able to observe microscopically a planar lamellar structure of sporadic occurrence and separation occurring in certain peristerite specimens.

The structural reasons for peristerite unmixing have not been clearly established. Ribbe (1960) suggests that it is due to the relatively large size difference between Al and Si atoms in the tetrahedral framework. The strains which occur on substitution of Al for Si are relieved by a distribution involving Al-rich (and Ca-rich) regions and Si-rich (and Na-rich) regions. This assumes that the structure of the An-rich component (25% An) is sufficiently different from pure albite

to allow the strain-free accommodation of the Al atoms, a fact which is largely confirmed by the structure analysis of an oligoclase (Waring, 1961).

The nature of the polymorphic transitions which low albite can undergo has been the subject of considerable work. MacKenzie (1957) synthesised under hydrothermal conditions albites intermediate between high and low; the existence of such transitional states had already been recognised by the heat treatment of almost pure soda-feldspars. However more recently the polymorphism has been recognized to be more complex than the single transformation previously proposed. In earlier work MacKenzie (1952) had observed that a synthetic albite crystallised above about 950°C became monoclinic when heated above this temperature, but reverted to triclinic symmetry on cooling. Later work by Schneider (1957) and Brown (1960a) confirmed these observations, and has suggested that a monoclinic form of $NaAlSi_3O_8$ can exist at room temperatures. Laves (1960a) has discussed the stabilities of the various forms of $NaAlSi_3O_8$, and concludes that there are two stable forms, the monoclinic form, monalbite, and the triclinic form, low albite, both of which may have high, transitional or low states depending on the Si–Al arrangement. These conclusions are criticised by Smith and MacKenzie (1961) and MacKenzie and Smith (1961). While these authors appear to accept the existence of a monoclinic form of $NaAlSi_3O_8$ at temperatures above about 950°C, they are unconvinced by the present experimental evidence about the stability of this form at room temperature.

Careful structural determination of both low and high albite Ferguson, Traill and Taylor (1958) confirmed that the transformation is primarily but not exclusively concerned with order-disorder relationships for the Si and Al atoms. The structural significance of monalbite may be that in some way it is more disordered in these arrangements than high albite, though the precise nature of the disorder must await determination.

For more An-rich specimens we are also concerned with the peristerite solvus, and its position with respect to the polymorphic tronsformations. Gay and Smith (1955) suggested that the solvus lies below the low-high albite inversion, and that homogeneous specimens with a low-albite structure can exist in this composition field. Schneider (1957) investigated the charges in lattice geometry of each of the

submicroscopic phases with heat treatment. Ribbe (1960) pointed out that process of homogenisation is difficult to follow by this method due to the similarity in cell geometry of the high temperature phases; indeed in some specimens schiller effects were found to persist after unmixing can no longer be detected. Both these latter authors were concerned with homogenisation by heat treatment at temperatures above the range expected for any low-high transformation, and their work does not necessarily provide any direct evidence on the position of the solvus. Brown (1960b), working with natural specimens, showed, that oligoclases which display only the earliest forewarnings of unmixing have lattice constants which fit those of ordered plagioclases, and supports the view that under equilibrium cooling conditions exsolution follows the formation of a homogeneous ordered crystal.

At higher temperatures, the "displacive" transformation high albite-monalbite persists into the oligoclase field. Schneider (1957)
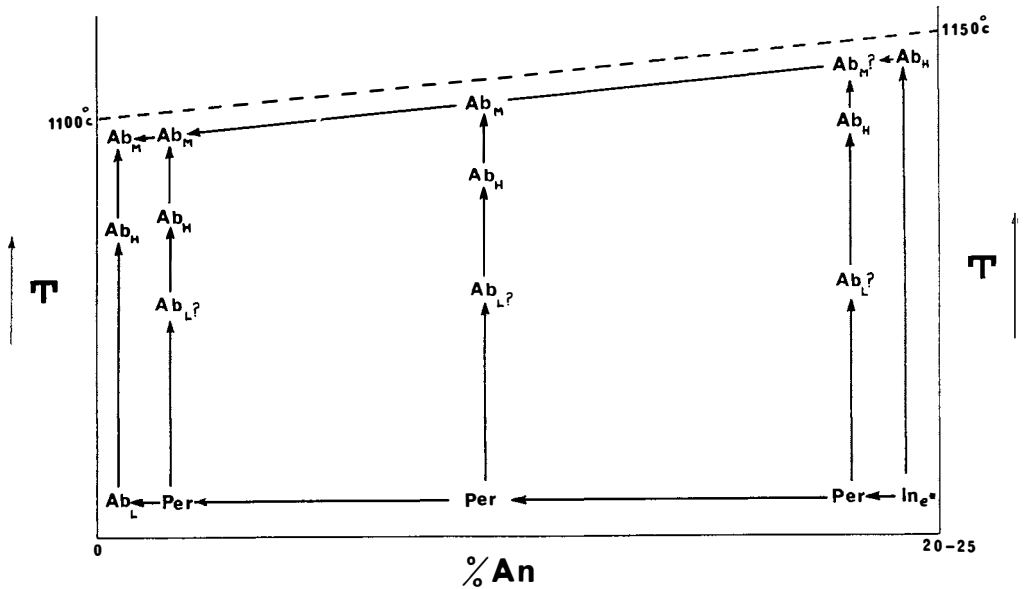

Figure 4. Diagrammatic representation of sub-solidus relationships from 0 % An to 20–25 % An.

The dotted line represents the solidus. The various stuctural modifications are denoted as:—Intermediate plagioclase with diffuse (e) type reflexions, In_{e*}, peristerite unmixing, Per, low albite, Ab_L, high albite Ab_H and monoclinic albite Ab_M.

showed that it extended up to at least 13% An, and Brown (1960a) has given some evidence that it probably extends to about 20% An though the precise limits remain uncertain.

The probable form of the equilibrium relationships is indicated diagrammatically in Figure 4.

Discussion

At present, while the various structural modifications can be recognised and the general features of their sub-solidus relations established, there can be little certainty in the prediction of the structural state to be assumed under given conditions of crystallisation. Over most of the field equilibrium cooling conditions cannot be established in the laboratory; indeed Smith and Gay (1958) have suggested that below about 45–50% An even the most slowly cooled natural specimens have not been able to attain equilibrium. This means that the results obtained by the heat-treatment of natural low temperature specimens must be regarded with caution, and it is difficult to see how further experimental work can resolve all the problems that remain. Obviously progress can be made in some regions e.g. in the high albite-monalbite transformation, but in other regions the nature of the structural re-arrangements may preclude a definitive solution.

This has some bearing on the determination of "structural state" for a plagioclase, in which the measurement of some physical parameter (e.g. one of the optical properties or an interplanar spacing) allows the specimen to be classified with respect to the limiting states, high or low. The structural condition of the specimen determines the value of the physical parameter. Measurements of two different properties for the same specimen cannot necessarily be expected to lead to the same classification of structural state though fortunately they often do (see Gay and Muir, 1962). The major part of the variation of the physical parameter may be associated with a structural transformation for a particular specimen, so that before any real physical significance can to an experimentally determined state, much more data on the dynamics and mechanism of the transformations is needed. It will be even more difficult to assess the value of such determinations if the specimen has followed a non-equilibrium path to its final

position. It is clear that at present the structural state of a plagioclase can only be reliably interpreted in combination with other information from associated minerals concerning the cooling history of the rock in which the assemblage is found.

Discussion

Olav H. J. Christie

When heated for long periods at elevated temperatures, single crystals of albite develop cross-hatched twinning upon quenching. This indicates that the heated crystals have been monoclinic at the temperature of heating (Schneider (1957)). Furthermore, the crystaline product obtained by devitrification of albite glass at elevated temperature under water pressure seems to be monoclinic at high temperature (MacKenzie 1952)). As a consequence of these observations Dr. Gay has suggested that the stable modifications of the albite rich plagioclases are monoclinic at high temperatures. There are, however, reasons to believe that it is premature to draw this conclusion.

It has been shown that the temperature of the postulated (high albite) triclinic—monoclinic inversion depends on the length of heat treatment; thus, albite heated for one month at $1000°–1050°$ C may be monoclinic above and triclinic below $900°$ C; the same crystal heated at the same temperature for, say, four months may be monoclinic down to $-100°$ C, below which it is triclinic. In his comment to this observation Laves writes: Es wird dabei angenommen, dass dieser Temperatureffekt vorwiegend auf Erhöhung der Al-Unordnung zurückzuführen ist, und nicht auf Änderung der chemischen Zusammensetzung — z. B. Verlust von Na_2O oder von natürlichen Verunreinigungen, etwa OH oder H_2O — was aber wohl noch nachgeprüft werden müsste (Laves (1960)).

A few experimental runs in our laboratories seem to indicate that considerable loss of sodium by volatilazation takes place under the experimental conditions leading to the monoclinic phases which are discussed by Laves. Analysis of the products before and after heating show that at least 10% of the original Na_2O content has been volatilized from powdered albite heated for three months at $1050°$ C. The loss of Na_2O from the outer shell of the grains produce a remnant

composition more nearly that of a eutectic composition near the albite point in the system Na_2O–Al_2O_3–SiO_2. This seems to be the reason why albite single crystals melt at their surfaces as a result of heat treatment (see also Robinson (1962)).

It has been advocated (e.g. W. L. Brown, personal communication, June 1962) that the formation of a melt is a surface phenomenon which has no bearing to the composition of the interior of the crystal. However, Na is capable of diffusing rapidly at high temperatures, as demonstrated by homogenization of coarse perthites in three days at $1000°$ C. Therefore, when Na_2O is volatilized from the surface, there is likely to be a tendency for the Na ions to migrate within the crystals and to establish a concentration gradient from the core to the margins. The evaporation of sodium from the surface, therefore, may have a marked influence on the composition of the interior of the crystal.

Since loss of Na_2O accompanies prolonged heating, and prolonged heating results in a lowering of the triclinic—monoclinic inversion temperature, it is possible that a deficiency of Na_2O has a marked influence on it. It is not known if a monoclinic pure albite exists at any temperature or whether it is necessary that the monoclinic phase produced from albite holds less Na_2O than does pure albite.

In the study of the triclinic—monoclinic inversion of Na–K feldspars by MacKenzie (1952) synthetic albite was produced hydrothermally at $700°$, $800°$, $950°$ and $1025°$ C. Runs with these albites in a diffractometer supplied with devices for heating the sample during the exposure to X-rays showed that the deviation from monoclinic symmetry (obliquity) decreased with increasing temperature of the powder speciment of the diffractometer runs. The obliquity was also dependent on the conditions of hydrothermal synthesis, thus, albite synthesized at $700°$ and $800°$ C would, according to the curves drawn by MacKenzie, reach monoclinic symmetry at an extrapolated temperature above the melting point of albite. The albite synthesized hydrothermally at $950°$ and $1025°$ C would be monoclinic at temperatures below the melting point of albite. These results clearly indicate that the products obtained from an albite glass by hydrothermal treatment at different temperatures are different in one way or another. It is possible that there is a close relation between temperature of hydrothermal synthesis and sodium deficiency: higher temperature

of hydrothermal treatment causes greater leaching of sodium, which in turn causes a lower measured temperature of the triclinic-monoclinic inversion.

The experimental evidences underlying the suggestion that acid plagioclases are monoclinic at high temperatures are not unambiguous and more experimental work is needed to justify any final conclusions.

F. Laves:

1) In the 4. paragraph Dr. Christie points to the fact that Na is capable to diffuse rapidly at high temperatures, as evidenced by the rapid homogenization of perthites. However this evidence is irrelevant to the argument here under consideration as in the case of perthites the diffusion is due to an Na/K exchange process without a necessity of changing the framework composition and of oxygen diffusion. In the case here under consideration one (or both) of two processes must take place: (1) moving of Na^{1+} *and* O^{2-}, i.e. production of oxygen deficiency in the tetrahedral $(Al, Si)_2O_4$-framework, or (2) replacement of Na^{1+} by H^{1+}.

2) On the lines of arguments used by Dr. Christie it might be premature too to conclude that a *pure triclinic albite* can exist at high temperature.

3) The best way to check the question if differences in Na_2O deficiency play a role on the triclinic monoclinic transformation temperatures appears to me right now to do experiments with which would be investigated if a monoclinic form could be reversed to the triclinic one by heating it in a Na_2O environment.

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